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DIFFERENTIAL ABSORPTION LIDAR (DIAL) QUANTIFICATION OF VOC FUGITIVE EMISSIONS FROM SMALL SOURCES IN LOS ANGELES AREA, USA, OCTOBER 2015

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JANUARY 2017

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ABSTRACT

This report presents the results of non-methane VOC emission measurements from small sources in Los Angeles area, USA, carried out using the NPL Differential Absorption Lidar (DIAL). The measurements were conducted between the 8th and 19th October 2015

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ISSN 2059-6030

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CONTENTS

TABLES ..... **V**
FIGURES ..... **VI**
EXECUTIVE SUMMARY ..... **VII**
1 INTRODUCTION **1**
1.1 OVERVIEW OF MEASUREMENT APPROACH 2
1.2 OVERVIEW OF TABLES AND FIGURES 2
2 VOC MEASURMENTS FROM E. CRESTON AVE. - OIL WELLS & TANKS **4**
2.1 LOCATION SS01 RESULTS AND DISCUSSION 6
3 VOC MEASURMENTS FROM E. 29TH ST - STORAGE TANK OF WATER PROCESSING FACILITY **7**
3.1 LOCATION SS02 RESULTS DISCUSSION 9
4 VOC MEASURMENTS FROM GARDENA AVE. - OIL WELLS AND TANKS **10**
4.1 LOCATION SS03 RESULTS DISCUSSION 12
5 VOC MEASURMENTS FROM HOME DEPOT PARKING LOT - OIL WELLS, DRILLING RIG & TANKS **13**
5.1 LOCATION SS04 RESULTS DISCUSSION 15
6 VOC MEASURMENTS FROM TRADER JOES PARKING LOT - OIL WELLS & TANKS **17**
6.1 LOCATION SS05 RESULTS DISCUSSION 19
7 VOC MEASURMENTS FROM SHOPKEEPER RD. - OIL WELLS & TANKS **20**
7.1 LOCATION SS06 RESULTS DISCUSSION 21
8 VOC MEASURMENTS FROM SHOPKEEPER RD. - OIL WELLS & TANKS **22**
8.1 LOCATION SS07 RESULTS DISCUSSION 24
9 VOC MEASURMENTS FROM VONS #1638 – GAS STATION **25**
9.1 LOCATION SS08 RESULTS DISCUSSION 27
10 VOC MEASURMENTS FROM COSTCO #1050 – GAS STATION **28**
10.1 LOCATION SS09 RESULTS DISCUSSION 30
11 CONCLUSION **31**
12 APPENDIX 1: DESCRIPTION OF THE DIAL TECHNIQUE **32**
12.1 OVERVIEW OF THE DIAL TECHNIQUE 32
12.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS 32
12.3 DESCRIPTION OF FACILITY OPERATED BY NPL 33
12.4 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS 36
12.5 CALIBRATION AND VALIDATION 37

13 APPENDIX 2: VOC SPECIATION USING PUMPED SORPTION TUBES.....39
13.1 SPECIATION RESULTS FROM THE ATD TUBE SAMPLES 39

TABLES

Table 1.1 Summary of DIAL measurement locations. 2
Table 2.1 Emission rate determined from SS01 on 8th of October. 4
Table 2.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 6
Table 3.1 Emission rate determined from SS02 on 9th of October. 7
Table 3.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 9
Table 4.1 Emission rate determined from SS03 on 14th of October. 10
Table 4.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported. 12
Table 5.1 Emission rate determined from SS04 on 15th of October. 13
Table 5.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported. 15
Table 6.1 Emission rate determined from SS05 on 18th of October. 17
Table 6.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 19
Table 7.1 Emission rate determined from SS06 on 18th of October. 20
Table 7.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 21
Table 8.1 Emission rate determined from SS07 on 18th of October. 22
Table 8.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 24
Table 9.1 Emission rate determined from SS08 on 19th of October. 25
Table 9.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 27
Table 10.1 Emission rate determined from SS09 on 19th of October. 28
Table 10.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported. 30
Table A1.1 Ultraviolet capability of NPL DIAL Facility 36
Table A1.2 Infrared capability of NPL DIAL Facility 36

FIGURES

Figure 1.1 NPL DIAL facility on a site. 1
Figure 2.1 Measurement configuration for location SS01 on 8th of October. 4
Figure 2.1a1 Observed VOC concentration for Scan 152 representing SS01/LOS4. 5
Figure 2.1a2 Visualisation of emission rate for Scan 152 representing SS01/LOS4. 5
Figure 2. 2 Time series VOC emission rate measured from location SS01/LOS1, LOS2 and LOS4..... 6
Figure 3.1 Measurement configuration for location SS02 on 9th of October. 7
Figure 3.1a1 Observed VOC concentration for Scan 171 representing SS02/LOS1. 8
Figure 3.1a2 Visualisation of emission rate for Scan 171 representing SS02/LOS1. 8
Figure 3. 2 Time series of VOC emission rate from SW corner tank. 9
Figure 4.1 Measurement configuration for location SS03 on 14th of October. 10
Figure 4.1a1 Observed VOC concentration for Scan 251 representing SS03/LOS2 over the 150-250 m range from the DIAL. 11
Figure 4.1a2 Visualisation of emission rate for Scan 251 representing SS03/LOS2 over the 150-250 m range from the DIAL. 11
Figure 5.1 Measurement configuration for location SS04 on 15th of October. 14
Figure 5.1a1 Observed VOC concentration for Scan 257 representing SS04/LOS2. 14
Figure 5.1a2 Visualisation of emission rate for Scan 257 representing SS04/LOS2. 15
Figure 6.1 Measurement configuration for location SS05 on 18th of October. 17
Figure 6.1a1 Observed VOC concentration for Scan 277 representing SS05/LOS1. 18
Figure 6.1a2 Visualisation of emission rate for Scan 277 representing SS05/LOS1. 18
Figure 7.1 Measurement configuration for location SS06 on 18th of October. 20
Figure 8.1 Measurement configuration for location SS07 on 18th of October. 22
Figure 8.1a1 Observed VOC concentration for Scan 295 representing SS07/LOS2. 23
Figure 8.1a2 Visualisation of emission rate for Scan 295 representing SS07/LOS2. 23
Figure 9.1 Measurement configuration for location SS08 on 19th of October. 25
Figure 9.1a1 Observed VOC concentration for Scan 302 representing SS08/LOS1. 26
Figure 9.1a2 Visualisation of emission rate for Scan 302 representing SS08/LOS1. 26
Figure 10.1 Measurement configuration for location SS09 on 19th of October. 28
Figure 10.1a1 Observed VOC concentration for Scan 308 representing SS09/LOS1. 29
Figure 10.1a2 Visualisation of emission rate for Scan 308 representing SS09/LOS1. 29
Figure A1.1 Illustration of the emission rate calculation approach..... 36
Figure A1.2 Schematic showing relationship between emission rate and wind direction 37
Figure A2.1 Volume fraction of VOCs in the four samples..... 40

EXECUTIVE SUMMARY

Background
Refineries, ports, and smaller stationary sources are key contributors to the stationary source emission inventory in the South Coast Air Basin (SCAB). However, their emissions are not fully characterized and the air quality in the SCAB remains among the worst in the USA. Thus, characterizing the actual magnitude of volatile organic compounds (VOCs) and other hazardous air pollutants (HAPs) emissions is crucial for attaining EPA air quality standards and for improving the well-being of people living in the SCAB. Optical remote sensing (ORS) methods, such as Differential Absorption Lidar (DIAL), offer a powerful set of capabilities for identifying, mapping and quantifying a wide range of emissions.

During the past few years the South Coast Air Quality Management District (SCAQMD) has been developing a fenceline monitoring program to better characterize and quantify actual gaseous emissions from a variety of stationary sources in the SCAB. As part of this program, different contractors were selected to conduct measurements of VOCs and other HAPs emissions from a variety of small sources such as gas stations, oil wells, small oil processing facilities, etc. using different ORS methods. The National Physical Laboratory (NPL) was selected to conduct validation and intercomparison work using the DIAL method. For this purpose, measurement surveys of nine different "small sources" sites such as gas stations, oil wells and storage tanks were carried out between 8th and 19th October, 2015.

Method
DIAL is a well-established and proven optical remote sensing technique that has been used by NPL in numerous emission surveys around the globe. The DIAL method allows spatially resolved concentration measurements of a target gas to be made along the path of an eye-safe laser beam transmitted into the atmosphere. During the measurement, the laser is operated alternately at two adjacent carefully chosen wavelengths. One, called the 'on-resonant wavelength', is a wavelength which is absorbed by the target species. The other, the 'off-resonant wavelength', is a wavelength which is not absorbed significantly by the target species. The difference in the absorption of the two wavelengths is related to the concentration of the gas. Spatial resolution along the beam path is obtained by pulsing the laser beam. Ultimately, emissions fluxes are determined by scanning the laser beam through the atmosphere to build up a concentration map, and combining this with measurements of the wind speed and direction.

Results and Discussion
DIAL surveys of "small sources" sites in the SCAB included measurements of a large and a medium size gas stations; observations of three urban oil fields consisting of oil wells and intermediate storage tanks; measurements of oil well drilling operations; and a survey of a small oil processing facility.

An average emission rate of about 5 kg/hr was observed from several measurements of a relatively large Costco gasoline station on the 19th of October; such emission was continuous but variable in time. On the same day a set of measurements from a smaller Vons gas station showed a lower emission rate averaged at less than 1 kg/hr.

Measurements of an oil field consistent of oil wells and tanks showed variable emission rates that were well-correlated with the tank filling and unloading cycle with lower emissions observed when the tank was unloading. The emission rates measured from a tank in an oil gathering and processing facility similarly varied by about a factor of 10 during the few hours of measurements. The highest emission rates measured from the two tanks were about 18 kg/hr and 155 kg/hr respectively. Intermittent emissions from tanks were also observed at a different oil field.

Observed emissions from oil wells appeared to be on average lower and more constant in time than the emissions from tanks. The measured emission rates from active oil wells ranged from less than 2 kg/hr

up to about 14 kg/hr. On one occasion, a part of the 92 kg/hr intermittent emission measured at an oil field on the 18th of October was most likely due to one or more oil wells.

A drill rig emission was measured on the 15th of October showing a highly variable emission rate ranging from about 2 kg/hr to 27 kg/hr. From the same oil field, consisting of oil wells and tanks, an unidentified source was measured several times from an area where no obvious potential sources could be identified on site or from satellite images. The average emission rate from this source was about 35 kg/hr quantified from the DIAL scans when this source was clearly spatially separated from other emission sources in the area. It is possible that one of the non-active plugged wells in the field was the source of the observed emissions. Further investigation is needed to confirm this theory.

In conclusion, the DIAL was quickly deployed at each agreed site, it was able to carry out measurements at one or more sites every day, independent of the meteorological conditions. DIAL measurements provided invaluable comparison and validation data for the other ORS techniques participating in the study. The DIAL was able to observe and quantify temporal variations in the emission rates for the variety of small sources as well as to identify and quantify intermittent sources.

1 INTRODUCTION

This report presents the results of a measurement campaign carried out using the National Physical Laboratory's (NPL) differential absorption lidar (DIAL) system (shown in Figure 1.1) to monitor emission rates of non-methane VOCs (referred only as VOC in the rest of the document) from small sources in Los Angeles area, USA, in October 2015. The DIAL measurements were conducted as a part of South Coast Air Quality Management District (SCAQMD) field measurements project which aimed to characterize and quantify emissions from a variety of small sources in the South Coast Air Basin (SCAB) such as gas stations, oil wells, small oil processing facilities, etc. NPL was selected to conduct validation and intercomparison work using DIAL method. Surveys of nine different sites including gas stations, oil wells and storage tanks were carried out between 8th and 19th October, 2015. The primary objective of the study was to carry out direct intercomparison measurements with other optical remote techniques of emission rates from several small sources.

A brief overview of the measurement approach and the DIAL measurement locations used during the campaign is given below. Sections 2 to 10 present summaries tables, figures and discussion of the VOC measurement results for each site. Technical details for the measurement methodology are presented in Appendix 1, which provides an overview of the DIAL technique, and discusses the calibration and validation procedures. Appendix 2 presents the results of speciation measurements of air samples using pumped absorption tubes.

Figure 1.1 NPL DIAL facility on a site.

1.1 OVERVIEW OF MEASUREMENT APPROACH

The NPL DIAL was used at seven different sites to determine VOC emission rates from different areas of each site. The sites were selected to enable comparison with other techniques and the choice of sites was agreed between project participants on a daily basis. The DIAL was quickly deployed and setup at each site and it was able to carry out measurements at one or two sites every day. Table 1.1 lists these DIAL measurement locations and provides the GPS locations for each position.

Emission rates were determined by scanning the DIAL measurement beam in a vertical plane downwind of the target sources, and measuring the total concentration of VOC in that plane. DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. A scaling factor to go from the standard DIAL VOC coefficients to the measured mixtures is then applied based on the results of absorption tube analysis as described in Appendix 2. All the VOC data presented in this report has been corrected using the appropriate scaling factors and the scaling factor uncertainties have been propagated in quadrature for all the standard deviations presented.

The logarithmic wind field profile used for the emission rate calculations (see Appendix 1) was determined using sensors mounted on the 12 m DIAL mast and the portable wind sensor that was placed on site near each measurement location. The wind direction measured from the portable and DIAL wind sensors were used to define the wind direction for the emission rate measurements. During the six measurement days the wind direction was variable but predominantly from the W/SW.

Table 1.1 Summary of DIAL measurement locations.

DIAL Location	Description	GPS Position
SS01	E. Creston Ave, Signal Hill	33° 47' 59.59" N , 118° 10' 14.41" W
SS02	E.29th St, Signal Hill	33° 48' 35.59" N , 118° 10' 30.98" W
SS03	Gardena Ave, Signal Hill	33° 48' 6.04" N , 118° 10' 7.79" W
SS04	Home Depot Car Park, Signal Hill	33° 48' 43.82" N , 118° 11' 4.44" W
SS05	Trader Joes Car Park, Long Beach	33° 45' 22.84" N , 118° 6' 25.22" W
SS06	Shopkeeper Rd, Long Beach	33° 45' 27.82" N , 118° 6' 26.72" W
SS07	Shopkeaper Rd, Long Beach	33° 45' 27.38" N , 118° 6' 26.30" W
SS08	Vons #1638 Lakewood Car Park	33° 50' 8.20" N , 118° 6' 57.70" W
SS09	Costco #1050 Lakewood Car Park	33° 51' 5.50" N , 118° 8' 12.40" W

1.2 OVERVIEW OF TABLES AND FIGURES

The lines-of-sight (LOS) used at each measurement location are shown in Figures 2.1 to 10.1. These figures also show the average wind direction measured over the full time frame during which the measurements from a given location took place. The DIAL maximum scan range depends on the atmospheric conditions, it varies from day to day and it can also change during the same day.

Some exemplar contour plots and visual representations of the emissions observed in the downwind DIAL measurements are provided. The contour plots (a1 figures) and the 3D visualizations (a2 figures) use a common colour scale (shown in the a1 figures).

Tables 2.1 to 10.1 report the emission rates determined for each scan made during each measurement location. The scan numbers are not necessarily sequential because some scans were recorded for data quality checks and also some scans may have been aborted by the operator. No valid scan has been eliminated from the report. The tables also list the locations and the LOS used for each measurement. Negative emission rate values can occur because of the random noise on a small signal and these are reported in the tables; however, in the summary Tables 2.2 through 10.2 non-physical negative results are reported as zero. The wind directions reported in the tables are from the sensor used for the

emission rate calculations. The wind speeds reported in the tables are from the DIAL wind sensor. The notes in each table are only indicative of the area measured in a specific LOS to aid the reader in visualising the general location from where the plumes are coming. Reference should be made to the results discussion for more detailed explanations.

Tables 2.2 through 10.2 are summary tables providing the mean and standard deviation of the VOC emission rates determined from each location and LOS. The standard deviation given in the tables is the standard deviation of the individual emissions from which each mean emission rate value has been determined. The standard deviation will include effects of the source variability, DIAL measurement uncertainty, tubes scaling factor uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements. Because the DIAL flux measurement depends on several different experimental conditions, the detection limit can be experimentally estimated when the measured standard deviation is similar to the measured value. The standard deviation thus defines the detection limit for that set of measurements.

2 VOC MEASURMENTS FROM E. CRESTON AVE. - OIL WELLS & TANKS

On the 8th of October DIAL measurements of oil wells and tanks at Creston Avenue in Signal Hill, CA were carried out from location SS01 with S/SE wind, as shown in Figure 2.1 and summarized in Table 2.1.

Table 2.1 Emission rate determined from SS01 on 8th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
134	SS01/LOS1	11:09	11:16	1.8	150.1	2.08	Oil Well & Tanks South of Road
135	SS01/LOS1	11:17	11:23	1.8	158.1	3.61	Oil Well & Tanks South of Road
136	SS01/LOS1	11:25	11:31	1.5	177.8	3.64	Oil Well & Tanks South of Road
138	SS01/LOS2	11:39	11:46	1.1	168.1	4.41	Oil Well & Tanks South of Road
139	SS01/LOS2	11:47	11:54	1.9	145.6	8.56	Oil Well & Tanks South of Road
140	SS01/LOS2	11:54	12:01	2.4	168.1	4.38	Oil Well & Tanks South of Road
141	SS01/LOS2	12:01	12:08	2.2	155.1	2.03	Oil Well & Tanks South of Road
142	SS01/LOS2	12:08	12:15	2.1	180.0	4.15	Oil Well & Tanks South of Road
143	SS01/LOS2	12:15	12:22	2.3	177.5	12.31	Oil Well & Tanks South of Road
144	SS01/LOS2	12:25	12:32	2.6	141.5	9.25	Oil Well & Tanks South of Road
145	SS01/LOS2	12:32	12:39	3.0	152.7	12.13	Oil Well & Tanks South of Road
146	SS01/LOS2	12:39	12:48	2.8	162.7	15.18	Oil Well & Tanks South of Road
147	SS01/LOS2	12:48	12:57	2.5	162.2	14.14	Oil Well & Tanks South of Road
148	SS01/LOS3	13:01	13:09	2.7	156.9	0.73	Downwind Oil Well North of Road
149	SS01/LOS3	13:13	13:20	3.4	155.8	-0.66	Downwind Oil Well North of Road
150	SS01/LOS3	13:20	13:27	3.2	143.1	0.55	Downwind Oil Well North of Road
151	SS01/LOS4	13:32	13:40	2.2	154.5	9.82	Oil Well & Tanks South of Road
152	SS01/LOS4	13:40	13:47	2.4	155.0	13.65	Oil Well & Tanks South of Road
153	SS01/LOS4	13:48	13:55	2.0	145.1	1.19	Oil Well & Tanks South of Road
154	SS01/LOS4	13:55	14:02	1.5	169.8	2.00	Oil Well & Tanks South of Road
155	SS01/LOS4	14:02	14:09	1.4	163.3	3.22	Oil Well & Tanks South of Road
156	SS01/LOS4	14:09	14:15	2.1	146.0	6.36	Oil Well & Tanks South of Road
157	SS01/LOS4	14:16	14:23	2.0	176.7	18.11	Oil Well & Tanks South of Road
158	SS01/LOS4	14:23	14:30	1.1	164.6	17.45	Oil Well & Tanks South of Road
159	SS01/LOS4	14:30	14:37	1.0	187.7	8.74	Oil Well & Tanks South of Road
160	SS01/LOS4	14:37	14:44	0.9	209.5	7.87	Oil Well & Tanks South of Road
161	SS01/LOS4	14:44	14:51	1.2	261.3	2.30	Oil Well & Tanks South of Road

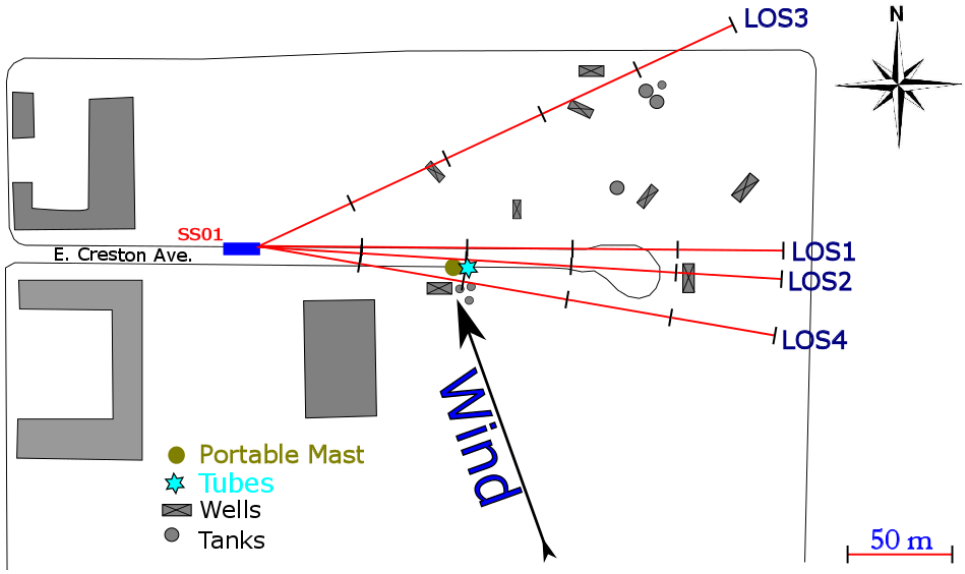

Figure 2.1 Measurement configuration for location SS01 on 8th of October.

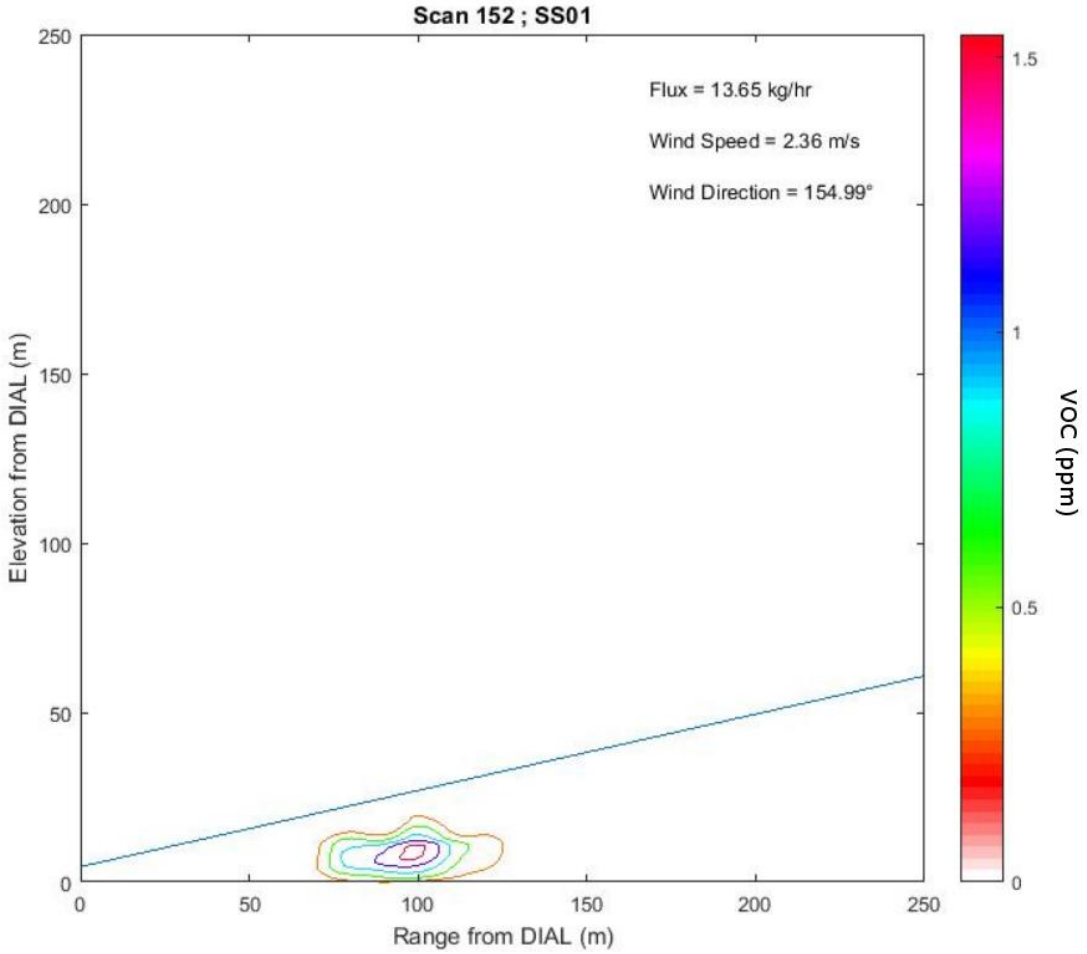

Figure 2.1a1 Observed VOC concentration for Scan 152 representing SS01/LOS4.

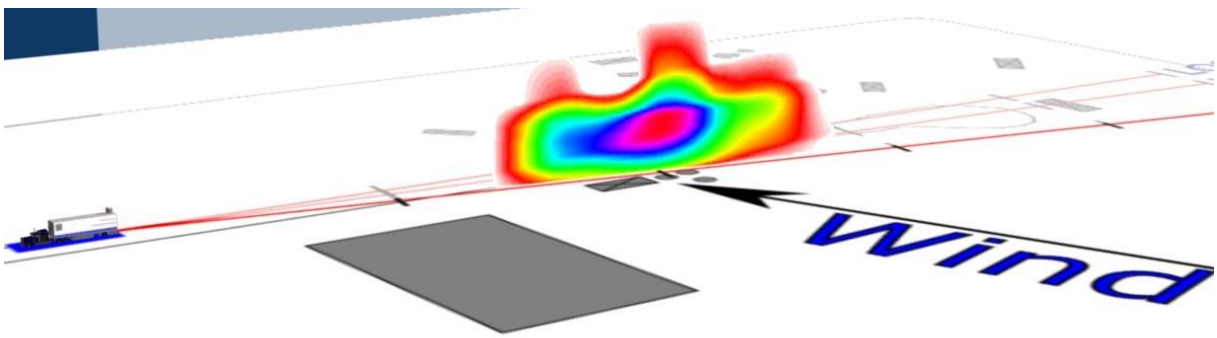

Figure 2.1a2 Visualisation of emission rate for Scan 152 representing SS01/LOS4.

2.1 LOCATION SS01 RESULTS AND DISCUSSION

Table 2.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
8-Oct	SS01/LOS1	Oil Well & Tanks South of Road	3.1	0.9	3
8-Oct	SS01/LOS2	Oil Well & Tanks South of Road	8.7	5.3	10
8-Oct	SS01/LOS3	Downwind Oil Well North of Road	0.2	0.8	3
8-Oct	SS01/LOS4	Oil Well & Tanks South of Road	8.8	6.6	10

Measurements along LOS1, LOS2 and LOS4 (see Figure 2.1) were conducted downwind of the oil well and the three tanks south of E. Creston Ave. The standard deviation of each set of measurements reported in Table 2.2 is high compared to the typical DIAL standard deviation (less than 30%) indicating a variable emission source. Figures 2.1a1 and a2 show examples of a contour plot and a 3D visualisation of the emission observed from Scan 152 (see Table 2.1). At the time of the DIAL measurements, SCAQMD also operated a FLIR camera, which was used to relate the observed emissions from vents of one of the tank with the movement of a product in the tank. Lower emissions were observed when the tank was unloading, presumably because the vent was under negative pressure. Figure 2.2 shows the time series of the measured VOC emission rates that ranged from 1.2 kg/hr to 18.1 kg/hr during the four hours observation period.

Measurements conducted along LOS3 (see Figure 2.1) were downwind of the oil well north of E. Creston Ave. and showed no significant emission.

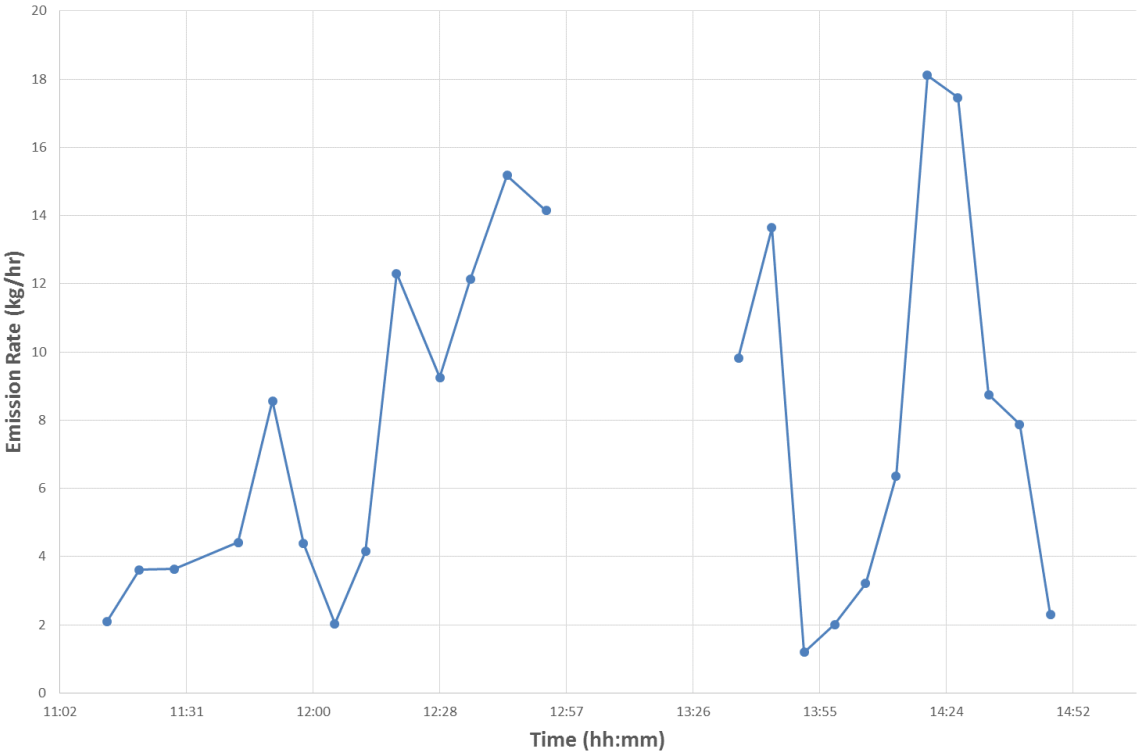

Figure 2. 2 Time series VOC emission rate measured from location SS01/LOS1, LOS2 and LOS4.

3 VOC MEASURMENTS FROM E. 29TH ST - STORAGE TANK OF WATER PROCESSING FACILITY

On the 9th of October measurements of emissions from an oil gathering station were conducted from location SS02 with a variable wind direction, mainly easterly in the morning with low wind speed and westerly in the afternoon with stronger wind speed. A summary of all measurements conducted at this location is presented in Table 3.1, and Figure 3.1 depicts the measurement setup.

Table 3.1 Emission rate determined from SS02 on 9th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
163	SS02/LOS1	10:21	10:31	0.4	116.5	-	Downwind Row of Tanks - Low WS
164	SS02/LOS1	10:41	10:51	0.9	54.8	5.22	Downwind Row of Tanks
165	SS02/LOS1	10:51	11:02	0.7	72.8	5.30	Downwind Row of Tanks
166	SS02/LOS1	11:02	11:12	0.6	33.5	12.36	Downwind Row of Tanks
167	SS02/LOS1	11:12	11:22	0.5	34.0	1.54	Downwind Row of Tanks
168	SS02/LOS1	11:23	11:33	0.6	36.0	25.90	Downwind Row of Tanks
171	SS02/LOS1	11:57	12:08	0.8	221.9	132.89	Downwind SW Corner Tank
172	SS02/LOS1	12:09	12:20	1.4	333.8	-	Wind Direction Almost Parallel to LOS
173	SS02/LOS1	12:20	12:31	1.0	311.2	26.58	Downwind SW Corner Tank
174	SS02/LOS1	12:32	12:43	1.6	294.1	40.04	Downwind SW Corner Tank
175	SS02/LOS1	12:43	12:54	2.1	317.0	15.59	Downwind SW Corner Tank
176	SS02/LOS1	12:54	13:06	1.6	304.5	38.74	Downwind SW Corner Tank
177	SS02/LOS1	13:06	13:17	1.4	270.8	40.27	Downwind SW Corner Tank
178	SS02/LOS1	13:17	13:28	1.8	306.8	74.79	Downwind SW Corner Tank
179	SS02/LOS1	13:29	13:40	1.7	298.2	17.55	Downwind SW Corner Tank
180	SS02/LOS1	13:40	13:51	2.5	291.8	49.04	Downwind SW Corner Tank
182	SS02/LOS1	14:05	14:16	3.7	284.4	90.56	Downwind SW Corner Tank
183	SS02/LOS1	14:17	14:28	3.3	288.0	107.73	Downwind SW Corner Tank
184	SS02/LOS1	14:28	14:39	3.2	295.3	155.11	Downwind SW Corner Tank
185	SS02/LOS1	14:40	14:51	3.5	311.8	105.71	Downwind SW Corner Tank

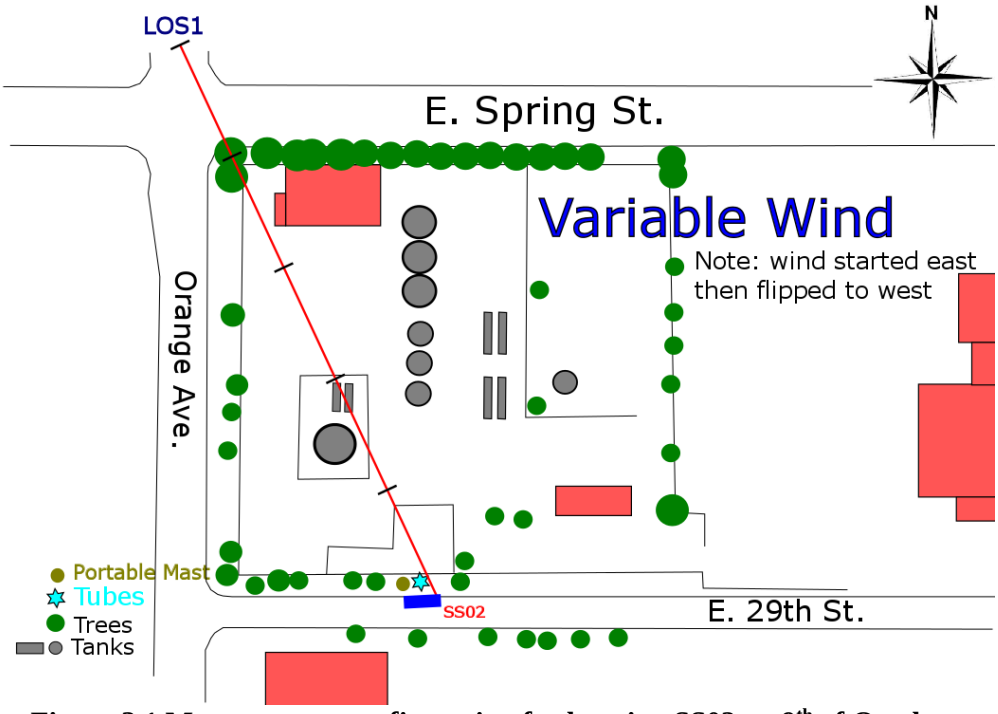

Figure 3.1 Measurement configuration for location SS02 on 9th of October.

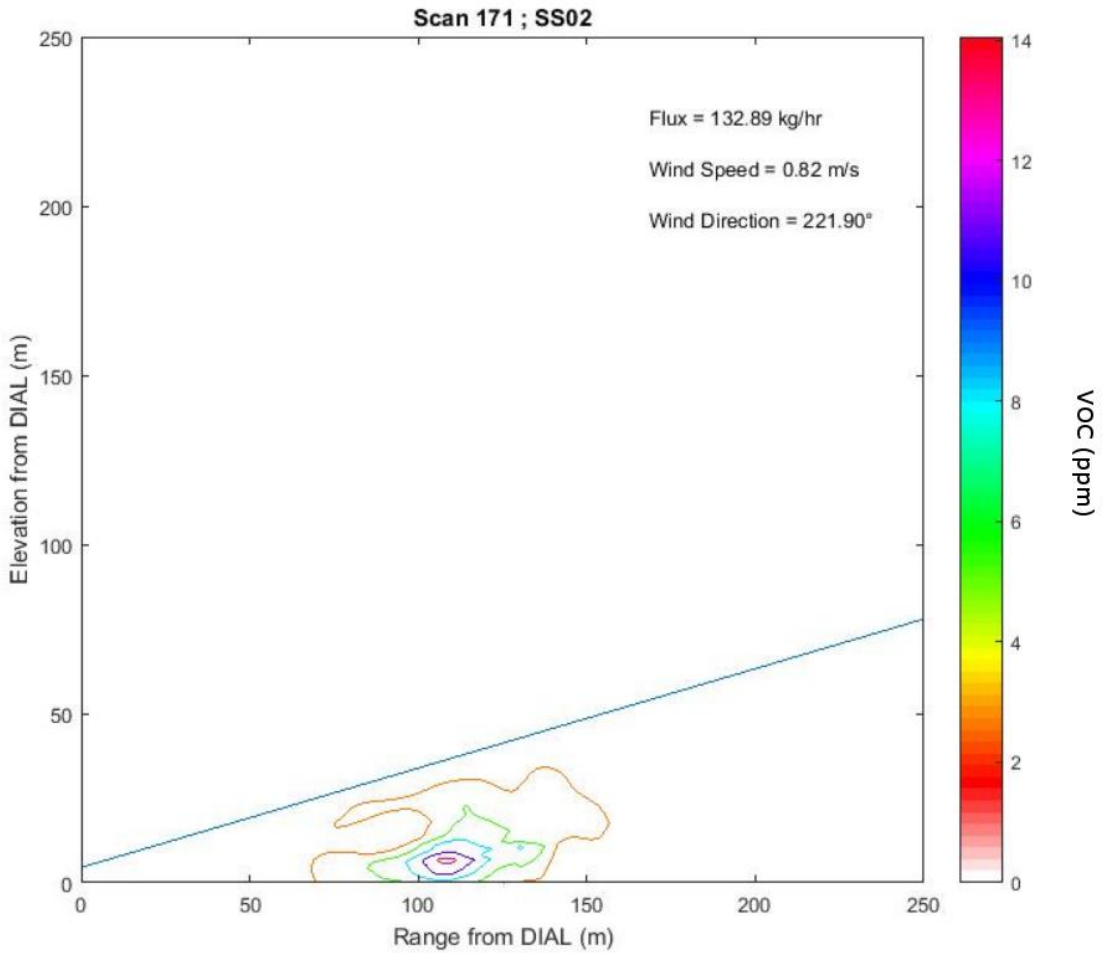

Figure 3.1a1 Observed VOC concentration for Scan 171 representing SS02/LOS1.

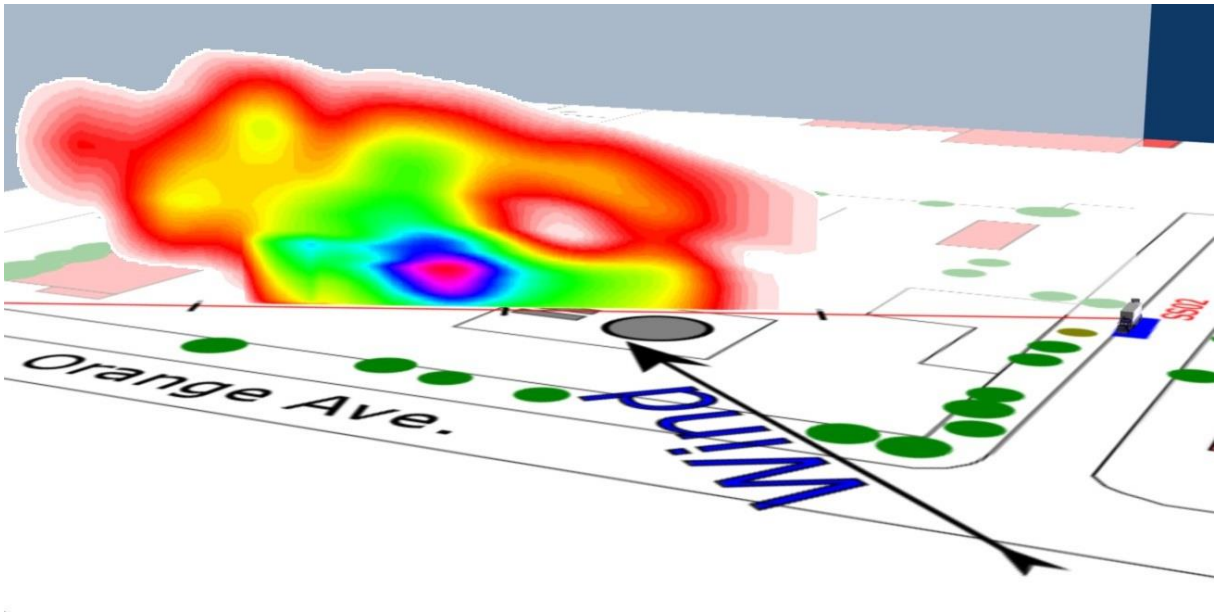

Figure 3.1a2 Visualisation of emission rate for Scan 171 representing SS02/LOS1.

3.1 LOCATION SS02 RESULTS DISCUSSION

DIAL measurements conducted on October 9th with easterly wind direction were downwind of a row of tanks (see Figure 3.1) and showed highly variable emission rates, which are summarized in Table 3.2.

Table 3.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
9-Oct	SS02/LOS1	Downwind Row of Tanks	10.1	9.7	5
9-Oct	SS02/LOS1	Downwind SW Corner Tank	68.8	46.3	13

The measurements carried out with the westerly wind were directly downwind of the tank in the SW portion of the facility (see Figure 3.1) and they showed a variable emission rate ranging from 15.6 kg/hr to 155.1 kg/hr. Figures 3.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 171 (see Table 3.1).The angle between LOS1 and the wind direction in some cases was relatively small and therefore the uncertainty on the emission could be higher than normal. Nonetheless, no correlation between the wind direction angles and the measured emission rates was observed, suggesting that the emission source was variable in time. Figure 3.2 shows the time series of the VOC emission rate from the SW corner tank. At the time of the DIAL measurements, SCAQMD also operated a FLIR camera, which observed emissions from the roof of the tank, probably due to a leaky valve.

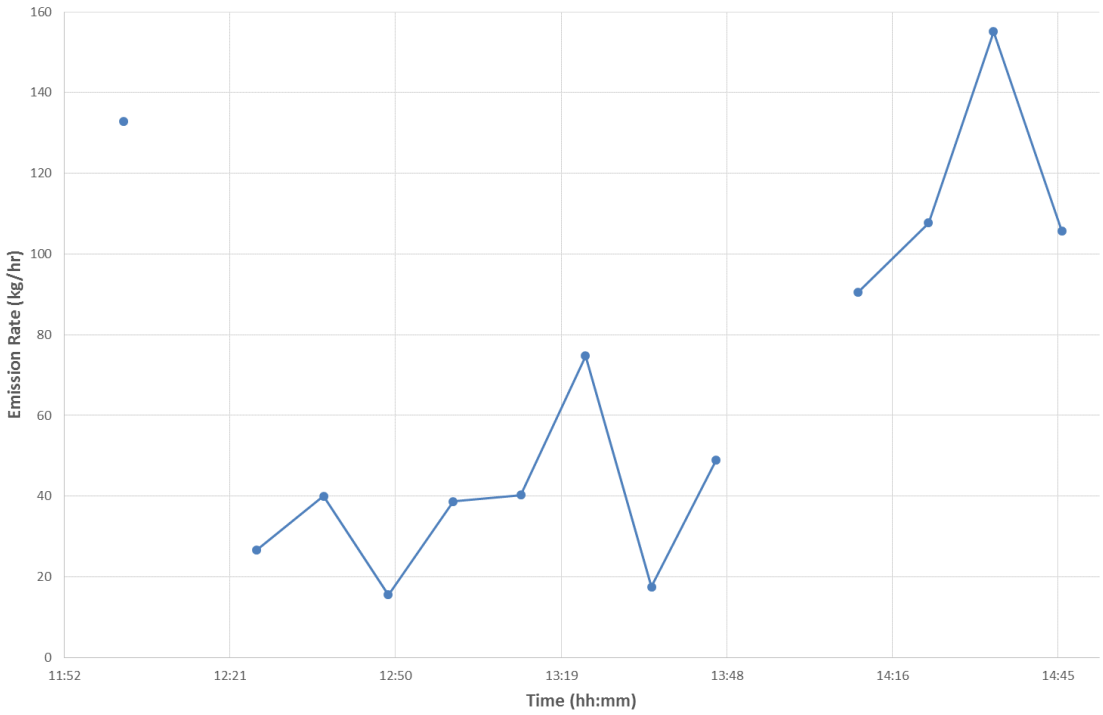

Figure 3. 2 Time series of VOC emission rate from SW corner tank.

4 VOC MEASURMENTS FROM GARDENA AVE. - OIL WELLS AND TANKS

On the 14th of October DIAL measurements of an area that included some of the oil field observed on October 9th were carried out from location SS03 with a north-westerly wind, as shown in Figure 4.1 and summarized in Table 4.1.

Table 4.1 Emission rate determined from SS03 on 14th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
240	SS03/LOS1	15:01	15:09	3.4	278.1	1.01	Downwind Wells West of Gardena Ave
241	SS03/LOS1	15:09	15:18	3.2	292.4	0.98	Downwind Wells West of Gardena Ave
242	SS03/LOS1	15:18	15:26	2.9	294.9	2.27	Downwind Wells West of Gardena Ave
243	SS03/LOS1	15:27	15:35	3.7	306.6	1.26	Downwind Wells West of Gardena Ave
244	SS03/LOS1	15:36	15:53	2.9	296.0	1.02	Downwind Wells West of Gardena Ave
245	SS03/LOS1	15:53	16:09	3.0	294.8	1.93	Downwind Wells West of Gardena Ave
246	SS03/LOS1	16:09	16:26	2.9	302.2	1.40	Downwind Wells West of Gardena Ave
247	SS03/LOS1	16:26	16:43	3.3	292.2	2.41	Downwind Wells West of Gardena Ave
249	SS03/LOS2	16:49	17:02	2.3	281.2	5.81	Wells South of E. Burnett St.
250	SS03/LOS2	17:02	17:16	2.9	294.2	6.28	Wells South of E. Burnett St.
250	SS03/LOS2					13.80	Well North of E Creston Ave
251	SS03/LOS2	17:16	17:29	2.6	304.1	4.21	Wells South of E. Burnett St.
251	SS03/LOS2					25.52	Well and Tank North of E Creston Ave

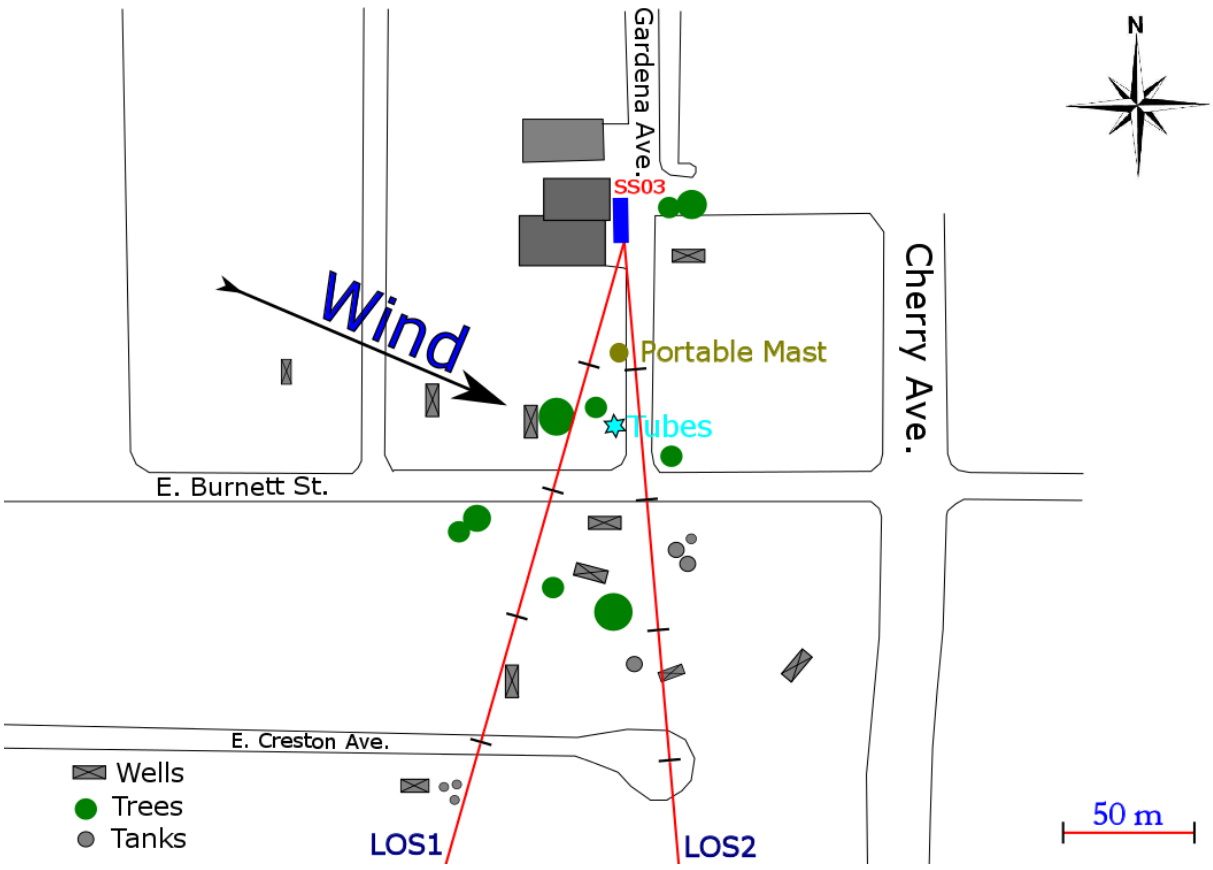

Figure 4.1 Measurement configuration for location SS03 on 14th of October.

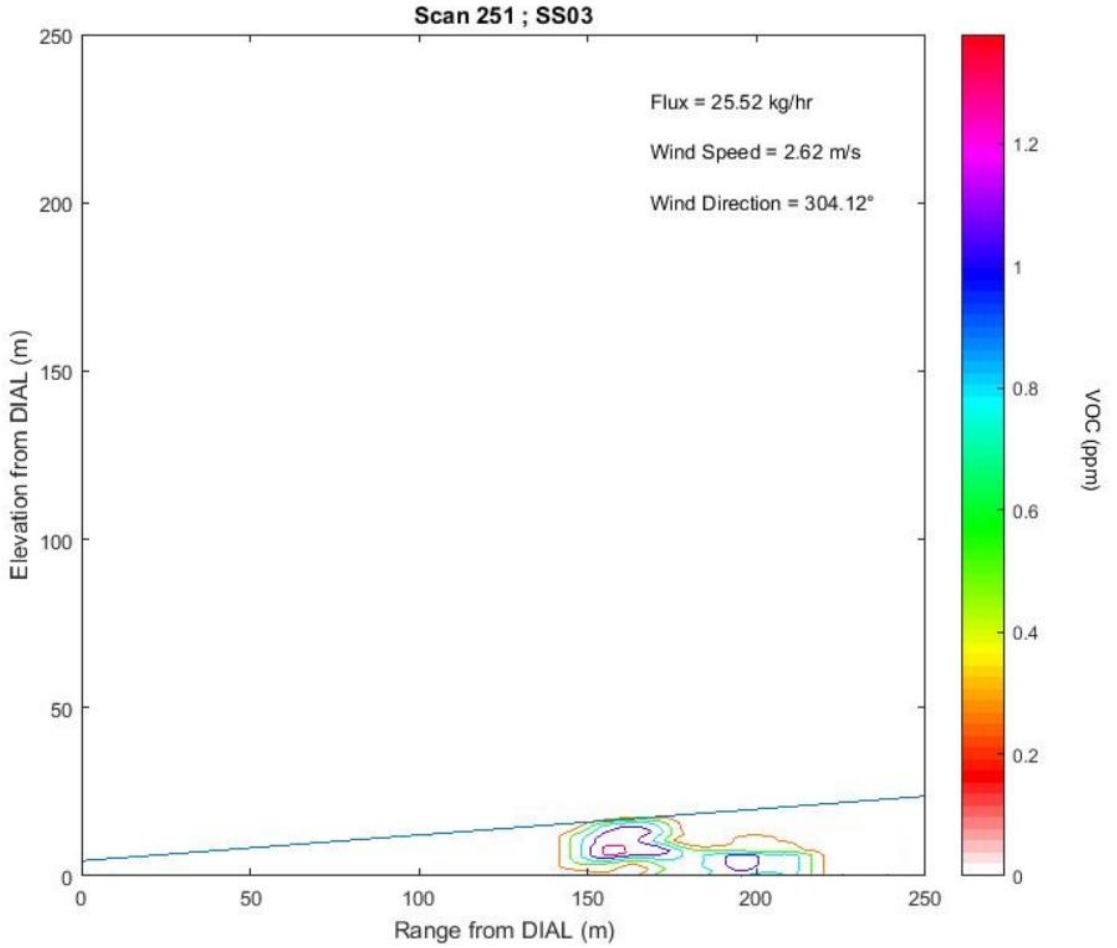

Figure 4.1a1 Observed VOC concentration for Scan 251 representing SS03/LOS2 over the 150-250 m range from the DIAL.

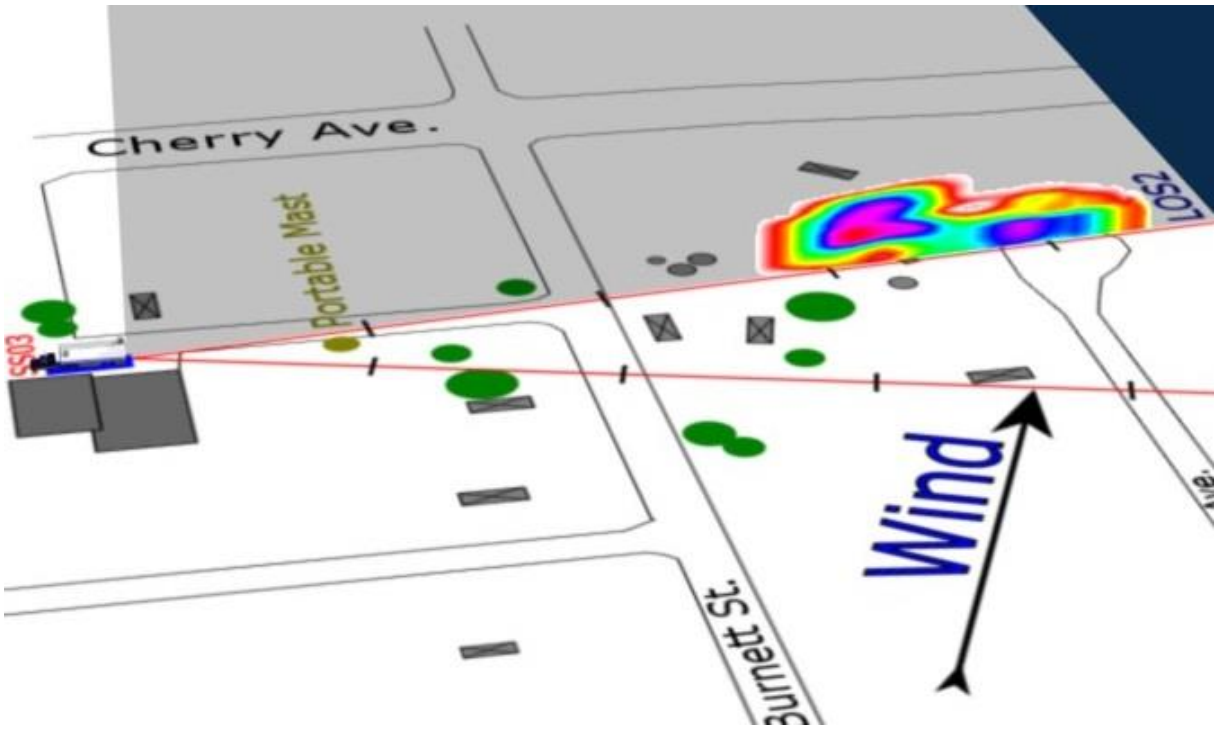

Figure 4.1a2 Visualisation of emission rate for Scan 251 representing SS03/LOS2 over the 150-250 m range from the DIAL.

4.1 LOCATION SS03 RESULTS DISCUSSION

Scans conducted along LOS1 were downwind of three wells west of Gardena Avenue and north of E. Burnett Street. The average emission rate was relatively small, 1.5 ± 0.6 kg/hr as reported in Table 4.2.

Table 4.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
14-Oct	SS03/LOS1	Downwind Wells West of Gardena Ave	1.5	0.6	8
14-Oct	SS03/LOS2	Wells South of E. Burnett St.	5.4	1.2	3
14-Oct	SS03/LOS2	Well North of E Creston Ave	13.8	-	1
14-Oct	SS03/LOS2	Well and Tank North of E Creston Ave	25.5	-	1

Measurements along LOS2 and data analysis range up to 150 m from the DIAL were downwind of the two wells south of E. Burnett Street. The average emission rate was 5.4 ± 1.2 kg/hr. The analysis of Scan 250 in the 150-250 m range from the DIAL showed a plume at about 200 m from the DIAL that could be associated to an emission from the well north of E. Creston Avenue next to LOS1 line in Figure 4.1. The emission rate from this source was 13.8 kg/hr. The analysis of Scan 251 in the 150-250 m range from the DIAL showed two plumes, one at about 200 m from the DIAL like in the case of Scan 250 associated to a well emission and the other one at about 160 m from the DIAL that could be associated to an emission from the tank north of E. Creston Avenue. Figures 4.1a1 and a2 show a contour plot and a 3D visualisation of the two plumes observed from Scan 251 in the 150-250 m range from the DIAL. The emission rate from these two sources was 25.5 kg/hr.

5 VOC MEASURMENTS FROM HOME DEPOT PARKING LOT - OIL WELLS, DRILLING RIG & TANKS

On the 15th of October DIAL measurements of an oil field consisting of oil wells and tanks were made from the Home Depot parking lot (location SS04 on Figure 5.1) with mainly a southerly wind which turned to west in the afternoon, as shown in Figure 5.1 and summarized in Table 5.1.

Table 5.1 Emission rate determined from SS04 on 15th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
253	SS04/LOS1	12:49	12:57	3.1	210.4	2.28	Downwind Drill Rig
253	SS04/LOS1					20.60	Including Unknown Source 200-250 m
254	SS04/LOS1	12:57	13:05	3.9	193.5	26.90	Downwind Drill Rig
255	SS04/LOS1	13:05	13:13	4.1	197.9	8.86	Downwind Drill Rig
256	SS04/LOS1	13:13	13:21	4.0	186.6	21.17	Downwind Drill Rig
257	SS04/LOS2	13:30	13:43	3.9	213.5	4.92	Downwind Drill Rig & Tanks
257	SS04/LOS2					25.87	Including Unknown Source 180-220 m
258	SS04/LOS3	13:52	14:05	4.2	202.2	10.02	Downwind Drill Rig & Tanks
259	SS04/LOS3	14:05	14:18	4.2	204.5	24.46	Downwind Drill Rig & Tanks
260	SS04/LOS3	14:19	14:32	4.5	210.7	10.18	Downwind Drill Rig & Tanks
261	SS04/LOS3	14:32	14:46	4.4	212.5	11.90	Downwind Drill Rig & Tanks
261	SS04/LOS3					42.60	Including Unknown Source 190-210 m
262	SS04/LOS4	14:59	15:13	4.1	197.3	1.71	Downwind East Wells
263	SS04/LOS4	15:14	15:27	3.9	214.5	2.15	Downwind East Wells
264	SS04/LOS4	15:27	15:40	3.0	218.3	1.85	Downwind East Wells
265	SS04/LOS4	15:41	15:54	3.6	279.6	17.39	Downwind All Wells & Tanks
265	SS04/LOS4					34.19	Unknown Source at About 250m
266	SS04/LOS4	15:54	16:07	4.3	282.1	24.27	Downwind All Wells & Tanks
267	SS04/LOS4	16:08	16:23	5.0	282.4	18.71	Downwind All Wells & Tanks
268	SS04/LOS4	16:23	16:38	4.8	284.1	20.78	Downwind All Wells & Tanks
269	SS04/LOS4	16:39	16:54	4.3	273.5	19.05	Downwind All Wells & Tanks
269	SS04/LOS4					33.88	Unknown Source at About 270m
270	SS04/LOS5	16:58	17:12	5.0	290.1	18.39	Downwind West Wells & Tanks
271	SS04/LOS5	17:13	17:19	4.5	286.7	17.02	Downwind West Wells & Tanks
271	SS04/LOS5					37.33	Unknown Source at About 250m
272	SS04/LOS5	17:20	17:26	4.1	291.3	21.21	Downwind West Wells & Tanks
272	SS04/LOS5					37.16	Unknown Source at About 260m

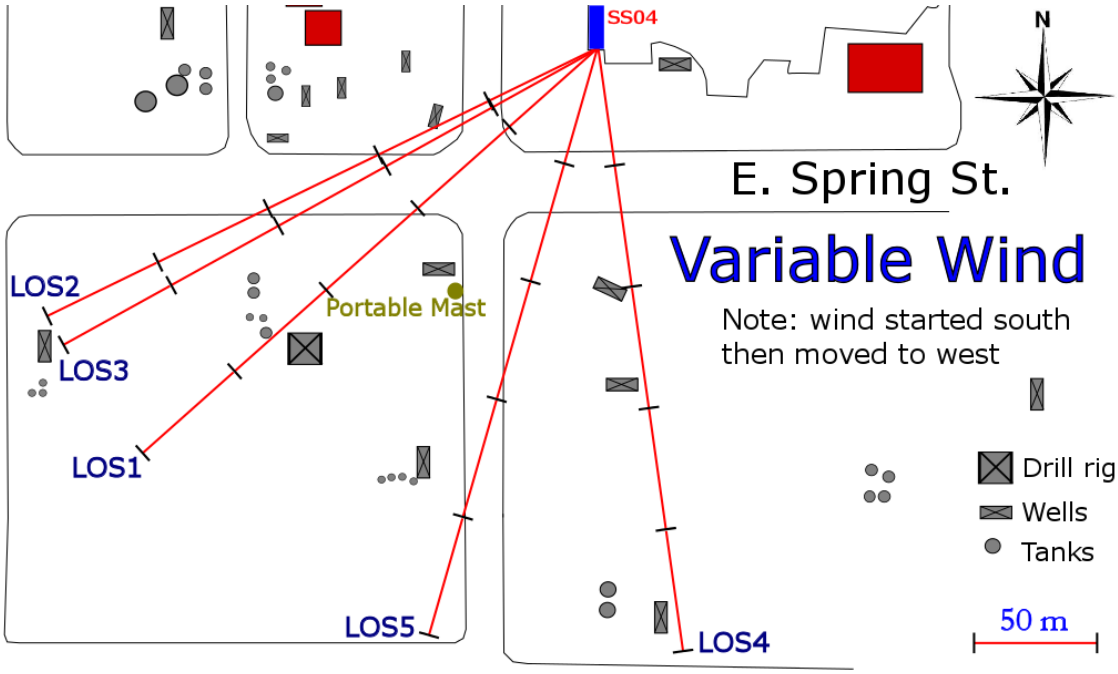

Figure 5.1 Measurement configuration for location SS04 on 15th of October.

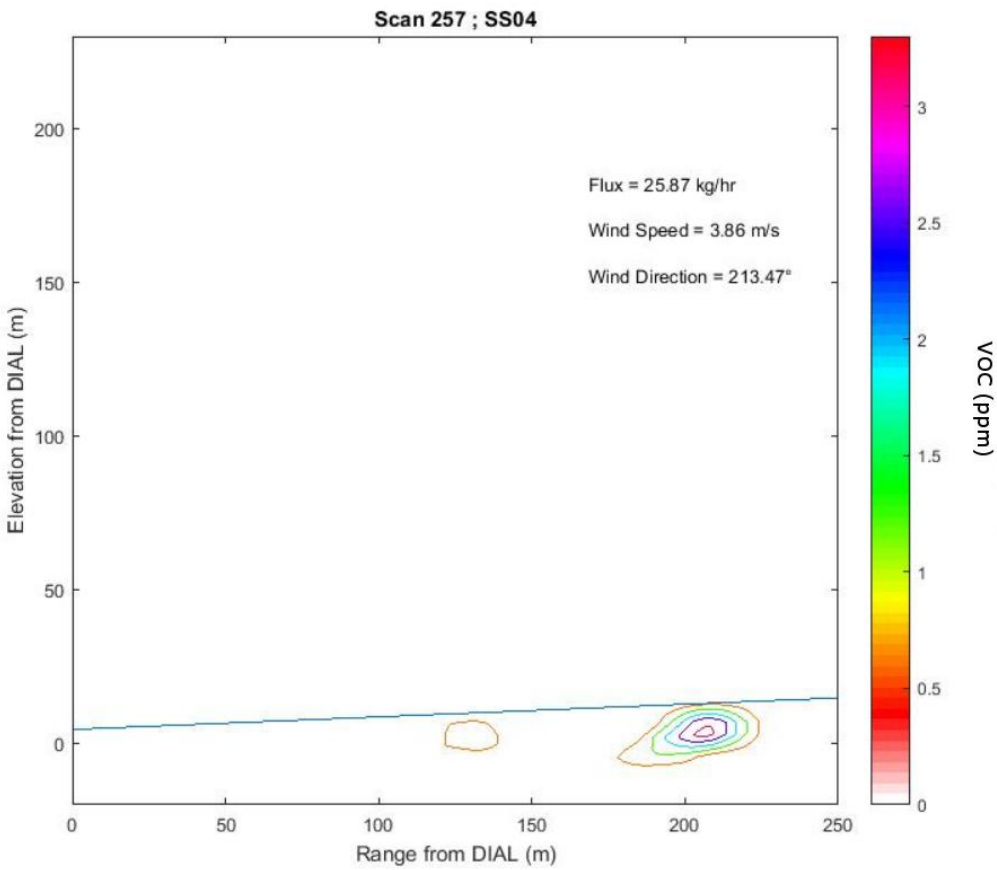

Figure 5.1a1 Observed VOC concentration for Scan 257 representing SS04/LOS2.

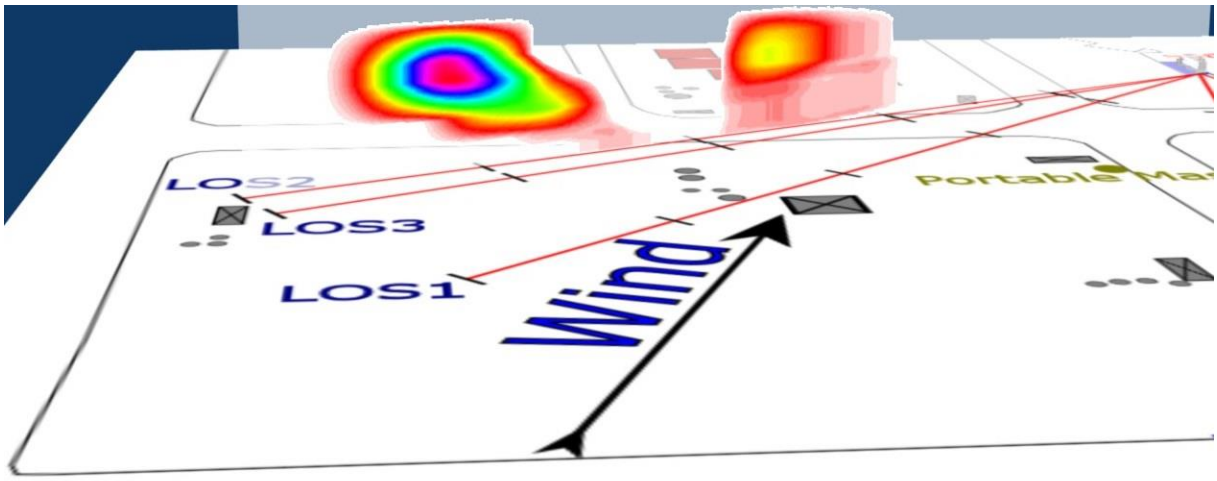

Figure 5.1a2 Visualisation of emission rate for Scan 257 representing SS04/LOS2.

5.1 LOCATION SS04 RESULTS DISCUSSION

Scans along LOS1 were directly downwind of the drill rig. The average emission rate was 14.8 kg/hr as shown in Table 5.2, with the standard deviation of 11.3 kg/hr, which is higher than the typical standard deviation of less than 30% for DIAL measurements, indicating a variable emission source. Measurements along LOS2 and LOS3 were downwind of the drill rig and also a few tanks just north of it. The emission rate was variable showing a similar pattern as the measurements along LOS1 indicating that likely most of the emission measured from LOS2 and LOS3 was due to the drill rig.

Table 5.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
15-Oct	SS04/LOS1	Downwind Drill Rig	14.8	11.3	4
15-Oct	SS04/LOS2	Downwind Drill Rig & Tanks	4.9	-	1
15-Oct	SS04/LOS3	Downwind Drill Rig & Tanks	14.1	7.0	4
15-Oct	SS04/LOS4	Downwind East Wells	1.9	0.3	3
15-Oct	SS04/LOS4	Downwind All Wells & Tanks	20.0	3.1	5
15-Oct	SS04/LOS5	Downwind West Wells & Tanks	18.9	2.6	3
15-Oct	SS04/LOS4/5	Downwind Unknown Source	35.6	1.9	4

Scans 253 (along LOS1), 257 (along LOS2) and 261 (along LOS3) detected a plume from an unknown source approximately in the 200 m region from the DIAL. Figures 5.1a1 and a2 show a contour plot and a 3D visualisation of the plumes from the drill rig and the unknown source observed from Scan 257. Considering the wind direction at the time of these measurements, the unknown source should be located in the SW corner area of the map in Figure 5.1. The emission from this source after subtracting the emission from the drill rig was approximately between 20 kg/hr and 30 kg/hr.

Measurements along LOS4 with a southerly wind were downwind of the easterly wells located near LOS4 and the average emission rate was 1.9 ± 0.3 kg/hr. The wind then shifted to the west giving an opportunity to measure all the tanks and wells west of LOS4 including the drill rig although there was no drilling activity observed during this set of measurements. The average emission rate was

20.0 ± 3.1 kg/hr and it was fairly stable in comparison with the earlier measurements made along LOS1, LOS2 and LOS3 while the drilling was ongoing.

The set of scans made along LOS5 with a westerly wind were downwind of the west wells and tanks. The average emission rate was 18.9 ± 2.6 similar to the emission measured along LOS4.

Scans 265 (along LOS4) and 269, 271, 272 (along LOS5) also detected a plume from an unknown source approximately in the 250 m region from the DIAL. This is consistent with an unknown source located in the SW corner area of the map in Figure 5.1 as measured from the three scans along LOS1, LOS2 and LOS3. The average emission rate measured from the four scans along LOS4 and LOS5 was 35.6 ± 1.9 kg/hr.

6 VOC MEASURMENTS FROM TRADER JOES PARKING LOT - OIL WELLS & TANKS

Table 6.1 Emission rate determined from SS05 on 18th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
274	SS05/LOS1	10:21	10:27	1.5	197.1	14.80	Downwind Tanks & 2 South Wells
275	SS05/LOS1	10:33	10:39	0.7	228.1	5.83	Downwind Tanks & 2 South Wells
276	SS05/LOS1	10:40	10:48	1.6	214.5	14.54	Downwind Tanks & 2 South Wells
277	SS05/LOS1	10:51	11:01	1.3	212.6	11.34	Downwind Tanks & 2 South Wells
278	SS05/LOS1	11:02	11:12	1.0	223.7	8.28	Downwind Tanks & 2 South Wells
279	SS05/LOS1	11:12	11:22	1.2	229.3	9.27	Downwind Tanks & 2 South Wells
280	SS05/LOS1	11:23	11:34	1.6	230.9	15.43	Downwind Tanks & 2 South Wells
281	SS05/LOS2	11:50	11:58	1.5	216.7	10.61	Downwind 2 South Wells
282	SS05/LOS2	11:59	12:13	1.4	215.0	8.95	Downwind 2 South Wells
283	SS05/LOS2	12:13	12:22	1.7	222.6	11.90	Downwind 2 South Wells
284	SS05/LOS2	12:22	12:30	1.9	229.2	14.94	Downwind 2 South Wells

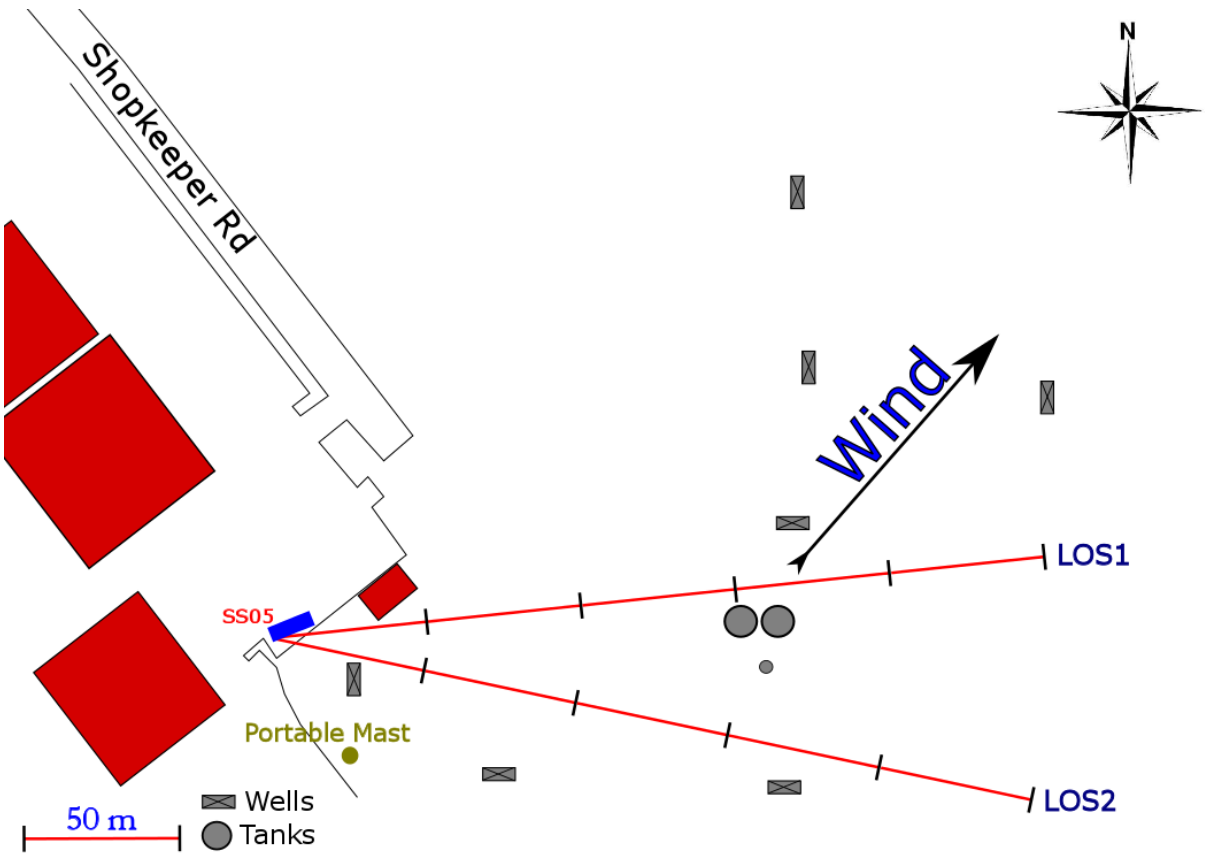

Figure 6.1 Measurement configuration for location SS05 on 18th of October.

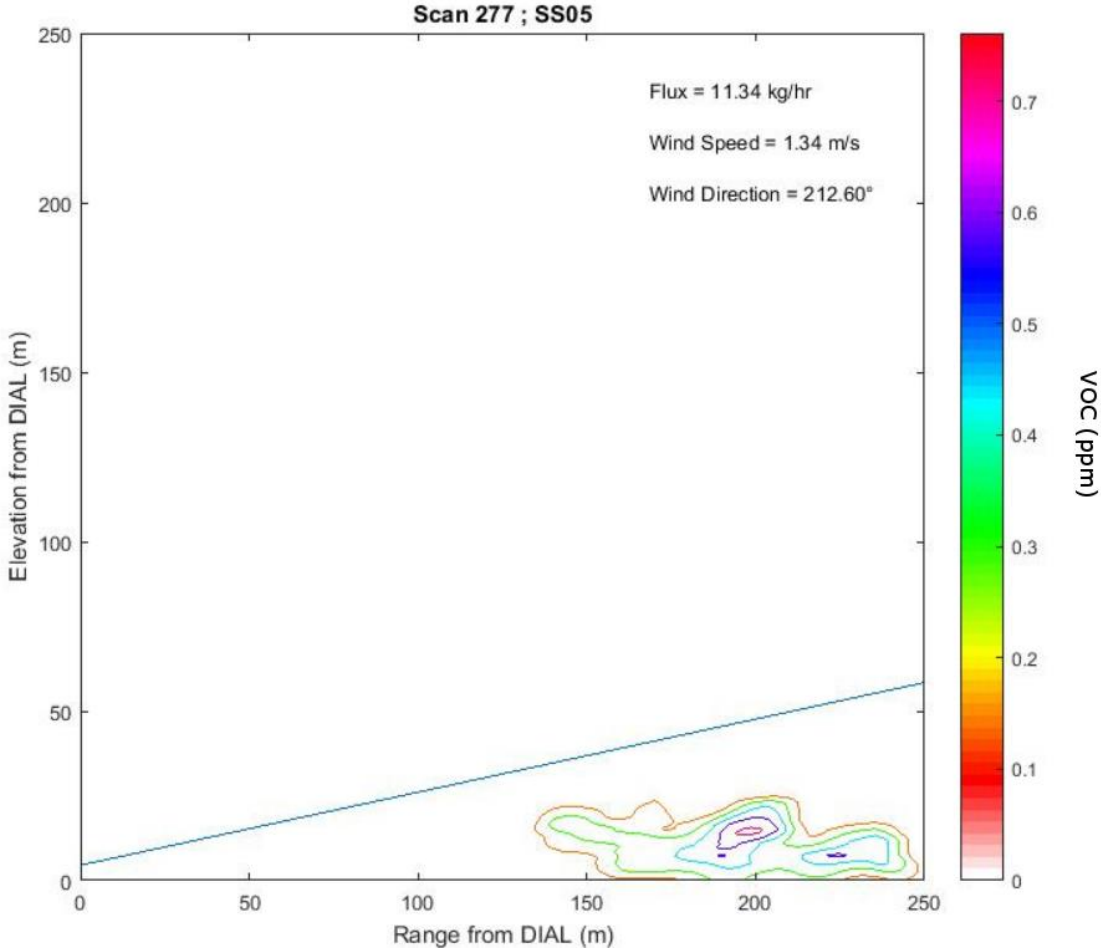

Figure 6.1a1 Observed VOC concentration for Scan 277 representing SS05/LOS1.

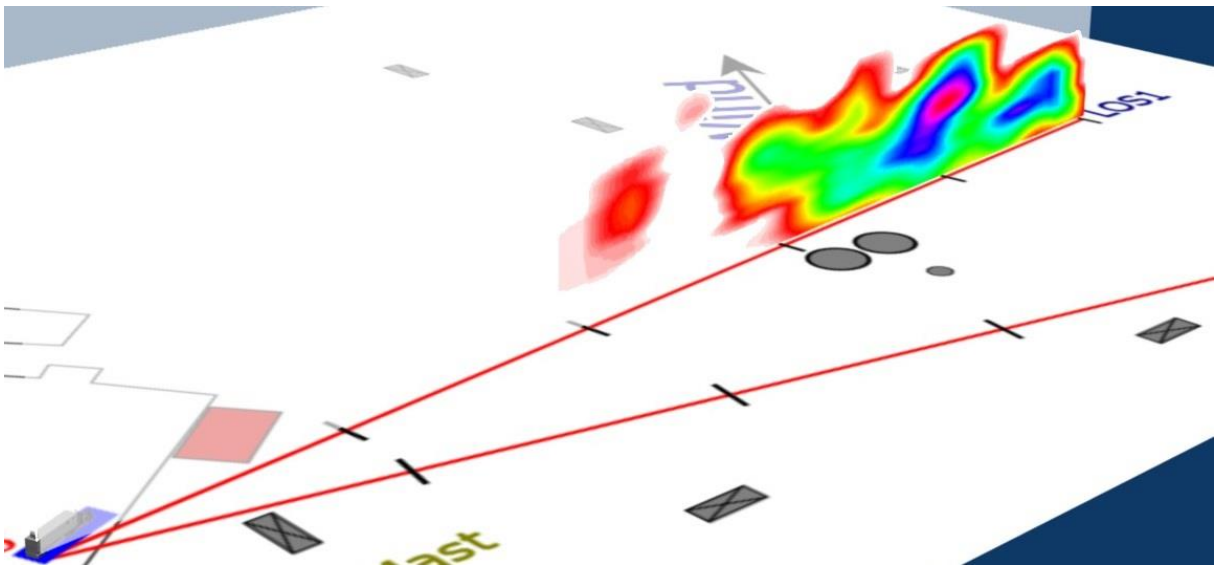

Figure 6.1a2 Visualisation of emission rate for Scan 277 representing SS05/LOS1.

6.1 LOCATION SS05 RESULTS DISCUSSION

Table 6.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
18-Oct	SS05/LOS1	Downwind Tanks & 2 South Wells	11.4	3.8	7
18-Oct	SS05/LOS2	Downwind 2 South Wells	11.6	2.7	4

On the 18th Oct measurements were carried out from location SS05 with a south-westerly wind, as shown in Figure 6.1 and summarized in Table 6.1. Scans along LOS1 were downwind of two south wells and a set of storage tanks and the average emission rate was 11.4 ± 3.8 kg/hr. Figures 6.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 277.

Measurements along LOS2 were downwind of only the two south well and the average emission rate was 11.6 ± 2.7 kg/hr. This compares very well with the emission measured along LOS1 indicating that the two wells were the main emission sources.

7 VOC MEASURMENTS FROM SHOPKEEPER RD. - OIL WELLS & TANKS

Table 7.1 Emission rate determined from SS06 on 18th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
286	SS06/LOS1	13:13	13:20	1.9	219.4	7.14	Tanks & Well N of Westminster Blvd.
286	SS06/LOS1					0.70	Well South of Westminster Blvd.
287	SS06/LOS1	13:23	13:32	1.5	244.4	9.53	Tanks & Well N of Westminster Blvd.
287	SS06/LOS1					-0.59	Well South of Westminster Blvd.
288	SS06/LOS1	13:32	13:42	1.5	243.6	11.21	Tanks & Well N of Westminster Blvd.
288	SS06/LOS1					0.13	Well South of Westminster Blvd.
289	SS06/LOS1	13:42	13:50	1.6	173.2	-	Wind Direction Almost Parallel to LOS

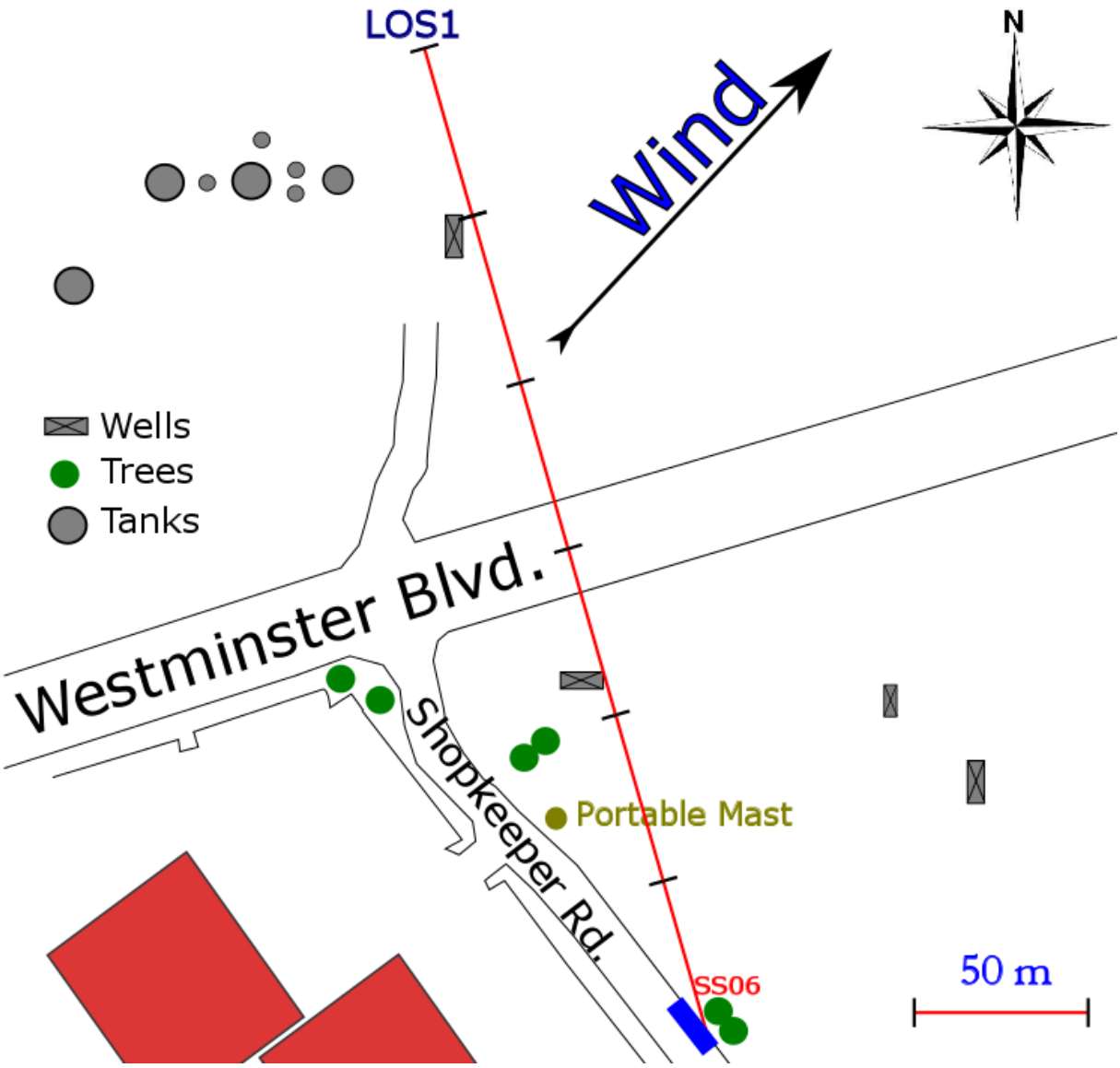

Figure 7.1 Measurement configuration for location SS06 on 18th of October.

7.1 LOCATION SS06 RESULTS DISCUSSION

Table 7.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
18-Oct	SS06/LOS1	Tanks & Well N of Westminster Blvd.	9.3	2.2	3
18-Oct	SS06/LOS1	Well South of Westminster Blvd.	0.1	0.6	3

On the 18th Oct measurements were also made from location SS06 with a south-westerly wind, as shown in Figure 7.1 and summarized in Table 7.1. Scans along LOS1 and an analysis range up 150 m from the DIAL were downwind the well south of Westminster Boulevard and no emission was detected above the DIAL detection limit.

Measurements along LOS1 with an analysis range above 200 m from the DIAL were downwind of the well and set of tanks north of Westminster Boulevard. The average emission rate was 9.3 ± 3.8 kg/hr as reported in Table 7.2.

8 VOC MEASURMENTS FROM SHOPKEEPER RD. - OIL WELLS & TANKS

Table 8.1 Emission rate determined from SS07 on 18th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
290	SS07/LOS1	14:16	14:25	2.4	182.9	19.65	Downwind Wells & Tanks
291	SS07/LOS1	14:25	14:33	2.5	219.0	13.67	Downwind Wells & Tanks
292	SS07/LOS1	14:34	14:42	2.3	228.3	12.83	Downwind Wells & Tanks
293	SS07/LOS1	14:42	14:50	2.5	190.9	12.64	Downwind Wells & Tanks
294	SS07/LOS1	14:50	15:01	3.2	180.7	16.78	Downwind Wells & Tanks
295	SS07/LOS2	15:10	15:16	2.3	206.8	92.04	Downwind Southern Wells & Tanks
296	SS07/LOS2	15:17	15:24	2.8	208.3	36.56	Downwind Southern Wells & Tanks
297	SS07/LOS2	15:24	15:31	2.8	231.2	14.78	Downwind Southern Wells & Tanks
298	SS07/LOS2	15:31	15:38	3.4	230.1	17.57	Downwind Southern Wells & Tanks

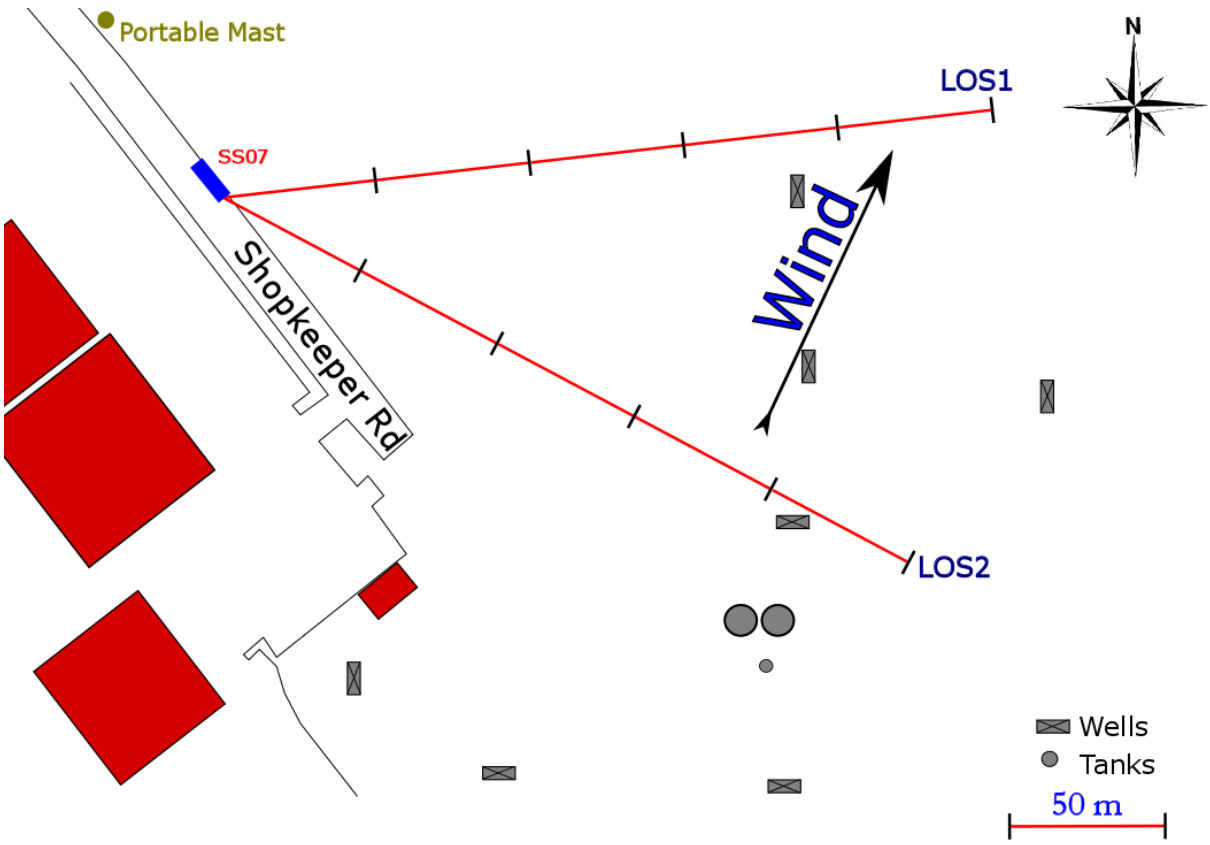

Figure 8.1 Measurement configuration for location SS07 on 18th of October.

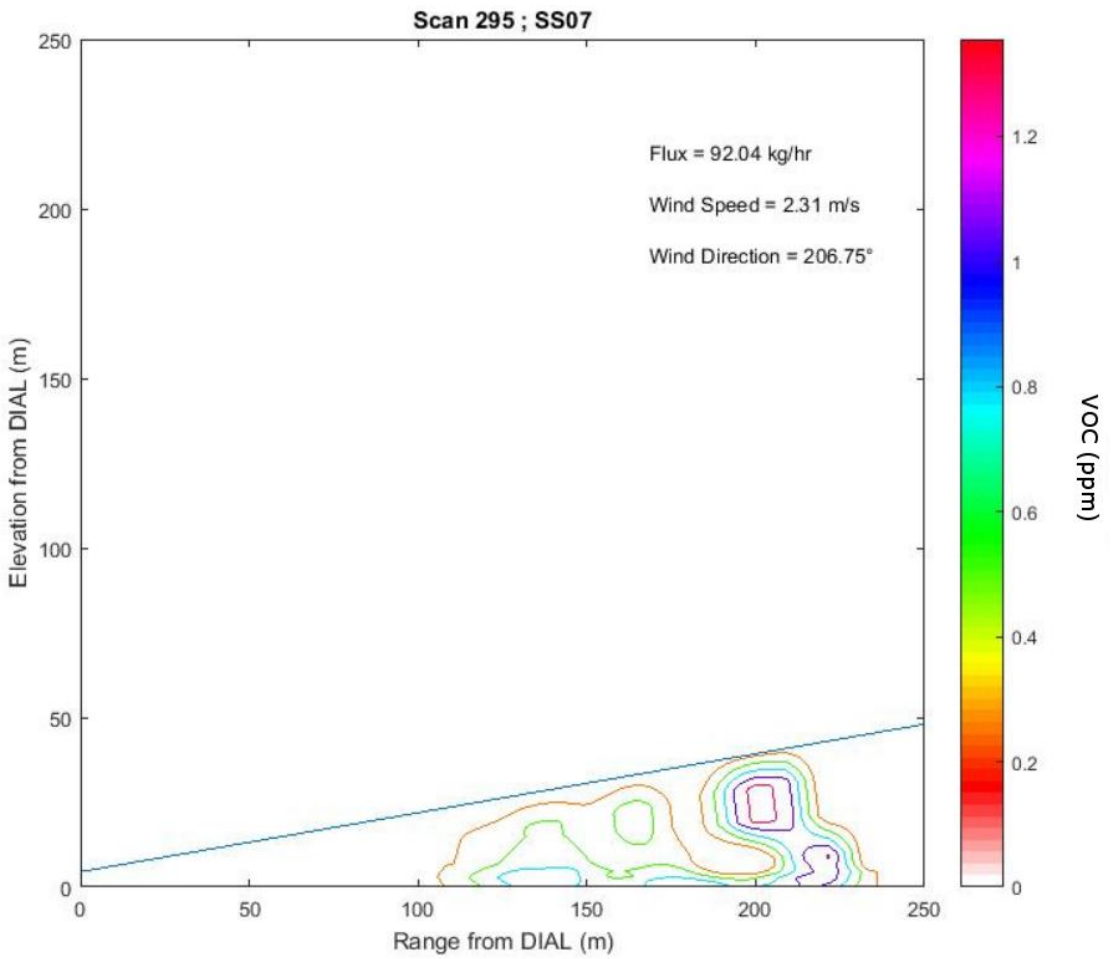

Figure 8.1a1 Observed VOC concentration for Scan 295 representing SS07/LOS2.

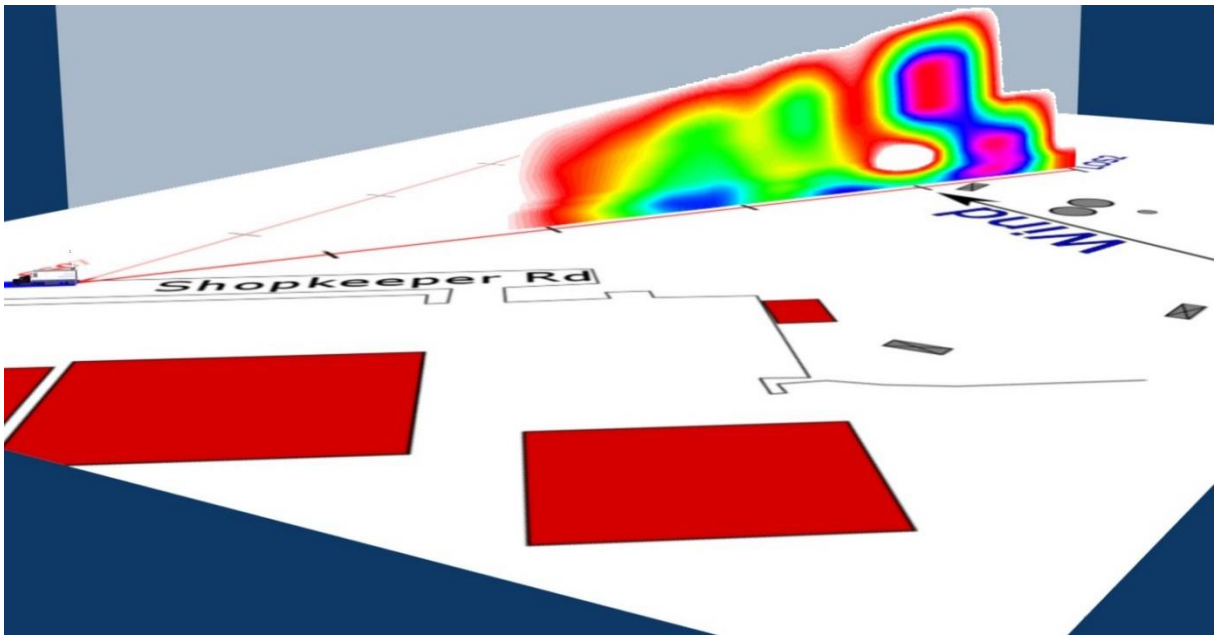

Figure 8.1a2 Visualisation of emission rate for Scan 295 representing SS07/LOS2.

8.1 LOCATION SS07 RESULTS DISCUSSION

Table 8.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
18-Oct	SS07/LOS1	Downwind Wells & Tanks	15.1	3.5	5
18-Oct	SS07/LOS2	Downwind Southern Wells & Tanks	40.2	36.0	4

On the 18th Oct afternoon the measurements were carried out from location SS07 with a south-westerly wind, as shown in Figure 8.1 and summarized in Table 8.1. Scans along LOS1 were downwind of several oil wells and the same set of tanks measured from location SS05/LOS1. The average emission rate was 15.1 ± 3.5 kg/hr as reported in Table 8.2.

Measurements along LOS2 were downwind of the same area measured from LOS1 apart for the northern wells. The emission rate calculated from Scan 295 was 92.0 kg/hr, Figures 8.1a1 and a2 show a contour plot and a 3D visualisation of such emission. The plume in the 200-230 m range from the DIAL could be due to the well just south of LOS2 or more likely, taking into consideration the plume elevation of about 20-30 m, the storage tanks. A quite large plume was also observed in the 110-180 m range from the DIAL that could be due to emission from the two wells in the SW area. The emission rate measured from Scan 296 decreased to 36.6 kg/hr and for the next two scans it further decreased back to the level measured from LOS1, indicating there was an intermittent source in addition to the general emissions.

9 VOC MEASURMENTS FROM VONS #1638 – GAS STATION

Table 9.1 Emission rate determined from SS08 on 19th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
300	SS08/LOS1	10:22	10:24	1.8	164.3	0.75	Downwind Vons Gas Station
301	SS08/LOS1	10:25	10:35	1.7	187.7	-	Wind Direction Almost Parallel to LOS
302	SS08/LOS1	10:35	10:45	1.6	145.4	1.22	Downwind Vons Gas Station
303	SS08/LOS1	10:54	11:05	3.1	172.2	0.44	Downwind Vons Gas Station
304	SS08/LOS1	11:05	11:15	2.4	170.1	0.53	Downwind Vons Gas Station

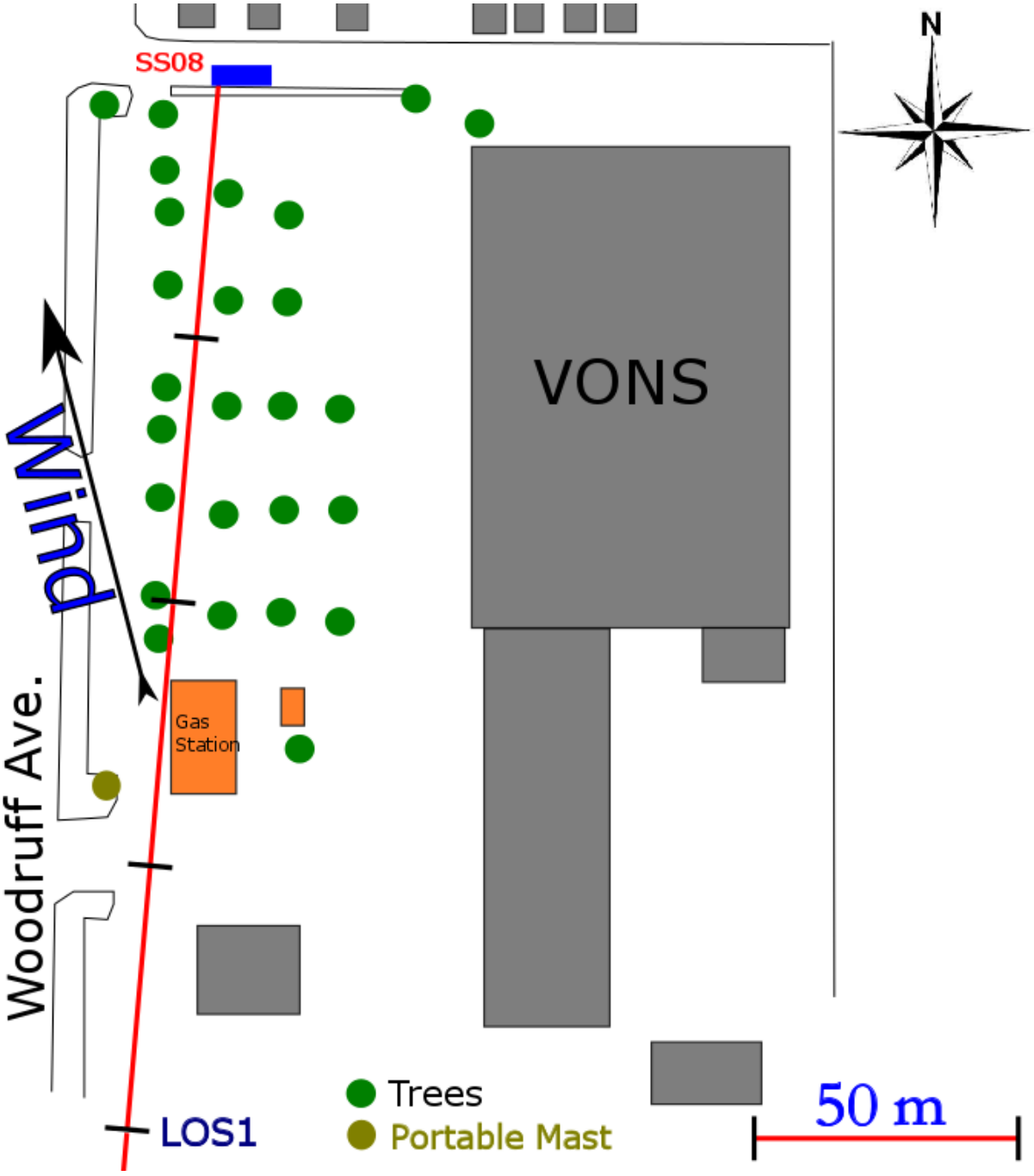

Figure 9.1 Measurement configuration for location SS08 on 19th of October.

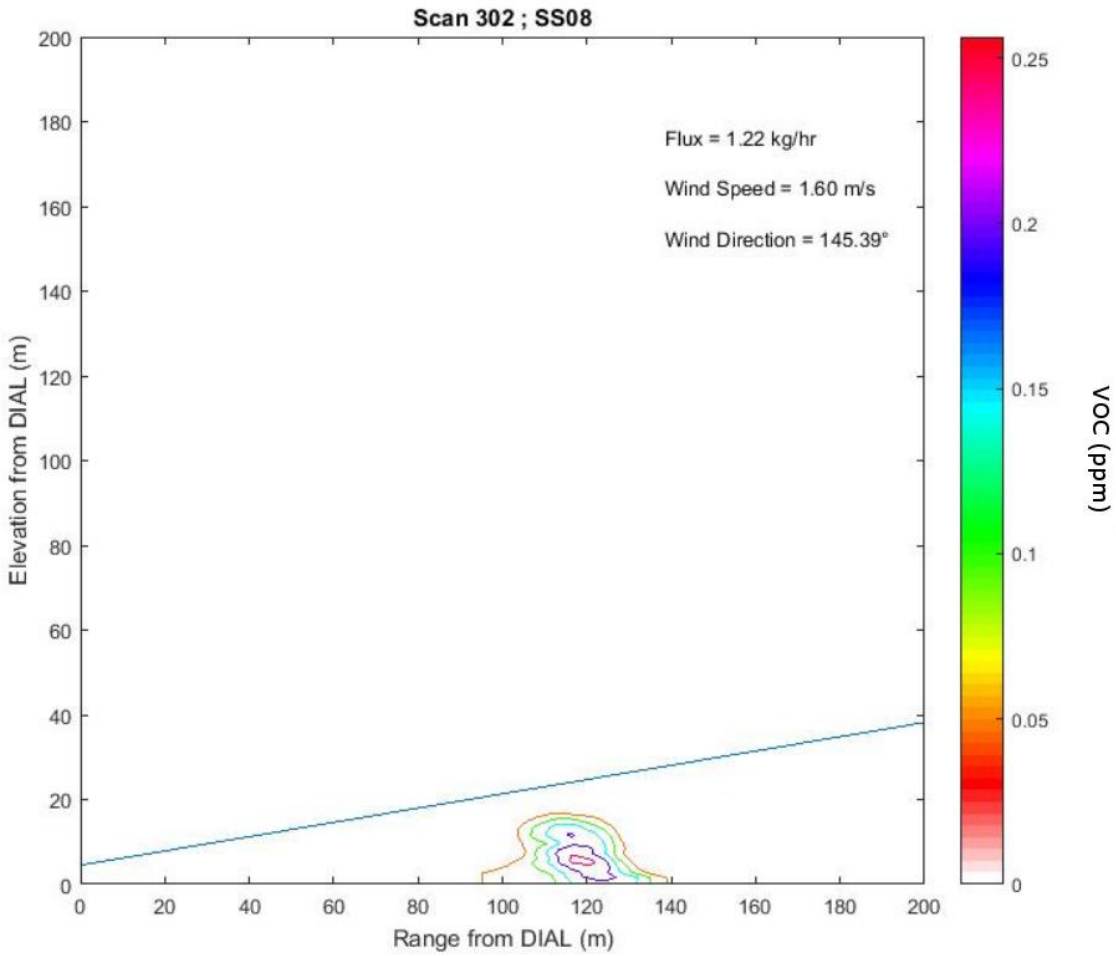

Figure 9.1a1 Observed VOC concentration for Scan 302 representing SS08/LOS1.

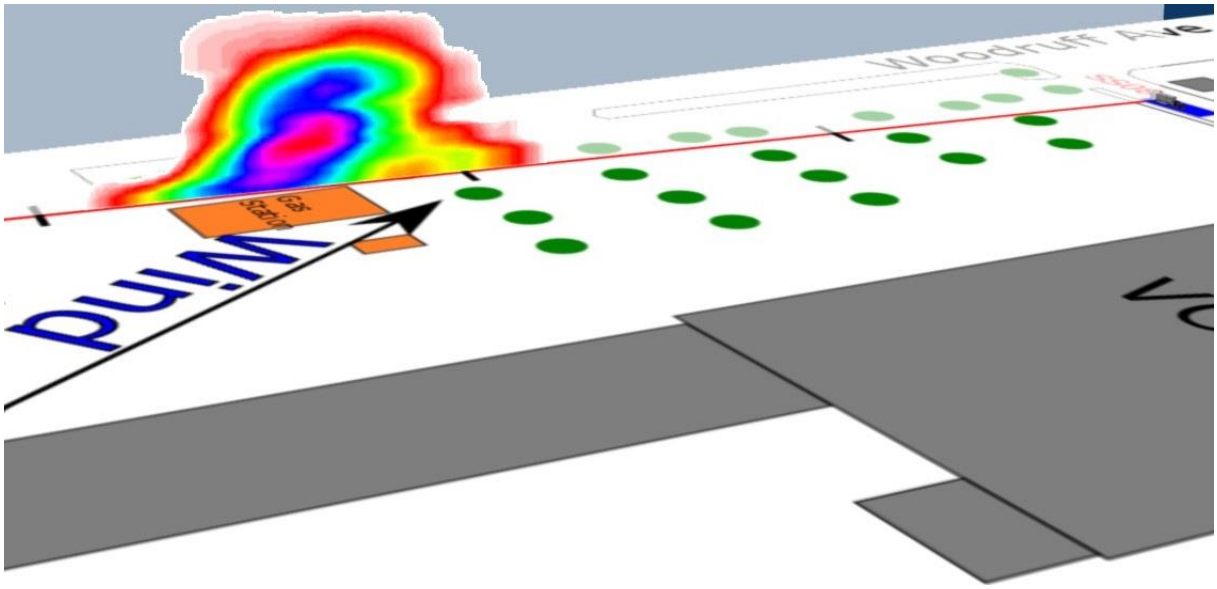

Figure 9.1a2 Visualisation of emission rate for Scan 302 representing SS08/LOS1.

9.1 LOCATION SS08 RESULTS DISCUSSION

Table 9.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
19-Oct	SS08/LOS1	Downwind Vons Gas Station	0.7	0.4	4

On the 19th Oct measurements carried out from location SS08 with a W/SW wind were downwind of Vons #1638 gas station, as shown in Figure 9.1 and summarized in Table 9.1. Although the wind direction was not ideal the DIAL was able to measure an average emission rate of 0.7 ± 0.4 kg/hr. Figures 9.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed in Scan 302 from the small gas station.

10 VOC MEASURMENTS FROM COSTCO #1050 – GAS STATION

Table 10.1 Emission rate determined from SS09 on 19th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
306	SS09/LOS1	12:37	12:45	3.0	219.1	6.96	Downwind Costco Gas Station
307	SS09/LOS1	12:46	12:54	2.9	206.5	6.50	Downwind Costco Gas Station
308	SS09/LOS1	12:56	13:03	4.4	183.0	5.21	Downwind Costco Gas Station
309	SS09/LOS1	13:13	13:20	2.8	210.7	4.00	Downwind Costco Gas Station
310	SS09/LOS1	13:21	13:28	4.0	184.5	2.32	Downwind Costco Gas Station
311	SS09/LOS1	13:28	13:36	3.9	194.7	3.44	Downwind Costco Gas Station
312	SS09/LOS1	13:36	13:44	3.3	201.6	3.50	Downwind Costco Gas Station
313	SS09/LOS1	13:45	13:52	3.8	201.0	4.18	Downwind Costco Gas Station
314	SS09/LOS1	13:53	14:00	2.2	214.0	3.71	Downwind Costco Gas Station
315	SS09/LOS1	14:00	14:08	3.6	215.6	3.83	Downwind Costco Gas Station
316	SS09/LOS1	14:08	14:16	2.6	214.4	5.19	Downwind Costco Gas Station
317	SS09/LOS1	14:16	14:24	3.8	220.9	6.76	Downwind Costco Gas Station
318	SS09/LOS1	14:24	14:31	4.2	212.1	2.97	Downwind Costco Gas Station
319	SS09/LOS1	14:32	14:39	2.6	215.8	5.30	Downwind Costco Gas Station
320	SS09/LOS1	14:39	14:47	2.8	222.7	3.70	Downwind Costco Gas Station
321	SS09/LOS1	14:47	14:55	2.9	224.4	5.85	Downwind Costco Gas Station
322	SS09/LOS1	14:55	15:03	3.5	214.4	6.46	Downwind Costco Gas Station
323	SS09/LOS1	15:03	15:10	4.0	220.1	4.28	Downwind Costco Gas Station
324	SS09/LOS1	15:11	15:19	3.5	227.2	6.87	Downwind Costco Gas Station
325	SS09/LOS1	15:19	15:27	3.0	223.3	6.07	Downwind Costco Gas Station
326	SS09/LOS1	15:27	15:34	3.4	209.9	3.56	Downwind Costco Gas Station
327	SS09/LOS1	15:34	15:42	3.7	214.1	2.79	Downwind Costco Gas Station
328	SS09/LOS1	15:43	15:50	2.5	228.9	3.82	Downwind Costco Gas Station
329	SS09/LOS1	15:50	15:58	2.9	227.5	2.33	Downwind Costco Gas Station

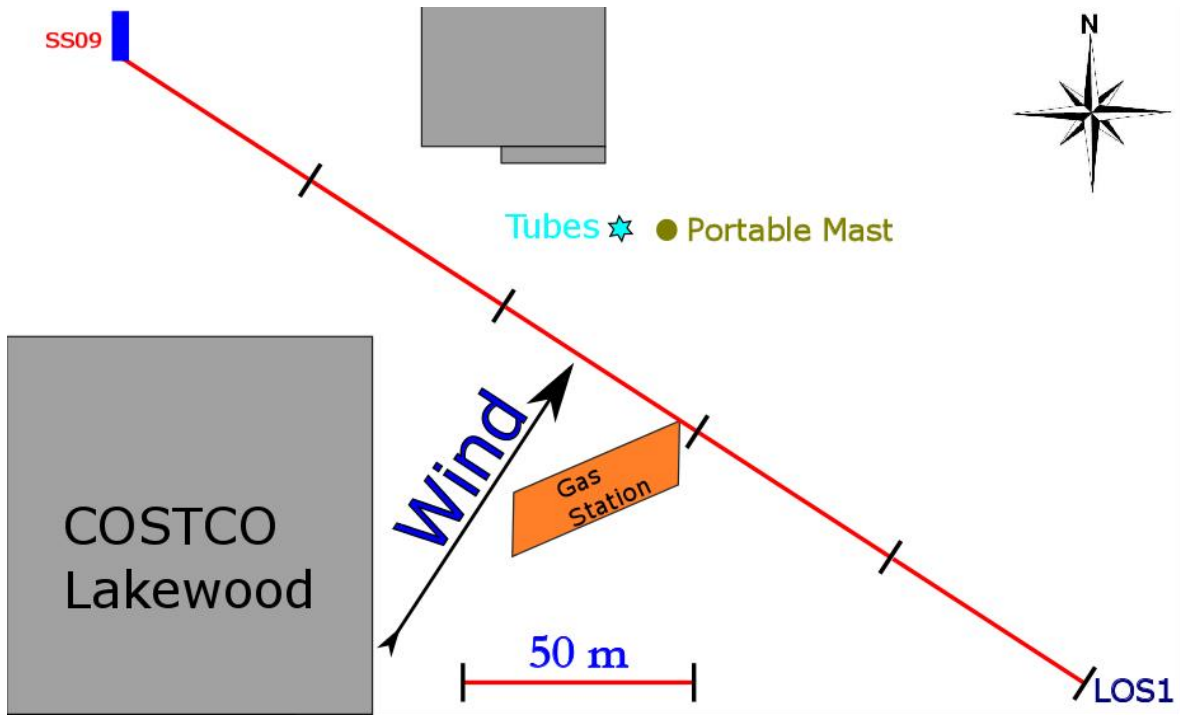

Figure 10.1 Measurement configuration for location SS09 on 19th of October.

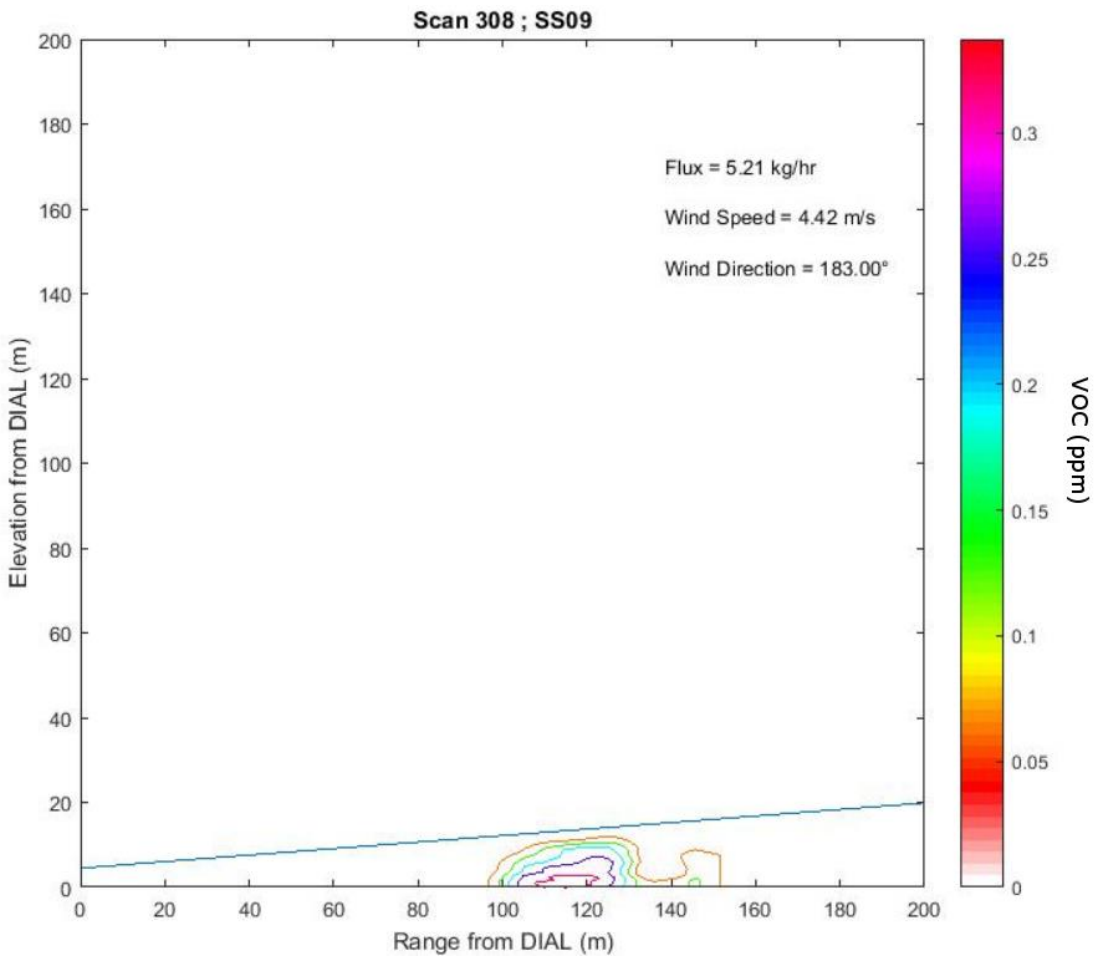

Figure 10.1a1 Observed VOC concentration for Scan 308 representing SS09/LOS1.

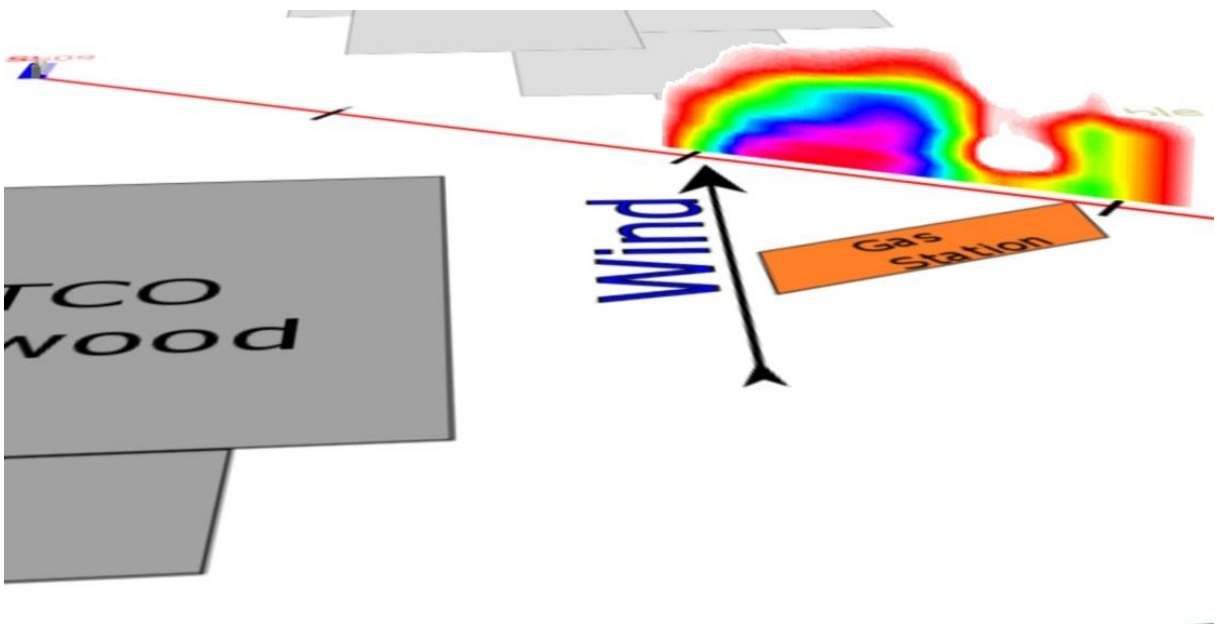

Figure 10.1a2 Visualisation of emission rate for Scan 308 representing SS09/LOS1.

10.1 LOCATION SS09 RESULTS DISCUSSION

Table 10.2 Summary of determined VOC emission rates. For each location and LOS the average flux and standard deviation are reported.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans
			kg/hr	kg/hr	#
19-Oct	SS09/LOS1	Downwind Costco Gas Station	4.6	1.2	24

On the 19th Oct measurements were also made from location SS09 with a south-westerly wind downwind of Costco #1050 gas station, as shown in Figure 10.1 and summarized in Table 10.1. This is a relatively large gas station and the average emission rate was 4.6 ± 1.2 kg/hr as reported in Table 10.2. The standard deviation is relatively high considering the high number of scans performed (24) suggesting that the variation in the emission rate from about 2 kg/hr to 7 kg/hr, was not only due to the variation in the DIAL measurements but also to source variation. Figures 10.1a1 and a2 show a contour plot and a 3D visualisation of the emission observed from Scan 308.

11 CONCLUSION

Measurements conducted in the South Coast Air Basin demonstrated that the DIAL is able to monitor emissions from small sources such as oil wells, storage tanks and gas stations under all the meteorological conditions experimented during the campaign. The DIAL was able to observe and quantify temporal variations in the emission rate as well as to identify and quantify intermittent sources.

The variable emission rates observed from location SS01 were correlated with the tank filling and unloading cycle with lower emissions observed when the tank was unloading. Tank emission rates measured from locations SS01 and SS02 varied by about a factor of 10 during the few hours of measurement. The highest emission rates measured from the two locations were about 18 kg/hr and 155 kg/hr respectively. Intermittent emissions from tanks were also observed in one scan from location SS03/LOS2 and in two scans from location SS07/LOS2.

Emissions from oil wells appear to be on average lower than the emissions from the tanks and usually more constant in time. Measurements of different sets of wells were made from locations SS03/LOS1, SS03/LOS2, SS04/LOS4, SS05/LOS2 and SS06/LOS1; the emission rates observed ranged from less than 2 kg/hr up to about 14 kg/hr. An intermittent emission from a well of about 14 kg/hr was observed in one scan from location SS03/LOS2. Additionally, part of the 92 kg/hr intermittent emission measured from one scan made from location SS07/LOS2 was probably due to one or more wells.

A drill rig emission was measured from locations SS04/LOS1/LOS2/LOS3 showing a highly variable emission rate ranging from about 2 kg/hr to 27 kg/hr.

An unknown source was measured several times from location SS04 and different LOS from an area where no obvious potential sources could be identify from satellite images. The average emission rate was about 35 kg/hr quantified from the scans where it was possible to spatially separate this source from other emission sources in the area.

An average emission rate of about 5 kg/hr was observed from several measurements of a relatively large gas station from location SS09; such emission was continuous but variable in time. A set of measurements from a smaller gas station showed a lower emission rate averaged at less than 1 kg/hr.

In conclusion, the DIAL was quickly deployed at each agreed site, it was able to carry out measurements at one or more sites every day and to quantify emissions from all the small sources under investigation providing invaluable comparison and validation data for the other techniques.

12 APPENDIX 1: DESCRIPTION OF THE DIAL TECHNIQUE

12.1 OVERVIEW OF THE DIAL TECHNIQUE

The Differential Absorption Lidar (DIAL) technique is a laser-based remote monitoring technique which enables range-resolved concentration measurements to be made of a wide range of atmospheric species. This section explains the theory of the DIAL technique and describes the NPL system in detail.

12.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS

The atmospheric return signal, P, measured by a DIAL system from range r and at wavelength x is given by the Light Detection and Ranging (Lidar) equation, a simplified form of which is given in Equation 1.

$$P_x(r) = E_x \frac{D_x}{r^2} B_x(r) \exp\{-2\int_0^r [A_x(r') + \alpha_x C(r')] dr'\} \quad \textbf{(1)}$$

where D_x is a range independent constant, C(r) is the concentration of an absorber with absorption coefficient α_x and $A_x(r)$ is the absorption coefficient due to all other atmospheric absorption, E_x is the transmitted energy and B_x is the backscatter coefficient for the atmosphere.

The equation has three basic components:

- a backscatter term based on the strength of the signal scattering medium
- parameters associated with the DIAL system
- a term which is a measure of the amount of absorption of the signal which has occurred due to the presence of the target species.

In the DIAL technique, the laser is operated alternately at two adjacent wavelengths. One of these, the "on-resonant wavelength", is chosen to be at a wavelength which is absorbed by the target species. The other, the "off-resonant wavelength", is chosen to be at a wavelength which is not absorbed significantly by the target species, and is not interfered with by other atmospheric constituents.

Pairs of on- and off-resonant signals are then acquired and averaged separately until the required signal to noise ratio is achieved.

The two wavelengths used are close together, hence the atmospheric terms $A_x(r)$ and $B_x(r)$ in the lidar equation can be assumed to be the same for both wavelengths. These terms are then cancelled by taking the ratio of the two returned signals.

The path-integrated concentration (CL) may be derived (Equation 2) by multiplying the logarithm of the ratio of the signals by the ratio of the absorption of the two wavelengths by the target species.

$$CL(r) = \frac{1}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^{N} \log \frac{S_{ON,i}(r)}{S_{OFF,i}(r)} \quad \textbf{(2)}$$

where N is the number of pulse pairs averaged, $\Delta\alpha = \alpha_{OFF} - \alpha_{ON}$ is the differential absorption coefficient and S represents the received power after energy normalisation of the on- and off-resonant signals respectively.

This path-integrated concentration represents the total concentration of the target species in the atmosphere along the measured line-of-sight out to the range r.

The range-resolved concentration can then be derived by differentiating the path-integrated concentration (Equation 3).

$$C(r) = \frac{dCL(r)}{dr} \qquad \textbf{(3)}$$

where C(r) is the concentration at range r along the line-of-sight averaged over the spatial resolution of the DIAL along its line-of-sight (typically 3.75 m).

12.3 DESCRIPTION OF FACILITY OPERATED BY NPL

The DIAL system operated by NPL is housed in a mobile laboratory. It can operate in the infrared and ultraviolet spectral regions allowing coverage of a large number of atmospheric species. A scanner system directs the output beam and detection optics, giving almost full coverage in both the horizontal and vertical planes.

The system also contains ancillary equipment for meteorological measurements, including an integral 10 m meteorological mast with wind speed, direction, temperature and humidity measurements.

The system is fully self contained, with power provided by an on board generator, and has full air conditioning to allow operation in a range of ambient conditions.

The following sections describe the DIAL system in more detail.

Source
The source employs a combination of Nd-YAG and dye lasers together with various non-linear optical stages to generate the tuneable infrared and ultraviolet wavelengths. The source has a pulse repletion rate of 10 Hz and an output laser pulse duration of ~10 ns. A small fraction of the output beam in each channel is split off by a beam splitter and measured by a pyroelectric detector (PED) to provide a value for the transmitted energy with which to normalise the measured backscatter return.

Detection
The returned atmospheric backscatter signal is collected by the scanning telescope. This directs the collected light into separate paths for the infrared and ultraviolet channels. The returned light passes through band pass filters relevant to each detection channel and is then focused onto the detection elements. Solid-state cryogenically-cooled detectors are used in the infrared channel and low-noise photomultipliers in the ultraviolet.

After amplification the signals from these detectors are digitised using a high speed digitiser. The digitiser is clocked using a clock generator triggered by the same trigger used to fire the lasers. This ensures the range gating is correctly synchronised to the laser pulse transmission. The signals from the PED monitoring the transmitted energy are also digitised and stored.

Data Analysis
The data acquired are analysed, using the DIAL techniques described below, to give the range-resolved concentration along each line-of-sight.

The data analysis process consists of the following steps:

i) Background subtraction

Any DC background value is subtracted from the signals. This measured background takes account of any DC signal offset which may be present due to electronic offsets and from incident background radiation. The background level is derived from the average value of the far field of the returned lidar signal where no significant levels of backscattered light is present.

ii) Normalisation for variation in transmitted energy
The two signal returns are normalised using the monitored values of the transmitted energy for the on and off resonant wavelength pulses. The mean transmitted energy is used to normalise the averaged return signal. For this application, this has been shown to be equivalent to normalising individual shots against transmitted energy and then averaging the normalised values.

iii) Calculation of path-integrated concentration
The path-integrated concentration of the target species, out to the range r, is calculated using equation 2.

The absorption coefficients used in this calculation are derived from high-resolution spectroscopy carried out using reference gas mixtures at NPL.

iv) Derivation of range-resolved concentrations.
The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight, as in equation 3.

v) Calculation of emission rates
Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. This is carried out using algorithms developed at NPL which reduce artefacts due to the difference in data density at different ranges, due to the polar scanning format of the data. The emission rate is then determined using the concentration profile together with meteorological data.

The emitted rate is calculated using the following mathematical steps:

(a) The product is formed of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.

(b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.

(c) This array of results is then integrated over the complete concentration profile to produce a value for the total emitted rate.

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. A logarithmic wind profile is used to describe the vertical distribution of the wind. Two wind speeds at different heights, usually from the fix mast sensors, are used to calculate the wind profile. The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

A summary of the ultraviolet and infrared performance capabilities of the NPL DIAL facility are given in Tables A1.1 and A1.2. The values given in these tables are based on the actual levels of performance of the system obtained during field measurements, rather than calculations based on theoretical noise performances. For simplicity the numbers are presented as a single concentration sensitivity and maximum range values. However, the detailed performance behaviour of a DIAL system is much more complex and there are a number of key points that should be noted:

- The DIAL measurement is of concentration per unit length rather than just concentration. So the sensitivity applies for a specified pathlength – 50 metres in this case. Measurements over a

shorter path would have a lower sensitivity, and would be more sensitive over a longer path length.

- Since the backscattered lidar signal varies with range, generally following a $(\text{range})^{-2}$ function, the sensitivity is also a function of range. The sensitivity values given in the tables apply at a range of 200 metres, and these will get poorer at longer ranges.
- The maximum range of the system is generally determined by the energy of the emitted pulse and the sensitivity of the detection system, except in the case of nitric oxide where range is limited by oxygen absorption at the short ultraviolet wavelengths required for this species.
- In all cases the performance parameters are based on those obtained under typical meteorological conditions. For the ultraviolet measurements the meteorological conditions do not have a great effect on the measurements as the backscattered signal level is predominantly determined by molecular (Rayleigh) scattering, and this does not vary greatly. However, in the infrared the dominant scattering mechanism is from particulates (Mie scattering). So the signal level, and therefore the sensitivity, is dependant on the particular loading of the atmosphere, and this can vary dramatically over relatively short timescales.
- The optical configuration of the DIAL system means there is a minimum range between 40-100 m before measurements can be made.

The NPL DIAL has a theoretical range resolution of 3.75 metres along the measurement beam, and a vertical and horizontal scan resolution which can be less than 1 metre at 100 metres. However, the actual range resolution determined by the signal averaging used, will depend on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 20-30 m.

The DIAL is able to make measurements of a wide range of compounds, including benzene and other aromatics, individual VOCs and total VOCs, see Tables A1.1 and A1.2. The methodology for obtaining measurements of the total VOC content from C3 to C15 is provided below. It consists of the combination of DIAL measurements with air sampling and GC analysis. The system is able to monitor individual aromatic compounds and VOC species, which have absorption features in the IR and UV spectral regions covered by the DIAL system. NPL has the spectral expertise, access to spectral libraries and an in-house spectroscopic capability to assess the DIAL sensitivity for additional individual species.

The general hydrocarbon measurement listed in Table A1.2 uses an infrared absorption that is similar for all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. The line strengths for these species are proportional to the number of carbon-hydrogen bonds present and this enables a total mass emission to be determined. As such it provides a measure of the mixture of volatile organic compounds (VOCs) that are present at an oil or petrochemical site. The pair of infrared wavelengths used for this DIAL measurement are selected so that the absorption per unit mass is relatively invariant with respect to the mix of different hydrocarbons that are present. However, the sensitivity of this measurement in terms of ppb of hydrocarbon depends on the mixture of species present, and the value given in the table reflects the typical mix of hydrocarbons found at oil refineries.

Although the general hydrocarbon measurement provides a good estimate of the overall amount of hydrocarbons present, the accuracy of this measurement can be improved, and the total VOC concentration calculated, by combining the DIAL measurements with the results of gas chromatography (GC) analysis of the emitted gases. The standard procedure for this involves taking whole air samples around the site in locations where the DIAL measurements show the emitted plumes are present. The VOCs present in these samples are identified and quantified by GC analysis. The results provide the relative levels of all the VOCs present with a concentration of 0.1 ppb or higher. The results of this analysis are combined with NPL's unique spectral library of quantified infrared absorptions of an extensive set of VOCs to calculate the combined absorption coefficient for the actual VOC mixture present at the site. Appling this absorption coefficient to the DIAL results enables the total VOC emission rates to be calculated.

Table A1.1 Ultraviolet capability of NPL DIAL Facility

Species	Sensitivity(1)	Maximum range(2)
Nitric oxide	25 ppb	500 m
Sulphur dioxide	10 ppb	3 km
Ozone	5 ppb	2 km
Benzene	10 ppb	800 m
Toluene	10 ppb	800 m

Table A1.2 Infrared capability of NPL DIAL Facility

Species	Sensitivity(1)	Maximum range(2)
Methane	50 ppb	1 km
Ethane	20 ppb	800 m
Ethene	10 ppb	800 m
Ethyne	40 ppb	800 m
General hydrocarbons	40 ppb	800 m
Hydrogen chloride	20 ppb	1 km
Methanol	200 ppb	500 m
Nitrous oxide	100 ppb	800 m

(1) The concentration sensitivities apply for measurements of a 50 metre wide plume at a range of 200 metres, under typical meteorological conditions.
(2) The range value represents the typical working maximum range for the NPL DIAL system.

12.4 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS

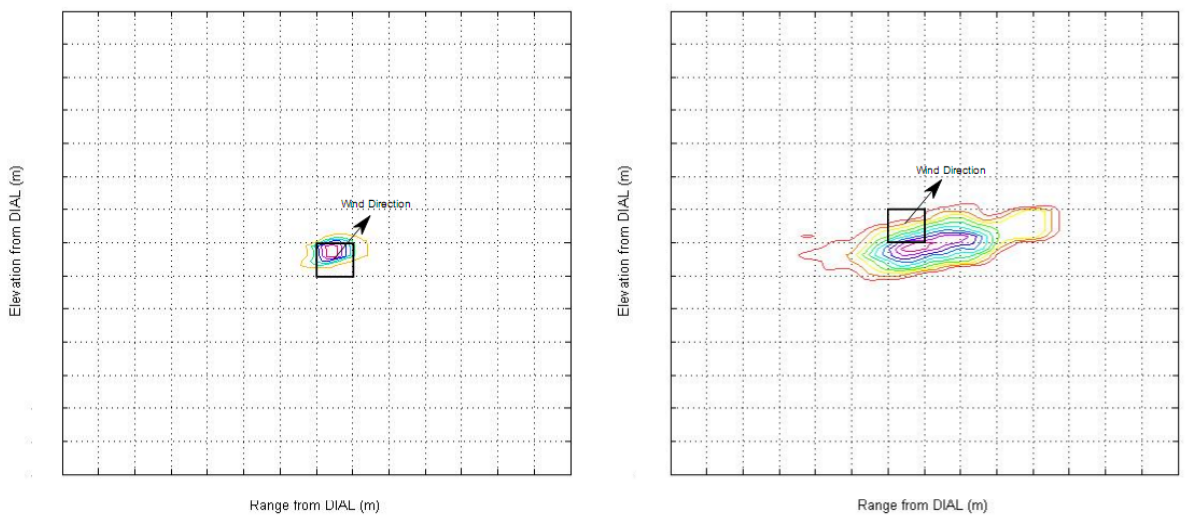

Figure A1.1 Illustration of the emission rate calculation approach

Where concentrations are provided as an indication of the levels observed in a measurement scan, the reported concentration in the measurement plane is the maximum concentration seen in a cell in the

measurement plane. The resolution of the planes used is equal to the DIAL system resolution and is 3.75 m, so each cell is 3.75 m square. Figure A1.1 shows how plume size affects the emission rate that is calculated. The concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell, and then the individual cell emission rates are summed to give the total emission rate through the plane. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated emission rate, and the other which has a larger plume, and therefore represents a larger emissions rate, although the peak concentration in both is similar, and indeed may even be higher in the small plume than the large plume.

Figure A1.2 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not perpendicular to the plane of the measurements. If only the concentration profile were observed the right hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the emission rate determined from this scan, resulting in the same emission rate being determined for both measurement orientations.

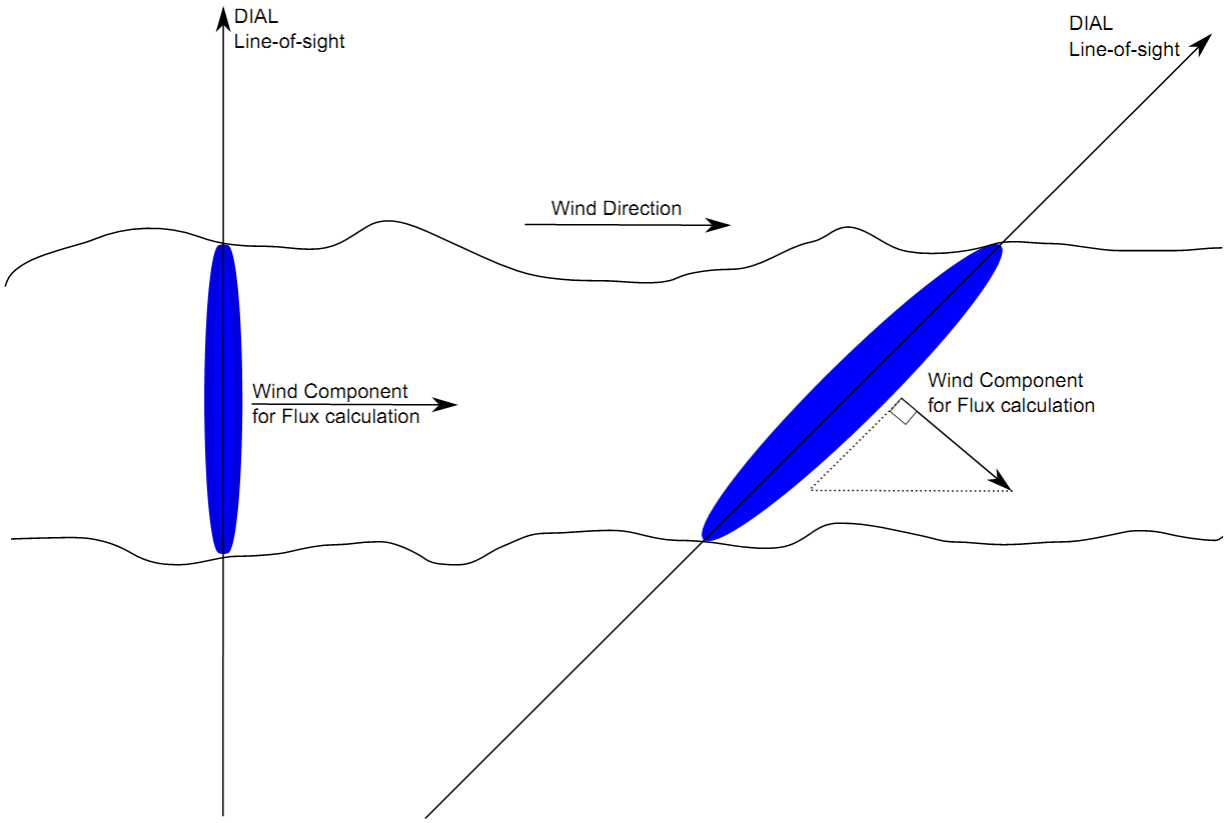

Figure A1.2 Schematic showing relationship between emission rate and wind direction

12.5 CALIBRATION AND VALIDATION

The NPL DIAL system has several in-built calibration techniques and procedures. The most important are the in-line gas calibration cells. The gas cells are filled with known concentrations of the target species, obtained from NPL standard gas mixtures, which are directly traceable to national standards. A fraction of the transmitted beam is split off and directed through a gas cell to a PED, in the same way as with the beam for the transmitted energy monitors. This provides a direct measurement of the differential absorption at the operating wavelengths by the target gas. The transmission through the

gas cells is continuously monitored during the operation of the system to detect any possible drift in the laser wavelengths. The calibration cells are also periodically placed in the output beam to show the concentration response of the whole system is as expected.

A number of field comparisons have been undertaken to demonstrate the accuracy of the measurements obtained with DIAL. Examples of these carried out by NPL are summarized below:

i) Intercomparisons have been carried out on chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range C_2 - C_8. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within ± 15%. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within ± 20%.

ii) The ultraviolet DIAL system was used to monitor the emission rates and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within ± 12%.

iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission rates to within ± 15%.

13 APPENDIX 2: VOC SPECIATION USING PUMPED SORPTION TUBES

The DIAL measures C2+ VOCs by measuring the differential absorption of two wavelengths of light. The wavelengths used, at around 3000 cm^{-1}, are chosen to measure, in effect, the C-H stretch in the hydrocarbons for C2 and above. The sensitivity of the DIAL is slightly different for different hydrocarbons, and for example an oxygenated hydrocarbon will give a different absorption per mass than a straight chain alkane. The differential absorption strength used in the DIAL VOC measurements was calibrated to give a mass emission rate for gasoline vapour. A different 'cocktail' of hydrocarbons could give a slightly different response per unit mass. Air samples were taken at locations which would provide an indication of the actual speciation of the emission fluxes sampled by the DIAL. If the actual (relative) composition is known from the air sample analyses, then it is possible to check that the absorption coefficients used are appropriate for the actual hydrocarbon mixture present, and adjust the coefficients if necessary.

Air samples were taken at a total of 4 small site locations SS01, SS02, SS03 and SS09 shown in Figures 2.1, 3.1, 4.1 and 10.1respectively. The air samples were taken using pumped Perkin Elmer Automatic Thermal Desorption (ATD).

The ATD tubes were sampled at a flow rate of 40ml/min to enable a reasonable duration of sample to be taken – typically 30 to 40 minutes. The samples were taken at a height of approximately 2m by mounting the sampling array on a tripod.

The sampler tubes were approximately 6mm in diameter and 90mm long. The sampler tubes contained approximately 200 milligrams to 300 milligrams of sorbent. Three sorbent tubes were used: a carbon molecular sieve (CarboSieve S3) to measure the lightest species, and two in series containing different sorbent materials, a porous polymer (Tenax TA) and a carbon black (Carbopack X). Different sorbents are needed to cover the diverse boiling point ranges and chemical functional groups of VOCs, and this combination gives a maximum Carbon number range of C_2-C_{22}.

13.1 SPECIATION RESULTS FROM THE ATD TUBE SAMPLES

The tube analyses were carried out by NPL's in house accredited analysis laboratory. Different methods of analysis were used for the CarboSieve S3 and Carbopack X (light hydrocarbons) tubes and the Tenax (heavy hydrocarbons) tubes.

The CarbonSieve S3 and Carbopack X method of analysis was based on EN ISO 16017-2 and was carried out using UKAS (United Kingdom Accreditation Service) accredited method QPDQM/B/526. This method combines Automatic Thermal Desorption with Gas Chromatography (GC), with a Flame Ionisation Detector (FID).

The analysis instrument used is an Automated Thermal Desorber autosampler coupled to a Gas Chromatograph usually with a flame ionisation detector. The VOCs are released from the sampler tube using a heated oven in an inert gas stream of helium. The VOCs are refocused onto a small cold trap prior to transfer onto the gas chromatography column. Generally a coated fused silica gas chromatography column of diameter 320 micrometers and length 60 meters is used to separate the individual VOCs collected. Using VOC standard materials, the identification of the individual VOC components are compared to the column elution time (retention time) of the standard VOC materials. The mass of VOCs collected is quantified using the flame ionisation detector. A series of calibrations standards are used to calibrate the flame ionisation detector response. The concentration of the VOC in ambient air is then calculated using from the mass collected and the volume of air sampled.

A similar procedure was used for the Tenax analyses, but in this case mass spectrometric (MS) detection was used after the GC separation instead of a FID. MS detection provides additional information on the mass of ionized fragments from the different species while retaining the elution

separation of the gases, which assists in the species identification within the potentially complex mixture of heavy organic components.

Over 30 different VOCs were identified in the four samples and to simplify the presentation of the data the aliphatic species have been separated into saturated and unsaturated compounds and then grouped by carbon number (from C2 to C10), and the aromatic species have also been grouped together. The results for the selected samples are given in Figure A2.1.

The results show that the observed VOC mixture covers a wide carbon number range (up to C10). Samples S05, S06 and S07 were representative of the emission from oil wells and tanks while S08 was representative of the emission from a gas station. As highlighted above, the DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. For each tube measurement a scaling factor to go from the standard DIAL VOC coefficients to the measured C2+ hydrocarbons mixtures was calculated and applied to the measurements at the location where the sample was taken. These factors were 1.10, 1.26, 1.44 and 1.24 for locations SS01, SS02, SS03 and SS09 respectively with an estimated uncertainty of 10%. For locations SS04, SS05, SS06 and SS07 where it was not possible to collect any tube sample representative of the emission, a contribution of the scaling factors from samples S05, S06 and S07 (representative of oil wells and tanks emission) was used, 1.27 ± 0.10. For the gas station measurements at location SS08 the scaling factor 1.24 from sample S08 was used with a 10% uncertainty.

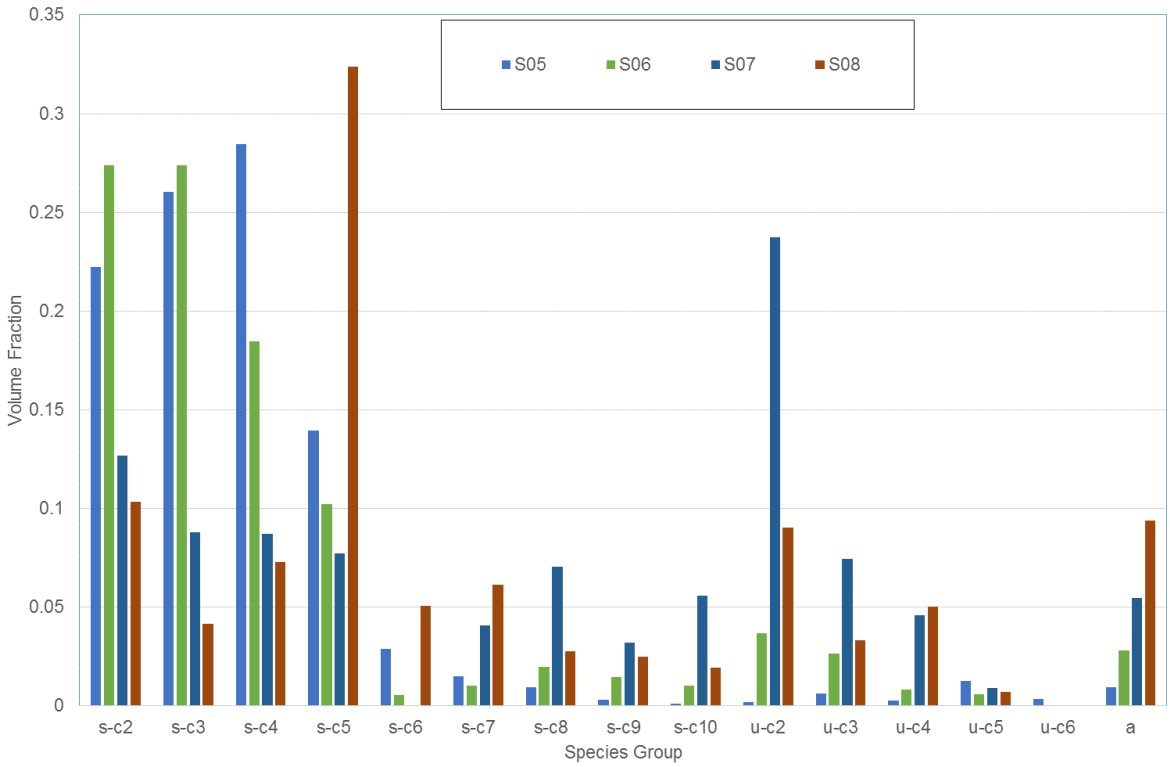

Figure A2.1 Volume fraction of VOCs in the four samples.