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Test Report

Commercial in confidence

Measurements of VOC emissions from petrochemical industry sites in the Houston area using Differential Absorption Lidar (DIAL) during Summer 2007.
DRAFT FOR COMMENT

FOR:	Texas Commission on Environmental Quality
FOR THE ATTENTION OF:	Russell Nettles
DATE OF TEST PERIOD:	16/07/07 to 18/08/07
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Date of Issue: 6 February 2008 **Signed:**

Checked by: **Name: Melanie Williams for Managing Director**

Contents

Contents 2
Introduction 3
Section 1. Measurements of VOC emissions from a Bulk Terminal, in the Houston non-attainment area. 4
Measurement description. 4
Definition of VOCs 4
Measurements on the 16th July. 6
Measurements on the 17th July 8
Measurements on the 18th July and 19th July 10
Night-time measurements on the 20th-21st July. 11
Section 2 Measurements of VOC emissions from a Refinery in the Houston non-attainment area. 12
Measurement description. 12
Measurements of product storage tanks. 14
Measurements of crude oil tanks 16
Measurements of VOC emissions from coker C 24
Measurements of VOC emissions from heated oil tanks 27
Measurement of VOC emissions from elevated flares. 28
Section 3 Measurements of Benzene emissions from Refinery 31
Measurement description 31
Benzene concentration measurements on 17th August. 31
Measurements of benzene fluxes from the coker 36
Section 4. Measurements of SO_2 from the Sulphur Recovery Unit 38
Annex 1. Description of the DIAL technique. 39
Overview of the Dial technique 39
Description of the theory of Dial measurements 39
Description of facility operated by NPL 40
Calibration and validation 45
NPL open-path calibration facility 47
Annex 2 Speciated VOC measurements and Flux Correction Factors 48
Flux Correction Factors 48
Sampling Procedure 53
Analysis of the ATD tubes 54
Annex 3. Meteorological Measurements 65

Introduction

This report presents the results of a measurement campaign carried out using the NPL differential absorption LIDAR (DIAL) system at two petrochemical facilities in the The Houston non-attainment area region of South East Texas, between 16th July to 18th August 2007. The project was carried out for the Texas Commission on Environmental Quality (TCEQ). This report covers the measurements undertaken by NPL, and does not cover additional measurements undertaken by other contractors.

The primary objective of the study was to assess emission fluxes of VOCs and benzene from a number of identified potential sources, including storage tanks, a delayed coker unit, waste water treatment areas and flares.

The report provides a summary of the VOC fluxes measured using the DIAL technique at a Bulk Terminal in the Houston non-attainment area (hereafter the Bulk Terminal) (Section 1) and a Refinery in the Houston non-attainment area (hereafter the Refinery) (Sections 2 and 3). Annex 1 provides an overview of the DIAL technique, and discusses the calibration and validation procedures. Annex 2 presents the results of speciation measurements of air samples, and Annex 3 presents a summary of the meteorological measurements undertaken during the campaign.

Section 1. Measurements of VOC emissions from a Bulk Terminal, in the Houston non-attainment area.

Measurement description.

DIAL measurements of the emissions of VOCs from storage tanks at the Bulk Terminal facility were carried out on 16th, 17th , 18th, 19th July and on the night of the 20th-21st July. The tanks selected by TCEQ/Bulk Terminal for measurement were naphtha storage tanks, numbers 22,23, 27, 28, and 29. Tank 3792 was also included in some of the measurements, though no specific identifiable emissions were observed that could be attributed to this tank.

Two measurement locations were used for the DIAL measurements; these were both on Avenue H, the southern road within the plant. The GPS coordinates for these measurement locations were:

DIAL Location 1.
North side of Ave H, due south of Tank 3770
29°21'23.64"N
94°55'2.82"W

DIAL Location 2
South side of Ave H, south of Tank 3792.
29°21'23.47"N
94°54'52.79"W

Measurements of VOC fluxes were carried out using the NPL DIAL as described in Annex 1. Fluxes were obtained by scanning the DIAL measurement line-of-sight in vertical planes, downwind of the target emissions sources. Measurements were also made upwind of the target sources to check for any upwind VOC fluxes. The measurement lines are shown in Figure 1.1.

Definition of VOCs

The DIAL technique, as operated during these measurements, provides a measurement of mass emission in gasoline vapour equivalent. The DIAL measures VOCs by measuring the differential absorption of two wavelengths of light sensitive to hydrocarbons of C3 and above.

This has been calculated for each air sample taken, and Annex 2 presents a set of correction factors for each measurement location. For the measurements at the Bulk Terminal the factors range from between 0.8 to 1.6.

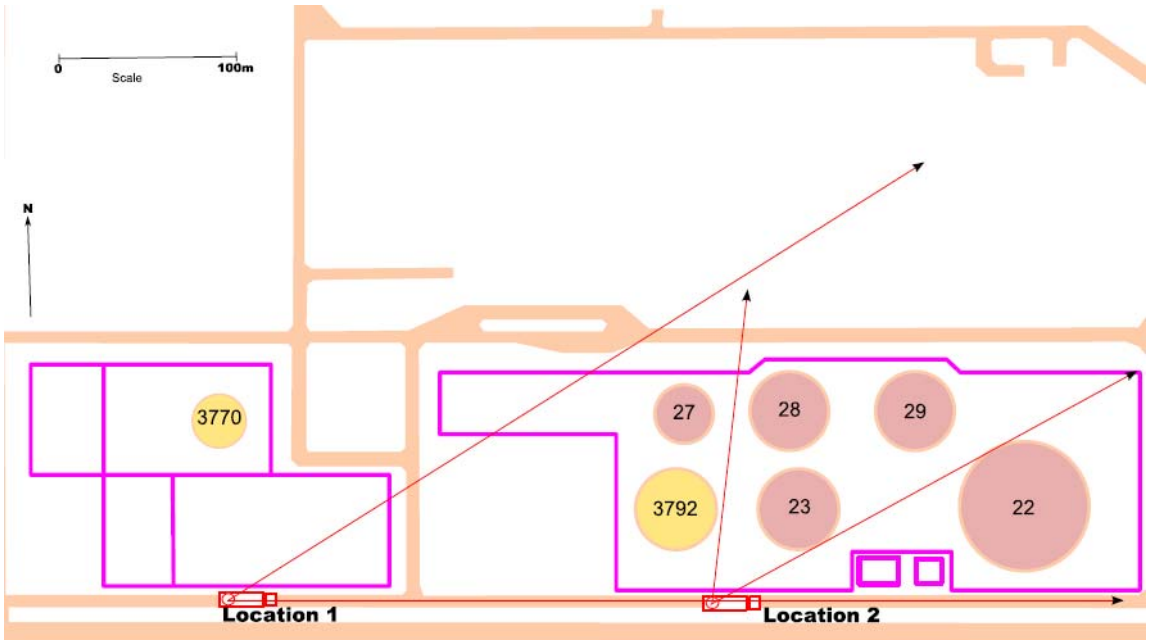

Figure 1.1.DIAL locations and scan lines used for VOC measurements at the Bulk Terminal.

Measurements on the 16th July.

From Location 1, scans were made which measured the emissions from tanks 23,27,28,29 and 3792. Tank 22 emissions would also have been observed if these had been significant. Table 1.1 presents these results. The wind direction was generally from the SE, with speeds of 3 to 6 m/s.

A small flux was measured, at a range consistent with emissions from tanks 27, 28 and 23. This is shown in Figure 1.2. No observable emissions were seen from tank 22 or tank 3792. The average emission observed was 28 lbs/hr with a standard deviation of ± 5 lbs/hr. It should be noted the standard deviation of the results includes both the inherent uncertainty in the DIAL measurements and any real variability in the emissions (whether due to source variability or variable dispersion).

Upwind scans (Scan IDs 16 and 21) gave results at or below the detection limit, which for the conditions prevailing at the Bulk Terminal was 1 lbs/hr.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
10	16:24	6.3	169.6	31	0.10	Downwind Tanks 23, 27, 28, 29
11	16:32	3.7	139.8	24	0.17	Downwind Tanks 23, 27, 28, 29
12	16:39	5.0	163.0	24	0.30	Downwind Tanks 23, 27, 28, 29
13	16:50	5.2	154.1	33	0.24	Downwind Tanks 23, 27, 28, 29
16	17:22	3.7	101.4	<1	0.14	upwind
21	17:42	3.4	114.4	<1	0.07	upwind
22	17:55	3.4	86.3	<1	0.15	Right next to tank 27

Table 1.1. VOC fluxes measured on 16th July at Bulk Terminal.

The DIAL provides a range resolved measurement of VOC concentrations. A DIAL scan can provide not only a measurement of the mass emissions flux, but also a visual indication of the location of the emission plume. Figure 1.2 shows an example of such a visualisation, for Scan ID 12 on the 16th July. The plot illustrates the vertical plane through which the DIAL scanned, and indicates the distribution of VOCs within this plume. The wind direction is indicated by the red arrow. The intensity of the colour plot is related to the concentration of the VOCs. The maximum VOC concentration in this plot is 300 ppb.

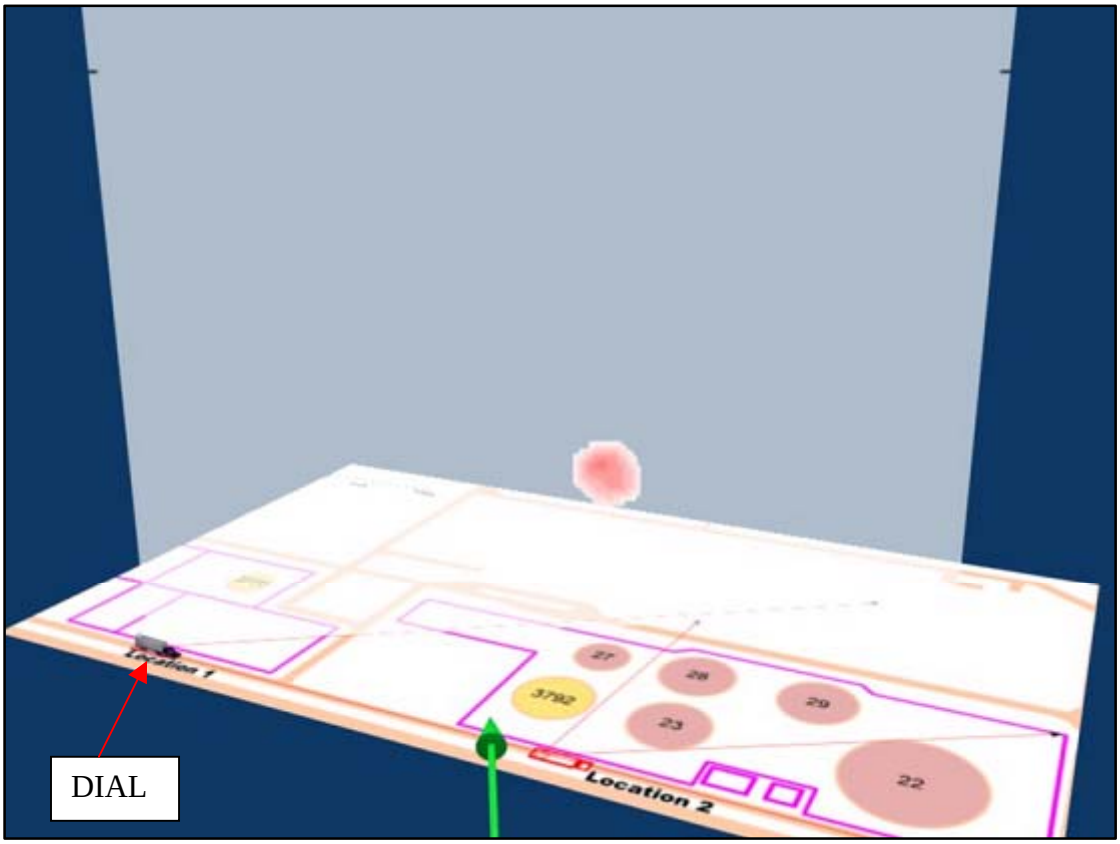

Figure 1.2. Example of the VOC distribution seen in a vertical scan at the Bulk Terminal (Scan 12, 16th July). The green arrow represents the average wind direction. The peak VOC concentration observed in this scan was 300 ppb.

Measurements on the 17th July

A further series of measurements were made of tanks 27,28,29 and 23 from Location 1. The wind was from the south, shifting slightly to south-westerly during the day with wind speeds ranging between 2.8 and 8.7 m/s. The results are presented in Table 1.2. The average flux observed for these tanks on the 17th July was 21 lbs/hr with a standard deviation of ± 5 lbs/hr. Upwind scans were below the detection limit, indicating no contribution from other sources.

In order to separate out and directly measure fluxes from tank 22, the DIAL was moved to Location 2, to the south of tank 3792. Scans could then be made isolating the emissions from tank 22. It should be noted that this measurement configuration is not ideal for flux measurements, as the measurement line of sight is very close to tank 22. Other locations were not possible due to construction work on the road to the north of tank 22. Scans made from location 1 had indicated that the emissions observed from tank 22 were not significant. This was apparent because no significant concentrations were observed at ranges which would have been consistent with a plume from tank 22. Moving to a measurement line of sight further away from tank 22, to the north of Ave G, would have reduced the chance of measuring any small emissions from tank 22 due to dispersion. The fluxes observed, even close to tank 22, were very small, with an average flux of 3 lbs/hr and a standard deviation of 1.3 lbs/hr. The peak concentrations observed were less than 100 ppb, and these emissions would generally be considered insignificant in the context of a DIAL survey.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
3	11:41	5.3	186.7	20	0.22	Downwind tanks 27/28/23
4	11:51	5.2	189.6	21	0.17	Downwind tanks 27/28/23
5	12:04	5.1	191.6	24	0.34	Downwind tanks 27/28/23
6	12:25	5.1	188.0	19	0.16	Downwind tanks 27/28/23
7	12:38	4.6	194.6	31	0.24	Downwind tanks 27/28/23
8	12:50	4.9	204.6	25	0.15	Downwind tanks 27/28/23
9	13:09	5.0	189.5	<1	0.01	Upwind
10	13:21	5.7	198.3	<1	0.03	Upwind
13	13:36	6.2	180.6	<1	0.01	Upwind
14	13:51	5.8	186.7	25	0.21	Downwind tanks 27/28/23
21	15:03	8.7	207.5	20	0.21	Downwind tanks 27/28/23
23	15:25	6.8	216.3	15	0.19	Downwind tanks 27/28/23
24	15:47	5.8	218.2	22	0.12	Downwind tanks 27/28/23
25	16:06	5.5	219.1	11	0.11	Downwind tanks 27/28/23
						Moved to Location 2
26	16:46	2.8	226.6	1	0.05	Downwind tank 22
27	17:04	3.7	220.3	4	0.09	Downwind tank 22
28	17:22	3.5	213.8	4	0.07	Downwind tank 22
29	17:41	3.4	209.6	3	0.07	Downwind tank 22

Table 1.2. VOC fluxes measured on 17th July at the Bulk Terminal.

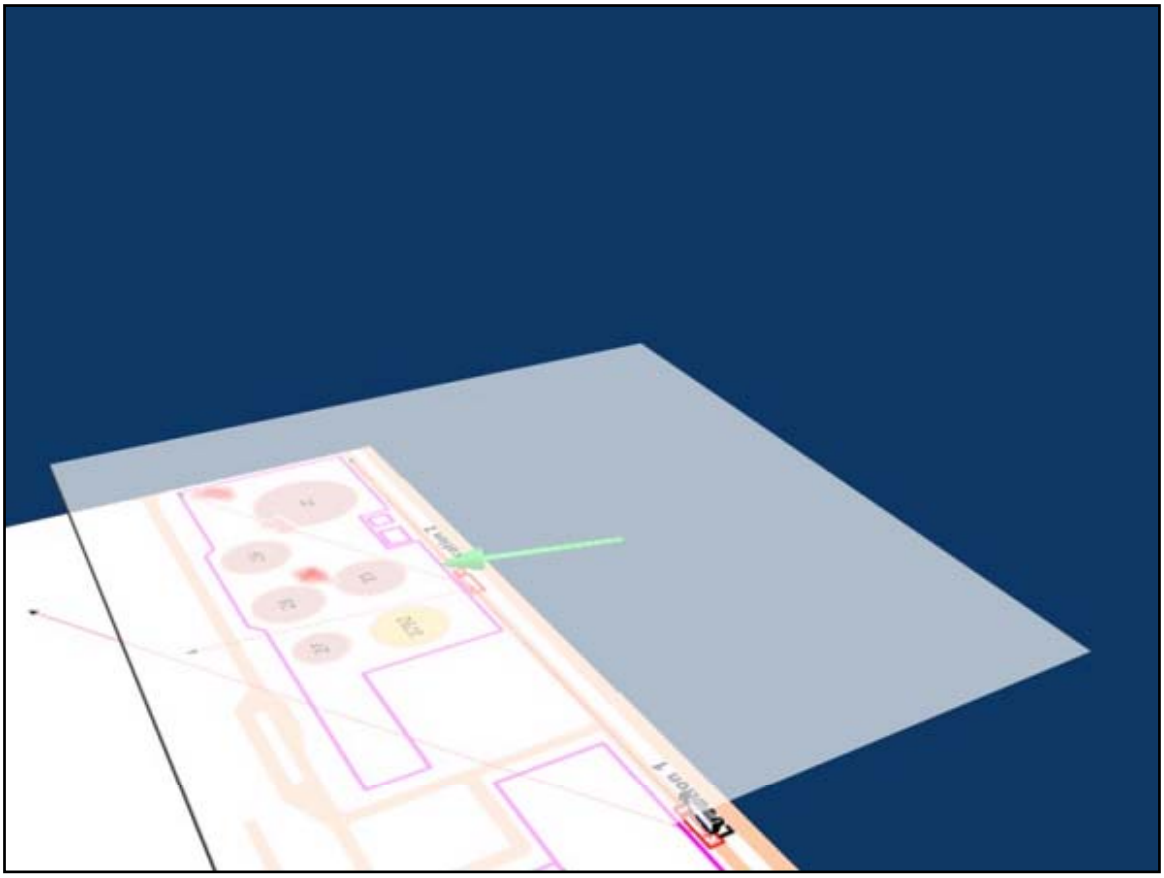

Figure 1.3. Example of a horizontal scan showing the VOC distribution above naphtha tanks at the Bulk Terminal (Scan 17, 17th July). The green arrow represents the average wind direction. The peak VOC concentration observed in this scan was 288 ppb.

Measurements on the 18th July and 19th July

Further scans were made of tank 22 on both the 18th and 19th July, tables 1.3 and 1.4 present these data. The average emissions fluxes measured were 5 lbs/hr with a standard deviation of 2.4 lbs/hr on the 18th and 3 lbs/hr with a standard deviation of 2.4 lbs/hr on the 19th.

Two scans were made on the 18th July to measure the emissions from tanks 23 and 28 from location 2. These scans may also have included the contribution from tanks 29 and 22. However, the emissions from these tanks would be quite dispersed and are probably not included in the measured fluxes. The scans are not ideal for flux determination, as the wind field would be very disturbed by the proximity of the tanks. The scans gave flux results that are much lower than those measured on the previous days for these tanks, with an average value of 3.5 lbs/hr. This indicates either, that the larger emissions originated from tank 27 (included in earlier measurements), and are not included in these scans. A more likely explanation, given subsequent measurements on the 19th, is that the wind field was not ideal and the scans did not capture the emissions from the tanks. On the 19th July similar scans measured an average emission flux of 18 lbs/hr, which is consistent with the measurements made on the 16th and 17th July for these tanks.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
3	09:54	5.6	131.3	5	0.03	Downwind tank 22
5	10:35	5.0	133.3	3	0.08	Downwind tank 22
6	10:56	5.1	136.3	7	0.09	Downwind tank 22
7	11:14	4.6	140.0	10	0.09	Downwind tank 22
8	11:36	3.8	141.8	<1	0.01	Upwind
9	11:46	4.3	140.9	<1	0.00	Upwind
10	12:00	3.8	139.4	4	0.07	Downwind tanks 28 and 23
11	12:12	3.7	136.2	3	0.04	Downwind tanks 28 and 23
13	13:49	4.7	212.9	4	0.03	Downwind tank 22
14	14:08	3.3	202.1	<1	0.01	Upwind
15	14:18	3.0	196.8	<1	0.02	Upwind
16	14:32	1.8	201.0	3	0.10	Downwind tank 22
17	14:50	1.6	162.2	3	0.06	Downwind tank 22
18	15:02	2.7	198.9	6	0.09	Downwind tank 22
19	15:14	2.3	185.8	<1	0.01	Upwind

Table 1.3. VOC fluxes measured on 18th July at the Bulk Terminal

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
31	14:42	3.4	123.8	1	0.06	Downwind tank 22
32	15:01	2.8	120.1	<1	0.05	Downwind tank 22 - wind shifted so upwind
33	15:22	3.1	149.6	<1	0.01	Upwind
34	15:32	3.3	172.0	<1	0.01	Upwind
35	15:42	2.4	170.7	5	0.08	Downwind tank 22
39	17:07	4.5	148.0	4	0.13	Downwind tank 22
40	17:28	3.6	132.4	20	0.23	Downwind tanks 28 and 23
41	17:47	3.8	125.2	16	0.20	Downwind tanks 28 and 23

Table 1.4. VOC fluxes measured on 19th July at the Bulk Terminal

Night-time measurements on the 20th-21st July.

A series of measurements was made on the night of the 20th-21st July from Location 2, the results of these scans are given in Table 1.5. These repeated the scans made from this location during the daytime. The wind was initially from further to the east, which was not ideal for this location, however it subsequently shifted further south, providing useable measurements of tank 22 and tanks 23/28. The average emission flux measured from tank 22 was 1 lbs/hr, which is at the detection limit.

The measurements of the emissions from tanks 23 and 28 gave an average emission flux of 14 lbs/hr, with a standard deviation of 7 lbs/hr. Although this emission is lower than that measured during the day. That, coupled with the variable wind pattern close to the tanks and the fact that the wind speed itself was lower during these measurements, suggests that conclusions about the relationship between day and night-time emissions cannot be drawn from these data, except to recognise that emissions are observed during the night-time, and therefore night time cannot be discounted from annualisation calculations based on day time measurements.

A series of air samples, using canisters and pumped sorbent tubes was also taken, and the results of these are reported in Annex 2. Figure A1.1 indicates the locations of these samples at the Bulk Terminal.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
49	0:05	3.0	99.5	1	0.03	Downwind tank 22
50	0:24	3.5	110.4	1	0.04	Downwind tank 22
51	0:43	3.1	104.7	1	0.06	Downwind tank 22
52	1:01	3.1	102.5	<1	0.00	Upwind
53	1:11	3.2	91.1	<1	0.01	Upwind
54	1:21	2.8	107.0	1	0.05	Downwind tank 22
55	1:40	2.7	102.6	2	0.05	Downwind tank 22
56	1:59	3.4	87.2	<1	0.04	Downwind tank 22
61	3:36	3.5	94.0	<1	0.01	Upwind
62	3:45	3.1	111.8	<1	0.01	Upwind
64	4:03	2.5	121.2	15	0.12	Downwind tanks 28 and 23
65	4:21	2.2	120.3	14	0.22	Downwind tanks 28 and 23
66	4:40	2.3	125.7	25	0.23	Downwind tanks 28 and 23
67	4:59	2.2	105.2	15	0.48	Downwind tanks 28 and 23
68	5:17	2.6	100.9	3	0.08	Downwind tanks 28 and 23
69	5:37	2.4	118.2	9	0.17	Downwind tanks 28 and 23
72	6:03	2.6	108.9	1	0.09	Downwind tank 22

Table 1.5. VOC fluxes measured on the night of 20th July at the Bulk Terminal

Section 2 Measurements of VOC emissions from a Refinery in the Houston non-attainment area.

Measurement description.

This section of the report describes the results of measurements of VOC emissions from various sources within the Refinery. Measurements of VOC emissions were carried out from the 25th July to the 11th August. Table 2.1 lists the measurements days and the sources monitored on each day. The DIAL measurement locations are identified on individual maps in the following Sections.

Date	DIAL Location	Sources monitored
25th July	Refinery Location 1	Product tanks
26th July	Refinery Location 1	Product tanks
28th July	Refinery Location 2	Crude oil tanks, coker
29th July	Refinery Location 2	Crude oil tanks
30th July	Refinery Location 3	Gasoline tanks and flare 6
31st July	Refinery Location 2, 2C	Crude oil tanks and coker
1st August	Refinery Location 2	Coker
2nd August	Refinery Location 4	Waste water treatment and crude oil tanks
3rd August	Refinery Location 2	Coker
5th –6th August (Night)	Refinery Location 2	Crude oil tanks
6th – 7th August (Night)	Refinery Location 3	Gasoline tanks, coker and flare 6
7th – 8th August (Night)	Refinery Location 5,6,7	Product tanks Hot oil tanks
9th August	Refinery Location 8	Flares
10th August	Refinery Location 8	Flares
11th August	Refinery Location 8	Flares

Table 2.1 Summary of DIAL VOC flux measurements at the Refinery

The GPS positions for the DIAL locations were:

Refinery Location 1
By Muster Point 8
29°22'1.48"N
94°56'23.11"W

Refinery Location 2
E 4th street, next to tank 1020
29°22'4.56"N
94°55'13.56"W

Refinery Location 2C
Further north on E 4th street
29°22'5.58"N
94°55'14.09"W

Refinery Location 3
Avenue J, North of tank 1045
29°22'10.26"N
94°55'29.40"W

Refinery Location 4
Avenue N, south of Surge Basin 2
29°21'52.38"N
94°55'17.22"W

Refinery Location 5
Outside Gate 16
29°22'3.78"N
94°56'27.42"W

Refinery Location 6
On W 4th St, by tank 17
29°22'21.36"N
94°56'10.98"W

Refinery Location 7
Avenue G, south of ARU
29°22'23.52"N
94°56'15.36"W

Refinery Location 8
Grant Avenue, South of tank 20.
29°22'35.45"N
94°56'29.47"W

The measurement results are presented in the following sections, grouped by the sources measured. It is important to note that the potential emission sources measured were identified by TCEQ and the refinery, and measurements were focussed on these sources. This study did not include a full survey of all sources within the refinery, and was not aimed at determining total refinery emissions.

Measurements of product storage tanks.

A small number of distillate product storage tanks were identified as being of interest. These included tanks 55 and 53. Scans were made of these tanks on the 25th 26th July and during the night of 7th August. These measurements were made from Location 1 on the 25th and 26th and from Location 5 on the 7th August. The results are presented in Table 2.2. The emissions from tank 55 were not significant, with average emission fluxes measured of 5 lbs/hr (not counting the negligible fluxes measured during very low and variable wind conditions). Upwind scans were in general below the detection limit, however one scan down Avenue K and upwind of the hydrogen plants No.1 and No.2 measured a small flux of 7 lbs/hr. Measurements of tank 55 during the evening of the 7th August showed similar emission fluxes, with an average of 6 lbs/hr. Tank 57 was too close to the DIAL to enable it to be measured on the 7th August. Measurements of tank 53 were made during the evening of the 7th August and an average flux of 24 lbs/hr with a standard deviation of 8 lbs/hr was measured. Upwind measurements were below detection limits.

			Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Date	Time	m/s	Degrees	lbs/hr	ppm	
79	25-Jul	17:15	4.5	128.4	2	0.07	Downwind Tank 55
80	25-Jul	17:26	4.1	140.0	3	0.06	Downwind Tank 55
82	25-Jul	18:07	4.7	166.4	2	0.05	Downwind Tank 55
84	25-Jul	18:16	4.9	169.3	<1	0.01	Downwind Tank 55
89	26-Jul	09:55	0.9	241.9	<1	0.01	Tank 55, Wind direction variable, low speed.
90	26-Jul	10:05	2.0	311.4	1	0.07	Tank 55, Wind direction variable.
91	26-Jul	10:15	1.6	286.8	<1	0.01	Tank 55, Wind direction variable.
92	26-Jul	10:27	1.8	304.3	<1	0.01	Tank 55, Wind direction variable.
93	26-Jul	10:43	1.3	256.8	<1	0.01	Tank 55, Wind direction variable, low speed.
94	26-Jul	10:58	0.7	282.6	<1	0.09	Scan down Avenue K, upwind tanks
95	26-Jul	11:09	4.9	117.0	7	0.23	Scan down Avenue K, upwind tanks
96	26-Jul	11:23	6.0	114.3	4	0.08	Scan between tanks 53,55. Downwind tank 55.
97	26-Jul	11:52	5.3	108.8	2	0.04	Scan between tanks 53,55. Downwind tank 55.
98	26-Jul	12:05	5.9	112.8	2	0.04	Scan between tanks 53,55. Downwind tank 55.
99	26-Jul	12:17	4.5	112.6	<1	0.01	Downwind tank 55
100	26-Jul	12:28	4.6	118.1	2	0.05	Downwind tank 55
101	26-Jul	12:38	5.2	112.2	1	0.02	Downwind tank 55
102	26-Jul	12:57	5.3	115.1	7	0.10	Downwind tank 55
106	26-Jul	14:26	7.4	136.4	5	0.05	Downwind tank 55
107	26-Jul	14:45	7.6	156.6	14	0.14	Downwind tank 55
108	26-Jul	15:03	6.3	155.0	6	0.05	Downwind tank 55
369	7-Aug	21:05	3.5	173.4	8	0.12	Downwind tanks 55, 66
373	7-Aug	21:42	3.5	175.9	4	0.08	Downwind tanks 55, 66
374	7-Aug	22:00	3.2	171.0	6	0.10	Downwind tanks 55, 66
375	7-Aug	22:23	3.3	167.8	<1	0.05	Upwind tanks
376	7-Aug	22:41	3.5	178.2	<1	0.06	Upwind tanks
377	7-Aug	23:03	3.1	188.3	13	0.11	Downwind tank 53
378	7-Aug	23:21	3.4	195.6	32	0.26	Downwind tank 53
379	7-Aug	23:40	3.3	195.4	29	0.38	Downwind tank 53
380	7-Aug	23:59	3.0	197.3	21	0.29	Downwind tank 53

Table 2.2 Measurements of VOC fluxes from product storage tanks

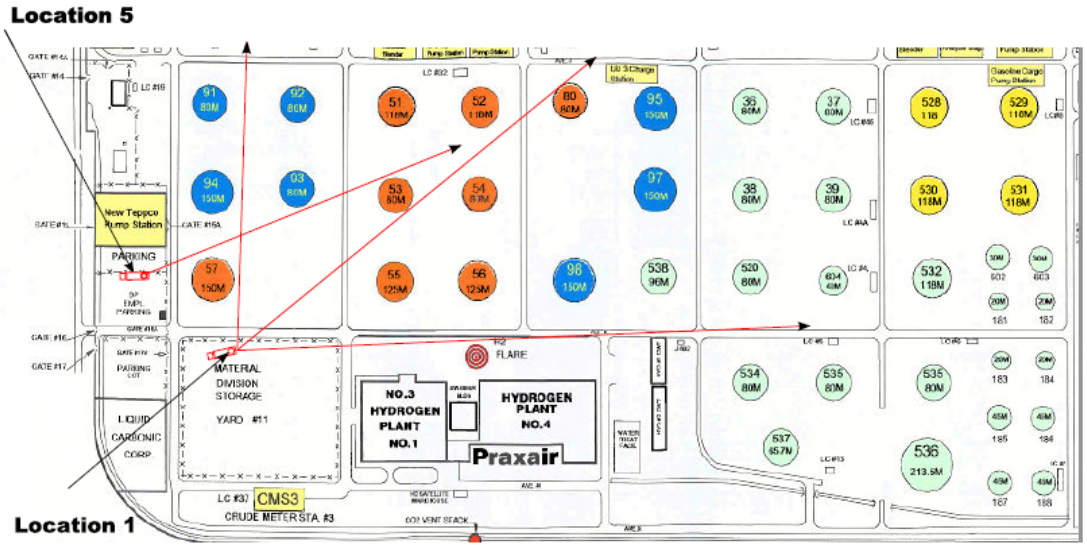

Figure 2.1. DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from the product storage tanks at the Refinery.

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Measurements of crude oil tanks

A series of measurements of the emissions from the crude oil storage tanks was made over several days. Measurements were made on the 28th 29th 31st July, 2nd August and on the night of the 6th August. The results of measurements of different tanks are summarised in Table 2.3, all flux results are presented in Table 2.4.

Measurements were made from Location 2, apart from the measurements of tanks 1020 and 1021 on the 31st July, for which the DIAL was moved north to Location 2C.

Tanks	Average emission flux Lbs/hr
1020	<2
1021	16
1024	5
1025	11
1052	22 28th July 39 2nd August 24 5th August, Night
1053	7
1055	<5

Table 2.3 Summary of VOC fluxes from crude storage tanks

In order to assign emission fluxes to individual tanks, some interpretation of the flux results in Table 2.4 has had to be made. In some cases, flux measurements were made which were downwind of a number of tanks. Where these tanks were also measured separately on other occasions then the split of the flux between the possible sources has been made based on these individual measurements. For the measurements made on the 2nd August from Refinery Location 4, the measurements of tanks 1055 and 1053 probably include a component of the emissions observed from tank 1052. The flux is not significantly higher than that measured from tank 1052 alone, and so it is clear there is no significant emission flux from either tank 1055 or tank 1053. This is consistent with the previous measurements of these tanks, which did not include emissions upwind from tank 1052. Similarly measurements of tanks 1020 and 1021 on the 29th July may have included some emissions from tanks 1025 and 1024, however, the wind direction was such that this is unlikely. The wind direction, and location of the observed flux, also indicate that most of the observed emission flux is attributable to tank 1021, and so the average emissions have been assigned to tank 1021. This is supported by measurement of tank 1020 only, on the 31st July, which gave very low fluxes, many below 1 lbs/hr.

No significant emissions were observed from tank 1055, which was in the near field during a number of scans.

In summary, most of the tanks observed during these measurements did not have significant emission fluxes, and in general, the emission fluxes from individual tanks were < 10 lbs/hr.

A VOC emission was observed from tank 1052, with an average emission of 39 lbs/hr observed on the 2nd August.

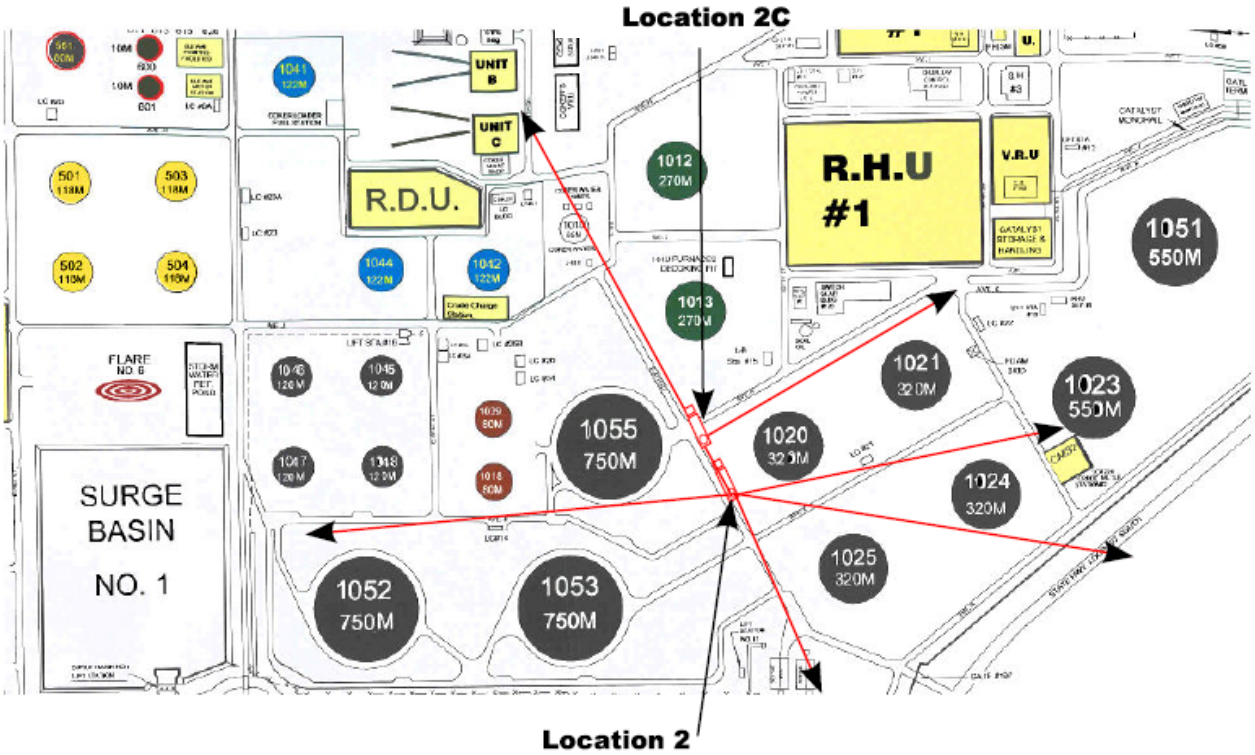

Figure 2.2.DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from the crude oil tanks at the Refinery.

Checked by:

Scan ID	Date	Time	Wind Speed m/s	Wind Direction Degrees	Emission rate lbs/hr	Concentration ppm	Notes
138	28-Jul	12:37	2.3	268.9	3	0.29	Downwind tank 1025
139	28-Jul	12:48	2.5	257.9	6	0.32	Downwind tank 1025
140	28-Jul	12:58	1.9	225.7	8	0.31	Downwind tank 1025
141	28-Jul	13:16	2.2	209.4	5	0.14	Downwind tank 1025
148	28-Jul	13:59	3.0	180.5	5	0.05	Downwind tank 1025
149	28-Jul	14:36	3.8	164.7	<1	0.01	Upwind tank 1025
152	28-Jul	15:51	3.3	216.0	17	0.14	Downwind coker
153	28-Jul	16:12	2.6	213.4	7	0.10	Downwind coker
154	28-Jul	16:30	3.0	204.1	8	0.12	Downwind coker
155	28-Jul	16:52	4.3	182.7	2	0.12	Downwind tank 1013/ upwind coker
156	28-Jul	17:19	4.6	169.0	7	0.32	Downwind tank 1053
157	28-Jul	17:39	4.3	163.8	13	0.24	Downwind tanks 1052 and 1053
158	28-Jul	18:03	4.1	168.4	23	0.08	Downwind tanks 1052 and 1053
159	28-Jul	18:23	3.8	170.5	31	0.17	Downwind tanks 1052 and 1053
160	28-Jul	18:42	3.8	175.4	<1	0.04	Upwind
163	29-Jul	12:44	1.8	138.4	3	0.12	Downwind tank 1053
164	29-Jul	12:56	3.0	124.3	6	0.16	Downwind tanks 1052, 1053
165	29-Jul	13:07	4.3	117.2	5	0.12	Downwind tank 1053
166	29-Jul	13:16	4.8	123.1	6	0.16	Downwind tank 1053
167	29-Jul	13:26	4.5	124.7	7	0.17	Downwind tank 1053
168	29-Jul	13:36	3.8	151.1	5	0.10	Downwind tank 1053
169	29-Jul	13:50	4.8	170.1	<1	0.05	Upwind 1053
170	29-Jul	13:59	5.2	150.9	<1	0.03	Upwind 1053
171	29-Jul	14:09	4.9	161.8	<1	0.03	Upwind 1053
172	29-Jul	14:19	5.4	156.7	3	0.04	Upwind 1053
173	29-Jul	14:34	4.1	156.4	12	0.23	Downwind tank 1025
174	29-Jul	14:43	4.0	167.1	13	0.50	Downwind tank 1025
175	29-Jul	15:12	4.1	173.8	8	0.19	Downwind tank 1025
176	29-Jul	15:23	3.2	161.6	9	0.28	Downwind tank 1025
178	29-Jul	15:44	3.4	135.6	15	0.23	Downwind tanks 1024, 1025
179	29-Jul	15:50	3.3	158.9	5	0.05	Downwind tank 1024
180	29-Jul	16:08	3.6	159.4	15	0.11	Downwind tanks 1024, 1025
181	29-Jul	16:27	4.0	159.7	14	0.08	Downwind tanks 1024, 1025
182	29-Jul	16:45	3.7	148.2	10	0.22	Downwind tanks 1020, 1021
183	29-Jul	17:13	4.3	153.0	19	0.11	Downwind tanks 1020, 1021
184	29-Jul	17:24	3.7	160.5	13	0.20	Downwind tanks 1020, 1021

Table 2.4 Measurements of VOC fluxes from crude oil storage tanks

Scan ID	Date	Time	Wind Speed m/s	Wind Direction Degrees	Emission rate lbs/hr	Concentration ppm	Notes
186	29-Jul	17:49	3.9	145.7	12	0.18	Downwind tanks 1020, 1021
187	29-Jul	17:59	3.8	150.9	19	0.18	Downwind tanks 1020, 1021
188	29-Jul	18:09	4.0	150.8	20	0.10	Downwind tanks 1020, 1021
231	31-Jul	12:25	3.2	87.8	<1	0.09	Downwind of tank 1053
232	31-Jul	12:35	3.0	114.9	3	0.09	Downwind of tank 1053
233	31-Jul	12:45	3.3	113.1	1	0.08	Downwind of tank 1053
235	31-Jul	13:14	3.5	106.2	<1	0.04	Downwind of tank 1020
236	31-Jul	13:27	3.7	107.4	2	0.10	Downwind of tank 1020
241	31-Jul	14:05	3.5	201.8	<1	0.28	Downwind of tank 1020
242	31-Jul	14:14	3.6	200.9	<1	0.17	Downwind of tank 1020
243	31-Jul	14:24	3.2	179.8	3	0.10	Downwind of tank 1020
258	31-Jul	17:30	4.2	169.5	4	0.08	Downwind of tank 1013
259	31-Jul	17:41	4.1	177.8	2	0.09	Downwind of tank 1013
260	31-Jul	17:50	3.8	172.2	2	0.08	Downwind of tank 1013
279	2-Aug	13:38	3.2	233.4	39	0.26	Downwind of tanks 1053, 1055, 1052
280	2-Aug	13:48	2.5	233.5	19	0.28	Downwind of tanks 1053, 1055, 1052
281	2-Aug	13:58	3.4	207.4	20	0.35	Downwind of tanks 1053, 1055, 1052
282	2-Aug	14:16	3.9	218.5	24	0.15	Downwind of tanks 1053, 1055, 1052
283	2-Aug	14:34	3.0	239.4	18	0.17	Downwind of tanks 1053, 1055, 1052
284	2-Aug	14:57	3.1	257.3	37	0.35	Downwind tank 1052
285	2-Aug	15:07	3.9	225.6	54	0.50	Downwind tank 1052
286	2-Aug	15:17	4.6	221.3	39	0.26	Downwind tank 1052
287	2-Aug	15:27	4.2	218.4	39	0.46	Downwind tank 1052
288	2-Aug	15:46	2.8	240.9	29	0.27	Downwind tank 1052
319	5-Aug	23:48	2.8	161.6	5	0.11	Downwind tank 1025
320	6-Aug	00:07	2.9	156.4	4	0.08	Downwind tank 1025
321	6-Aug	00:26	2.9	145.4	<1	0.05	Downwind tank 1025
322	6-Aug	00:45	3.3	163.3	2	0.29	Downwind tank 1025
323	6-Aug	01:06	3.8	156.7	4	0.12	Downwind tanks 1024 and 1025
324	6-Aug	01:25	4.2	165.1	11	0.11	Downwind tanks 1024 and 1025
325	6-Aug	01:44	3.7	158.8	4	0.08	Downwind tanks 1024 and 1025
326	6-Aug	02:05	4.1	169.8	<1	0.11	Upwind tanks
327	6-Aug	02:23	3.4	160.6	<1	0.08	Upwind tanks
328	6-Aug	02:45	3.9	167.6	44	0.19	Downwind tanks 1052 and 1053
329	6-Aug	03:03	3.6	164.2	22	0.30	Downwind tanks 1052 and 1053
330	6-Aug	03:41	3.1	167.8	12	0.17	Downwind tanks 1052 and 1053
331	6-Aug	03:59	3.4	165.7	19	0.30	Downwind tanks 1052 and 1053
332	6-Aug	04:19	3.6	166.4	1	0.11	Upwind tanks
333	6-Aug	04:37	3.9	183.4	<1	0.08	Upwind tanks
335	6-Aug	05:12	3.3	185.0	13	0.29	Downwind waster water vent (South of tank 1010)
336	6-Aug	05:30	3.4	181.2	5	0.08	Downwind waster water vent (South of tank 1010)
337	6-Aug	05:49	3.0	185.0	10	0.28	Downwind waster water vent (South of tank 1010)
338	6-Aug	06:09	2.9	185.0	1	0.08	Downwind tanks 1024 and 1025
340	6-Aug	06:32	2.2	202.0	1	0.10	Downwind tanks 1024 and 1025

Table 2.4 (continued) Measurements of VOC fluxes from crude oil storage tanks

Measurements of gasoline tanks and flare 6.

Measurements of gasoline storage tanks 501, 502, 503, and 504 were carried out from location 3 on the 30th July and on the night of the 6th August. The results are presented in Table 2.5.

The wind directions for these measurements were not ideal for flux determination; however, any significant emissions would have been observed. Upwind measurements from location 3 included measurements of emissions from flare 6, which was operational during the measurement periods. As can be seen from the results presented in Table 2.5, there was no significant VOC flux observed from these tanks; the measurements are consistent with an emission of approximately 5 lbs/hr from individual tanks. Night time measurements found slightly lower emissions; however as these measurements were close to the detection limit, drawing any conclusion from these results about night versus day emissions is not recommended. Owing to the wind direction during the night time measurements, it is also likely these scans would not have fully captured emissions from tank 502.

Measurements of emissions from flare 6 on the 30th July gave an average flux of 4 lbs/hr. During the night time measurements on the 6th August, an average flux of 22 lbs/hr was measured from flare 6.

It should be noted that these emissions could act as an upwind source for the gasoline tank measurements. However, they were spatially separated from the emissions from the gasoline tanks and were not included in these measured fluxes. Therefore this upwind source did not have to be subtracted from the tank measurements, which can lead to a significant source of uncertainty and is something that is avoided if possible.

			Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Date	Time	m/s	Degrees	lbs/hr	ppm	
193	30-Jul	11:41	2.2	188.0	<1	0.00	Upwind of tanks
196	30-Jul	12:05	2.5	249.8	2	0.07	Downwind tanks 501, 502, 503, 504
198	30-Jul	12:27	2.2	223.6	5	0.11	Downwind of tanks 501, 502, 503, 504
199	30-Jul	12:38	2.7	223.4	3	0.09	Downwind of flare 6
200	30-Jul	12:50	3.0	189.3	3	0.11	Downwind of flare 6
201	30-Jul	13:01	3.6	168.1	3	0.07	Downwind of flare 6
205	30-Jul	13:17	5.5	159.9	2	0.04	Downwind of tanks 501, 504
207	30-Jul	13:28	4.9	178.6	13	0.10	Downwind of tanks 501, 504
208	30-Jul	13:42	3.5	190.9	11	0.15	Downwind of tanks 501, 504
209	30-Jul	14:02	1.3	173.8	<1	0.03	Upwind of tanks
210	30-Jul	14:43	0.4	178.4	<1	0.11	Downwind of flare 6 (wind speed low)
211	30-Jul	14:52	2.3	219.0	3	0.18	Downwind of flare 6
212	30-Jul	15:03	3.2	206.7	11	0.08	Downwind of flare 6
213	30-Jul	15:16	3.9	204.2	2	0.05	Downwind of flare 6
215	30-Jul	15:55	3.3	191.5	3	0.05	Downwind of flare 6
216	30-Jul	16:44	4.5	201.7	3	0.04	Downwind of flare 6
217	30-Jul	16:55	4.2	208.5	4	0.10	Downwind of flare 6
218	30-Jul	17:08	4.1	205.4	5	0.08	Downwind tank 504
220	30-Jul	17:32	4.0	215.1	18	0.24	Downwind tanks 501, 502, 504
221	30-Jul	17:49	4.5	179.4	5	0.11	Downwind tank 504
224	30-Jul	18:11	4.5	217.7	16	0.19	Downwind tanks 501, 502, 504
344	7-Aug	00:25	3.6	139.3	37	0.45	Downwind flare 6, upwind of tanks 501-504
345	7-Aug	00:44	3.5	139.0	22	0.27	Downwind flare 6, upwind of tanks 501-504
346	7-Aug	01:02	2.8	131.6	13	0.26	Downwind flare 6, upwind of tanks 501-504
347	7-Aug	01:23	3.1	138.1	8	0.48	dnwnd 501, 502, 504(wind poor for flux)
353	7-Aug	02:56	2.7	135.7	1	0.13	Downwind of tanks 501, 502, 504 (wind direction not good for flux)
354	7-Aug	03:14	2.6	136.6	<1	0.12	Downwind of tanks 501, 502, 504 (wind direction not good for flux)
355	7-Aug	03:33	2.9	132.0	<1	0.05	Downwind of tanks 501, 502, 504 (wind direction not good for flux)
356	7-Aug	03:52	2.7	135.5	1	0.05	Downwind of tank 503 (wind direction not good for flux)
364	7-Aug	05:52	3.1	175.5	18	0.41	Downwind flare 6, upwind of tanks 501-504
365	7-Aug	06:10	2.8	178.2	18	0.23	Downwind flare 6, upwind of tanks 501-504
366	7-Aug	06:30	2.9	177.8	<1	0.09	Upwind flare 6

Table 2.5 Measurements of VOC fluxes from gasoline storage tanks

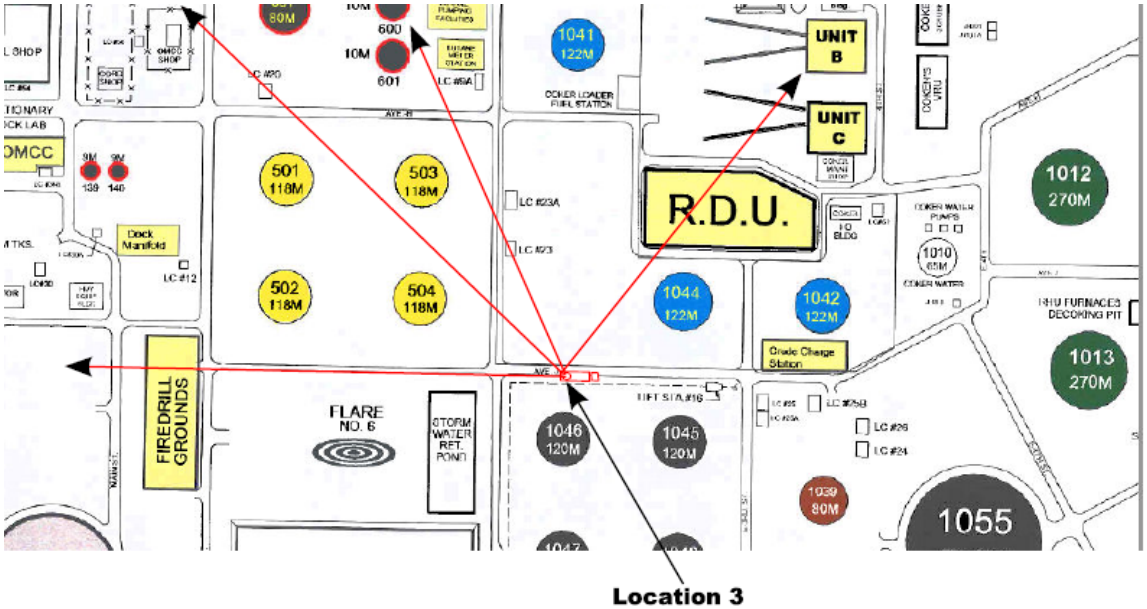

Figure 2.3. DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from the gasoline tanks at the Refinery.

Measurements of Water Treatment area.

Measurements were made of the water treatment plant on the 2nd August. Measurements were also made of crude tanks on this day and these have been reported in the relevant Section above.

The emissions fluxes observed from the waste treatment areas are given in Table 2.6. The average flux seen from the waste water treatment area, and specifically from the west side of the secondary and tertiary effluent treatment facilities, was 30 lbs/hr. Scans upwind of the water treatment plant measured less than 1 lbs/hr. Two scans were also made of the flux from the API separator located at the NE corner of Surge Basin 2, and these measured a small average emission flux of 7 lbs/hr.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Date and Time	m/s	Degrees	lbs/hr	ppm	
273	02/08/2007 12:18:14	3.2	214.5	<1	0.08	Upwind of waste water plant
275	02/08/2007 12:41:58	4.0	209.0	42	0.43	Downwind of waster water plant
276	02/08/2007 12:51:21	3.0	206.0	35	0.27	Downwind of waster water plant
277	02/08/2007 13:03:14	3.5	218.6	15	0.21	Downwind of waster water plant
299	02/08/2007 18:47:05	3.2	141.2	5	0.23	Downwind API separator
300	02/08/2007 19:05:29	2.5	168.3	8	0.24	Downwind API separator

Table 2.6 Measurements of VOC fluxes water treatment areas

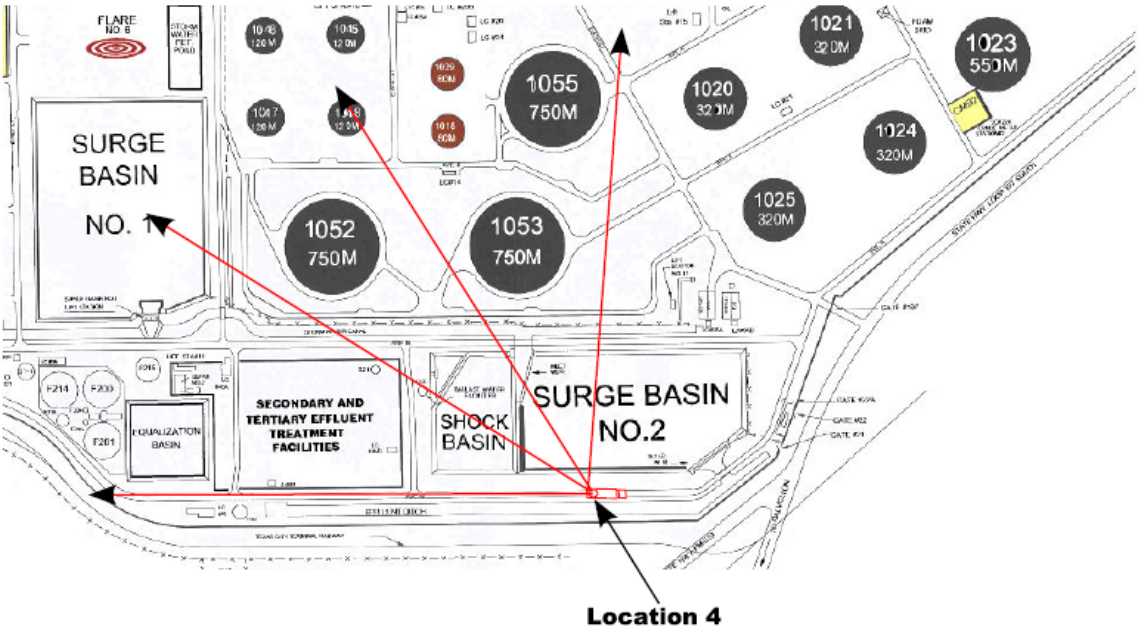

Figure 2.4. DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from the waste water treatment areas at the Refinery.

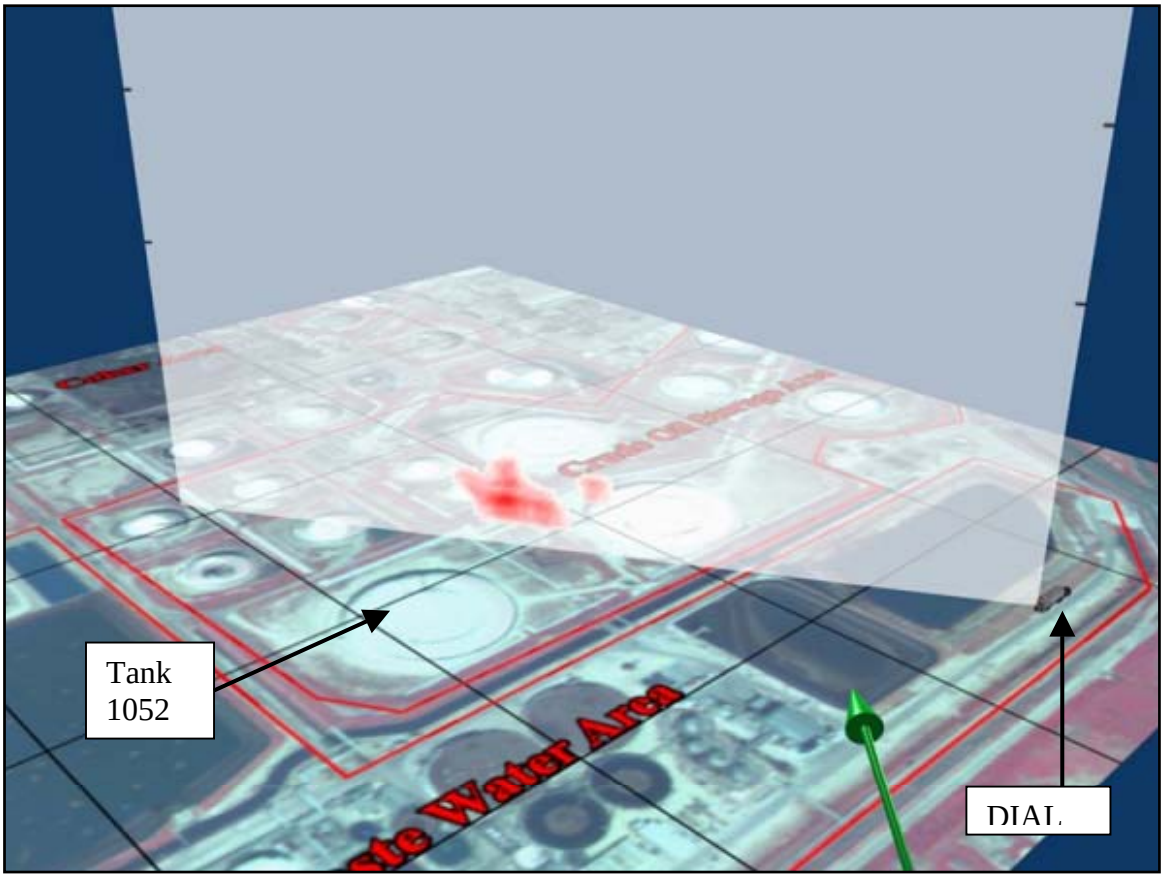

Figure 2.5. Example of the VOC distribution seen in a vertical scan at the Refinery (Scan 285). This scan measured the VOC emissions from tank 1052. The green arrow represents the average wind direction. The peak VOC concentration observed in this scan was 495 ppb.

Measurements of VOC emissions from coker C

Measurements were made of the VOC emissions from the operating coker, unit C, on the 28th July, 31st July, 1st 3rd August.

It had been suggested that refinery coker units could be a significant source of emissions, and figures of several hundred lbs/hr were discussed. One of the primary aims of these measurements was therefore to determine if the emissions from this coker were of a similar level. Over a number of measurement days, with different conditions, and through several cycles of the coker, the highest emission flux observed during a DIAL scan from the coker was 44 lbs/hr

The average emission fluxes observed from the coker are given in Table 2.7, and all individual flux results are presented in Table 2.8.

Date	Average emission flux from coker	Average upwind flux
28th July	10 lbs/hr	2 lbs/hr
31st July	31 lbs/hr	3 lbs/hr
1st August	12 lbs/hr	4 lbs/hr
3rd August	32 lbs/hr	8 lbs/hr
6th August - Night	4 lbs/hr	N/A

Table 2.7, Summary of VOC emissions fluxes measured from Coker 'C'

Measurements upwind of the cokers identified some small fluxes intermittently on the 31st July and 3rd August. These presumably arise from process units close to the cokers, including potentially, the coker vapour recovery unit. These upwind concentrations have not been subtracted from the observed coker results, however, their potential impact on the uncertainty of the results should be considered.

During the coker measurements on the 3rd August a small, localised emission was observed south of tank 1010. This was consistent with emissions from waste water vent pipes, located at the north end of E-4th street. The average emission flux observed from this source was 9 lbs/hr.

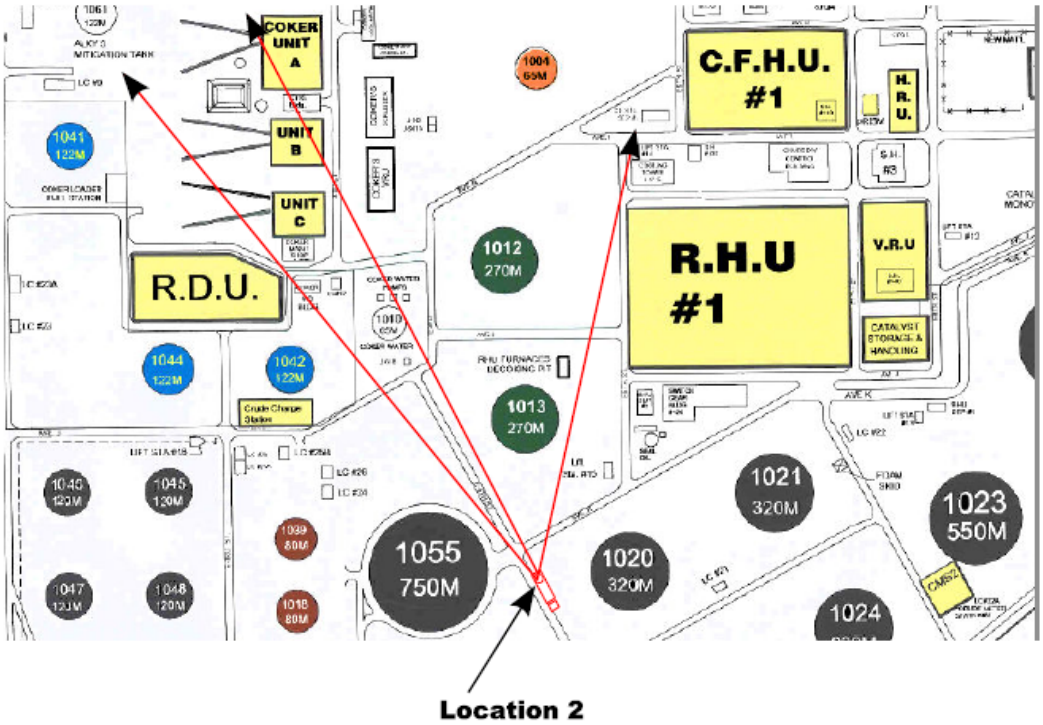

Figure 2.6.DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from coker C at the Refinery.

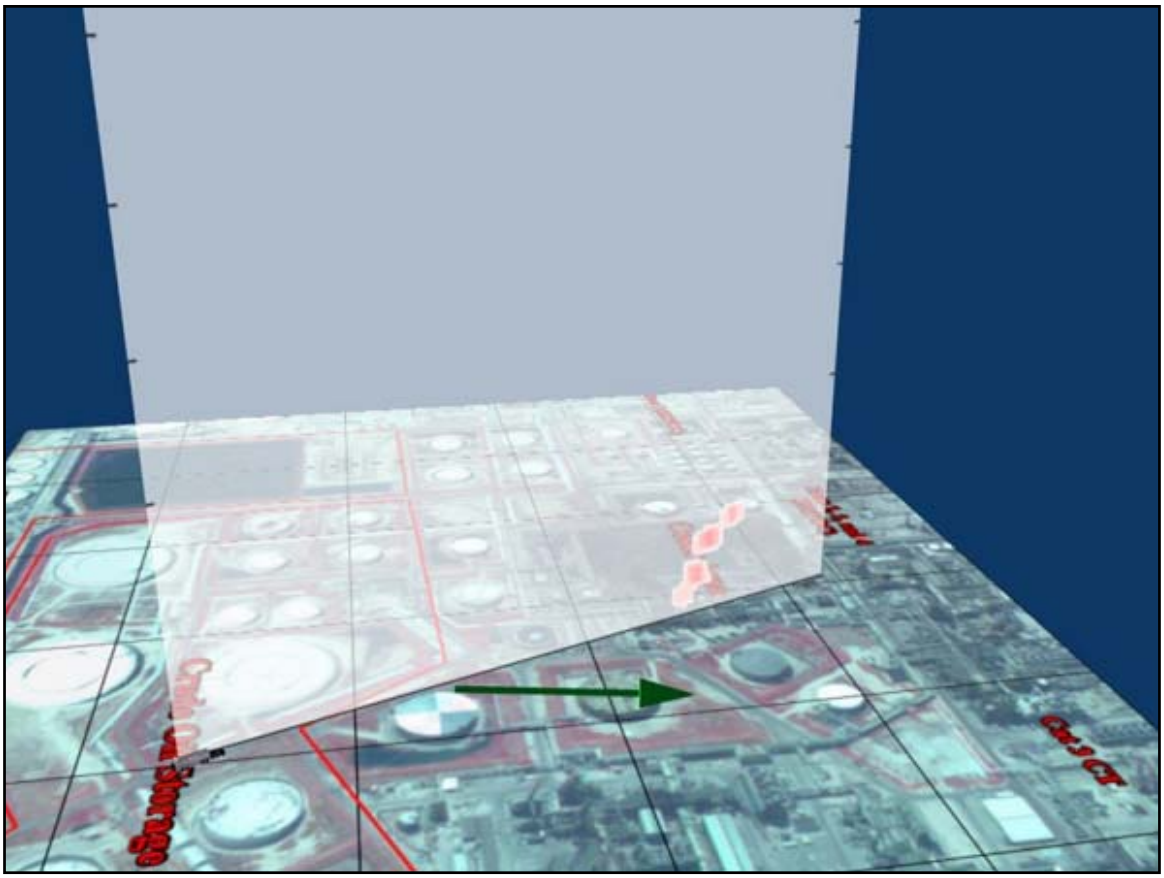

Figure 2.7. Example of the VOC distribution seen in a vertical scan at the Refinery (Scan 263), downwind of coker C. The green arrow represents the average wind direction. The peak VOC concentration observed in this scan was 234 ppb.

Scan ID	Date	Time	Wind Speed m/s	Wind Direction Degrees	Emission rate lbs/hr	Concentration ppm	Notes
152	28-Jul	15:51	3.3	216.0	17	0.14	Downwind coker
153	28-Jul	16:12	2.6	213.4	7	0.10	Downwind coker
154	28-Jul	16:30	3.0	204.1	8	0.12	Downwind coker
225	31-Jul	11:21	2.3	135.1	<1	0.21	Upwind of coker
226	31-Jul	11:31	1.6	119.0	1	0.26	Upwind of coker
227	31-Jul	11:41	1.9	90.8	8	0.34	Upwind of coker
228	31-Jul	11:52	1.6	75.5	<1	0.20	Upwind of coker
229	31-Jul	12:02	2.4	99.3	1	0.09	Upwind of coker
230	31-Jul	12:11	3.1	123.6	<1	0.05	Upwind of coker
244	31-Jul	14:35	2.8	158.9	30	0.33	Downwind of coker
245	31-Jul	14:44	4.4	155.2	42	0.25	Downwind of coker
246	31-Jul	14:54	4.5	142.4	32	0.21	Downwind of coker
247	31-Jul	15:06	4.4	138.7	25	0.27	Downwind of coker
248	31-Jul	15:16	4.2	150.7	44	0.35	Downwind of coker
249	31-Jul	15:26	4.3	171.8	20	0.29	Downwind of coker
250	31-Jul	15:45	4.3	169.9	26	0.18	Downwind of coker
251	31-Jul	15:59	3.8	172.3	29	0.16	Downwind of coker
252	31-Jul	16:27	4.2	179.9	N/A	0.75	Concentrations across vent pipes
253	31-Jul	16:38	3.8	175.5	N/A	0.37	Concentrations across vent pipes
254	31-Jul	16:48	3.6	169.5	N/A	0.19	Concentrations across vent pipes
255	31-Jul	16:59	3.5	176.4	13	0.34	Upwind of coker
256	31-Jul	17:08	3.6	169.3	<1	0.10	Upwind of coker
257	31-Jul	17:18	4.5	179.5	2	0.11	Upwind of coker
262	1-Aug	11:14	2.4	270.0	11	0.28	Downwind of coker
263	1-Aug	11:28	3.0	287.1	20	0.23	Downwind of coker
264	1-Aug	12:01	2.0	261.7	8	0.24	Downwind of coker
265	1-Aug	12:17	2.9	271.4	17	0.26	Downwind of coker
266	1-Aug	12:32	2.7	252.4	7	0.22	Downwind of coker
267	1-Aug	12:51	2.4	258.4	9	0.15	Downwind of coker
268	1-Aug	13:26	1.7	16.2	4	0.18	Upwind of coker
269	1-Aug	14:15	1.6	135.2	5	0.22	Upwind of coker (wind variable)
271	1-Aug	15:26	2.6	165.3	3	0.16	Upwind of coker (wind variable / rain)
302	3-Aug	11:05	4.3	75.0	20	0.68	Downwind of coker
303	3-Aug	11:24	4.2	75.8	22	0.22	Downwind of coker
304	3-Aug	11:57	4.5	93.4	37	0.43	Downwind of coker
306	3-Aug	12:35	3.7	92.4	11	0.46	Upwind of cokers
307	3-Aug	12:56	5.1	98.8	6	0.38	Upwind of coker
308	3-Aug	13:16	4.9	92.6	34	0.63	Downwind of coker
312	3-Aug	14:07	4.1	77.4	9	0.41	Flux from waster water vents (near tank 1010)
313	3-Aug	14:48	3.2	104.0	9	0.79	Flux from waster water vents (near tank 1010)
314	3-Aug	15:07	4.3	109.2	39	0.73	Downwind of coker
316	3-Aug	15:53	4.6	101.9	38	0.58	Downwind of coker
317	3-Aug	16:11	5.3	115.1	36	0.47	Downwind of coker
350	7-Aug	01:59	3.2	136.9	3	0.18	Downwind of coker
351	7-Aug	02:18	3.2	139.1	2	0.14	Downwind of coker
352	7-Aug	02:37	2.6	137.0	8	0.19	Downwind of coker
360	7-Aug	04:48	3.1	131.6	6	0.12	Downwind of coker
361	7-Aug	05:06	2.3	140.5	5	0.13	Downwind of coker
363	7-Aug	05:25	2.3	149.8	1	0.11	Downwind of coker

Table 2.8. Measurements of VOC emission fluxes from coker ‘c’.

Measurements of VOC emissions from heated oil tanks

A small number of heated tanks containing fuel oil were measured. These tanks were monitored on the night of the 7th August. The emissions from two tanks 43, and 60 were measured, and the results are given in Table 2.9.

The average emission flux from Tank 43 was 6 lbs/hr and from Tank 60 the average emission flux was 9 lbs/hr. Upwind fluxes were less than 1 lbs/hr. These results show the emissions from these tanks are very low and they are not significant sources of VOC emissions.

Scan ID	Date	Time	Wind Speed m/s	Wind Direction Degrees	Emission rate lbs/hr	Concentration ppm	Notes
							Moved to location 6, W 4th St.
382	8-Aug	02:00	3.6	213.1	3	0.11	Downwind tank 43
383	8-Aug	02:19	3.6	211.7	2	0.10	Downwind tank 43
384	8-Aug	02:30	3.7	211.4	1	0.06	Downwind tank 43
385	8-Aug	02:40	3.8	208.8	<1	0.01	Upwind tanks
386	8-Aug	02:49	3.5	209.0	<1	0.01	Upwind tanks
387	8-Aug	02:59	3.7	211.7	<1	0.02	Upwind tanks
388	8-Aug	03:16	3.0	215.3	8	0.16	Downwind tank 43
389	8-Aug	03:26	3.1	213.7	13	0.15	Downwind tank 43
390	8-Aug	03:36	2.7	213.5	7	0.13	Downwind tank 43
							Moved to location 7 Av G
399	8-Aug	05:14	2.2	204.3	9	0.11	Downwind tanks 60 and 63 - mainly tank 60
400	8-Aug	05:33	1.9	200.0	12	0.15	Downwind tanks 60 and 63 - mainly tank 60
401	8-Aug	05:42	2.1	203.9	15	0.17	Downwind tanks 60 and 63 - mainly tank 60
402	8-Aug	05:52	2.2	201.4	4	0.22	Downwind tanks 60 and 63 - mainly tank 60
403	8-Aug	06:01	2.0	186.0	9	0.23	Downwind tanks 60 and 63 - mainly tank 60
404	8-Aug	06:11	1.6	190.1	5	0.28	Downwind tanks 60 and 63 - mainly tank 60

Table 2.9. Measurements of VOC emission fluxes from hot oil tanks.

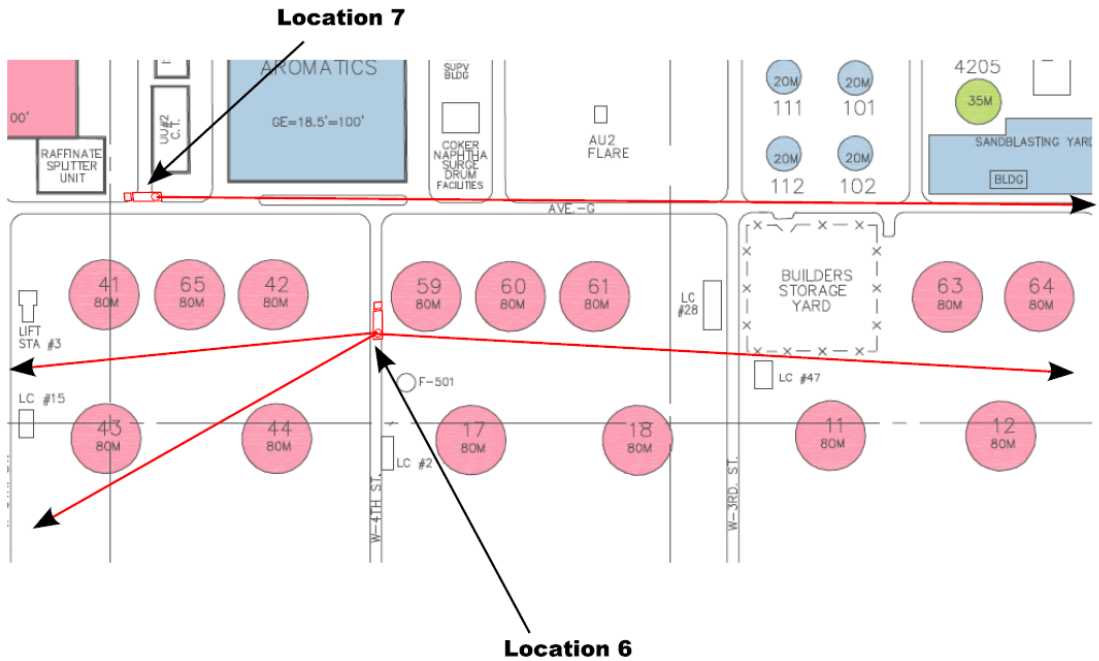

Figure 2.8. DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from the hot oil tanks at the Refinery.

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Measurement of VOC emissions from elevated flares.

Measurements of a temporary flare stack located in the NW corner of the refinery were undertaken. This flare had a very visible flame, and the aim was to determine any emission due to incomplete combustion in the flare. The DIAL was located in Grant Avenue and measured downwind and upwind of the flare to identify any plume of un-burnt hydrocarbons. These measurements identified very low levels of hydrocarbon downwind of the flare, and the VOC emission flux measured from this flare was ~ 6 lbs/hr. This is not surprising given that the flare was reported to be mainly burning hydrogen.

However, during the measurement of the temporary flare, a high concentration VOC plume was observed at a closer range than the temporary flare stack. This plume was consistent with emissions from another elevated flare, the ULC flare. This flare had an almost invisible flame during daylight, but was observed to be lit at night. Table 2.11 lists all the measured fluxes from these flares, and Table 2.10 provides a summary of the emissions from the ULC flare.

Date	Average VOC emission flux
9th August	147 lbs/hr
10th August	167 lbs/hr
11th August	263 lbs/hr

Table 2.10 Summary of measurements of VOC emissions from ULC flare.

The measurements of the ULC plume showed a fairly high degree of variability, and this will be due to a combination of variability in the flare emissions and the possibly to movement of the narrow plume during the period of each DIAL scan.

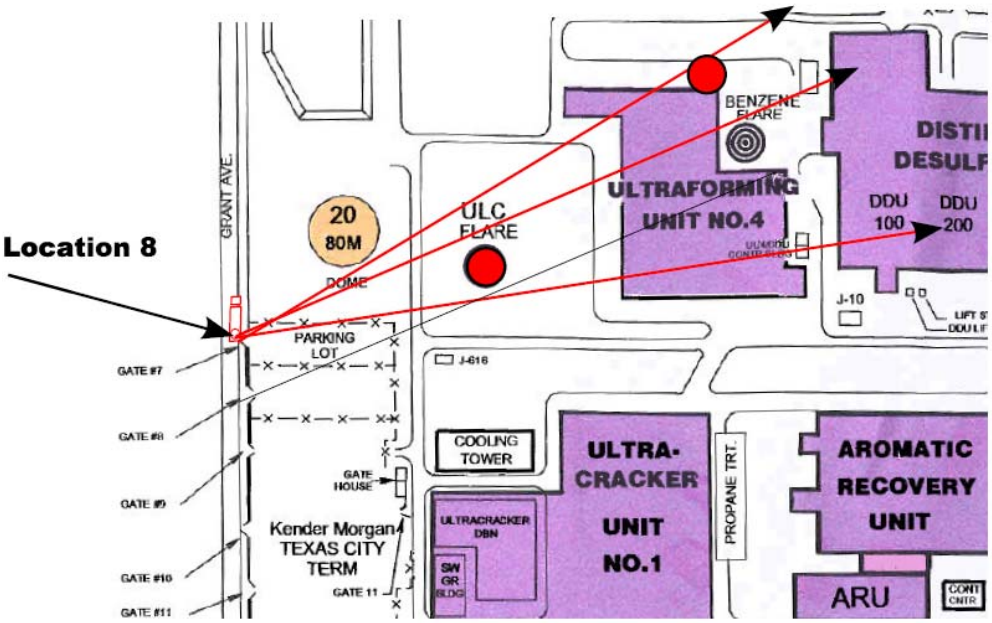

Figure 2.9. DIAL locations and scan lines used for DIAL measurements of VOC emission fluxes from flare stacks at the Refinery

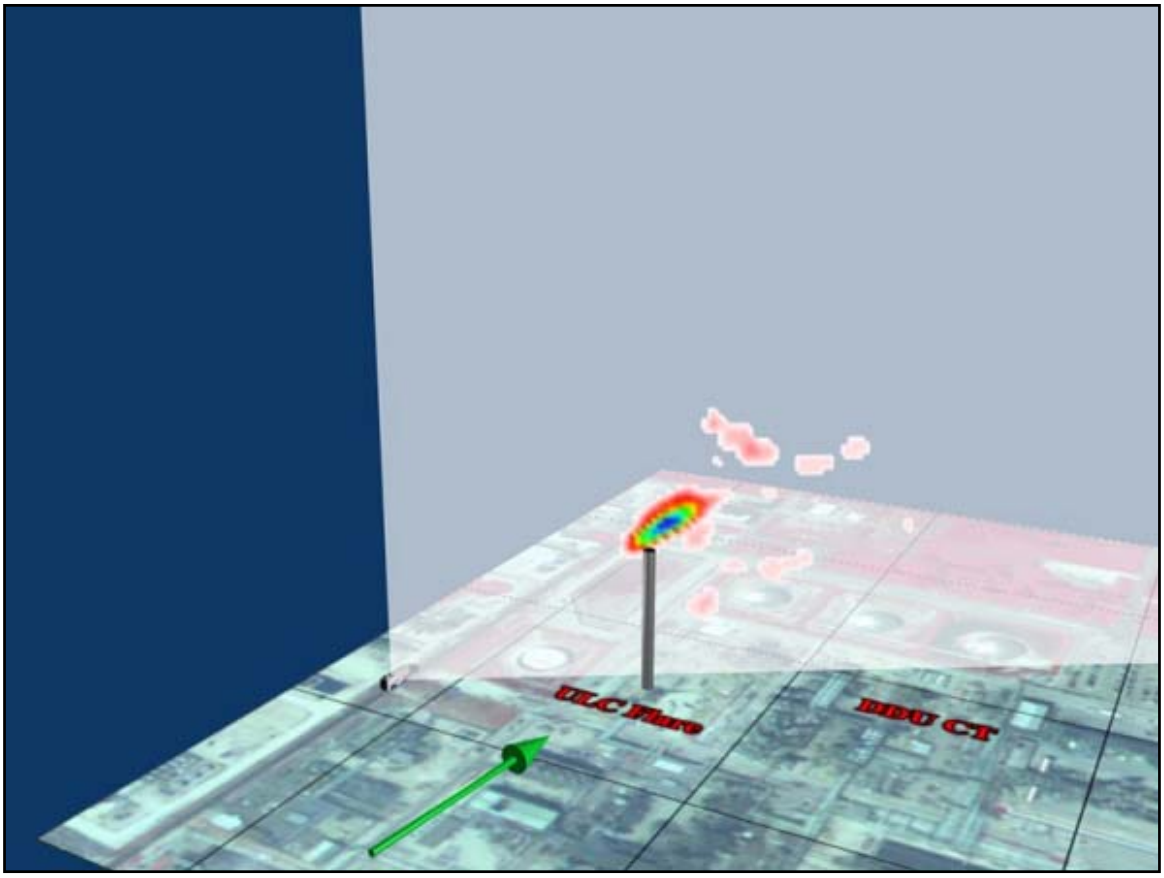

Figure 2.10 Example of the VOC distribution seen in a vertical scan at the Refinery (Scan 432) downwind of the ULC flare. The green arrow represents the average wind direction. The peak VOC concentration observed in this scan was 3.86 ppm.

Scan ID	Date	Time	Wind Speed m/s	Wind Direction Degrees	Emission rate lbs/hr	Concentration ppm	Notes
407	9-Aug	08:50	1.4	286.9	76	4.49	Downwind both flares
408	9-Aug	09:01	1.8	280.3	100	3.92	Downwind both flares
409	9-Aug	09:15	1.8	312.5	127	3.13	Downwind both flares
410	9-Aug	09:29	1.5	297.3	129	4.89	Downwind both flares
411	9-Aug	09:43	1.2	282.7	50	3.81	Downwind both flares
412	9-Aug	09:57	0.6	233.5	56	4.89	Downwind both flares
413	9-Aug	10:11	1.7	168.2	243	5.24	Downwind both flares
414	9-Aug	10:27	1.3	204.6	164	1.86	Downwind both flares
417	9-Aug	10:57	1.3	95.3	43	2.14	Downwind both flares
418	9-Aug	11:15	3.0	119.1	374	4.24	Downwind both flares
419	9-Aug	11:50	3.5	108.9	7	0.34	Upwind both flares
420	9-Aug	12:08	3.5	91.0	<1	0.40	Upwind both flares
421	9-Aug	12:29	3.1	98.7	13	0.36	Background (no plume)
431	9-Aug	14:17	4.1	113.5	126	1.61	Downwind both flares
432	9-Aug	14:53	4.4	121.8	243	3.86	Downwind both flares
433	9-Aug	15:11	4.4	124.7	181	1.69	Downwind both flares
436	9-Aug	15:59	4.4	122.7	1	0.28	Upwind both flares
437	9-Aug	16:18	3.9	126.5	23	0.29	Background (no plume)
439	10-Aug	09:51	3.8	325.4	567	8.16	Downwind both flares
440	10-Aug	10:12	2.7	353.7	159	3.84	Downwind both flares
441	10-Aug	10:31	3.1	350.7	172	3.84	Downwind both flares
442	10-Aug	10:40	3.1	9.0	190	3.40	Downwind both flares
443	10-Aug	11:00	2.8	10.9	<1	0.24	Upwind both flares
448	10-Aug	11:32	3.0	6.0	142	4.42	Downwind both flares
449	10-Aug	11:51	3.1	5.8	<1	0.36	Upwind both flares
450	10-Aug	12:01	2.6	2.8	95	2.80	Downwind both flares
451	10-Aug	12:20	3.2	25.7	<1	0.32	Background
452	10-Aug	12:29	3.0	22.3	102	1.17	Downwind both flares - further downwind
453	10-Aug	13:11	3.3	106.9	169	5.00	Downwind both flares
454	10-Aug	13:30	3.2	102.7	209	5.45	Downwind both flares
457	10-Aug	13:45	3.1	94.2	24	0.79	Downwind both flares (issues with sensitivity)
458	10-Aug	14:03	3.0	94.6	<1	0.57	Background
468	10-Aug	15:23	2.4	118.4	57	1.87	Downwind both flares
469	10-Aug	15:42	3.2	123.1	191	1.65	Downwind both flares
470	10-Aug	16:01	3.0	124.2	36	1.13	Downwind both flares
471	10-Aug	16:28	2.5	126.2	80	1.03	Downwind both flares
474	11-Aug	11:30	3.6	0.6	301	5.03	Downwind both flares
475	11-Aug	11:40	4.3	6.2	311	4.20	Downwind both flares
476	11-Aug	12:00	3.6	6.4	15	0.75	Downwind temporary flare only
477	11-Aug	12:21	3.8	10.2	4	0.27	Downwind temporary flare only
478	11-Aug	12:53	3.8	359.7	<1	0.20	Downwind temporary flare only
479	11-Aug	13:12	2.6	13.2	88	1.25	Downwind both flares
480	11-Aug	13:32	3.1	11.8	244	2.51	Downwind both flares
481	11-Aug	13:50	3.6	22.2	<1	0.19	Background scan
488	11-Aug	14:32	2.4	25.1	<1	0.31	Scan down Grant Avenue
493	11-Aug	15:53	2.1	30.3	<1	0.46	Scan downwind process stacks - A
494	11-Aug	16:07	1.4	37.5	<1	0.39	Scan downwind process stacks - B
495	11-Aug	16:23	2.5	112.3	1	0.58	Scan downwind process stacks - C
496	11-Aug	16:38	2.7	113.9	<1	0.45	Scan downwind process stacks - D
497	11-Aug	16:52	3.0	111.1	42	0.96	Downwind both flares, partial coverage of plume
498	11-Aug	17:10	3.3	121.0	14	0.37	Background
499	11-Aug	17:21	3.8	125.7	326	4.01	Downwind both flares
500	11-Aug	17:46	3.0	109.1	311	5.00	Downwind both flares
501	11-Aug	18:04	2.8	66.1	4	3.04	Background

Table 2.11. Measurements of VOC flux from ULC and temporary flares.

Section 3 Measurements of Benzene emissions from Refinery

Measurement description

Measurements of benzene were carried out on the 17th and 18th August 2007 at the Refinery. Measurements were made of the Aromatic Recovery Unit (ARU) on the 17th and the operational Coker (Coker Unit C) on the 18th. Measurements on the 17th were carried out in parallel with a UV Open Path DOAS spectrometer, operated by the EPA and were made for comparison purposes. Measurements on the 18th were carried out to obtain emissions flux measurements from the coker operations, and were timed to include the period during which the unit was cutting coke.

Benzene concentration measurements on 17th August.

The measurements on the 17th August were carried out to compare the concentrations measured by DIAL with those obtained by the open-path UV-DOAS system operated by Cary Secrest from EPA. Both systems were set up to measure a 200m path close to the ground, downwind of the ARU. Figure 1 shows the DIAL and DOAS locations and also the locations of 2 air samples, which were taken during the tests. The DIAL was located in Avenue C, South of Tank 5, GPS location 29°22'35.28"N, 94°56'2.10"W. The wind was from directions between 130° to 170° from N, at speeds of between 6 mph to 16 mph.

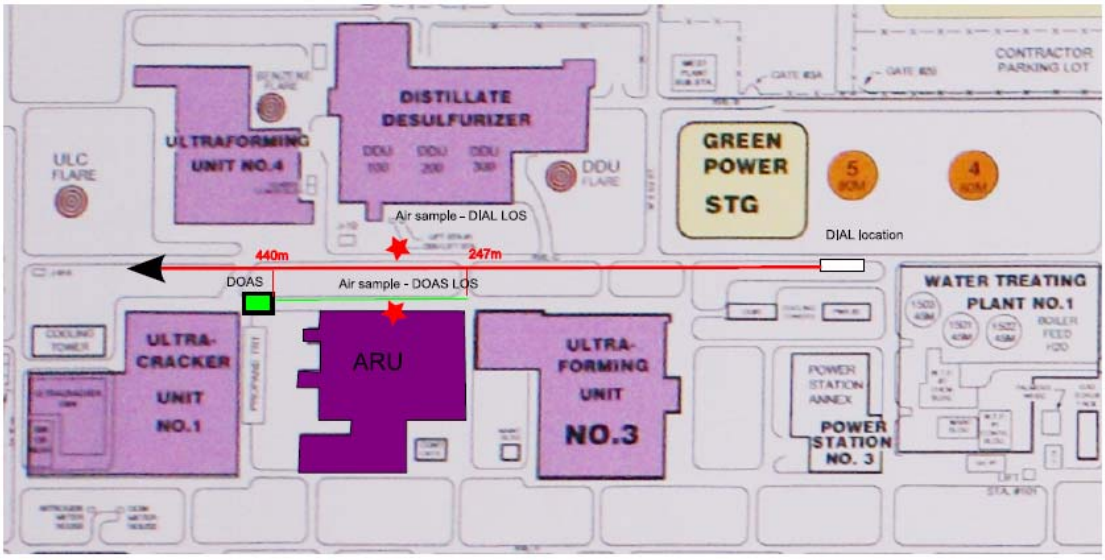

Figure 3.1, Location for measurements of benzene concentrations from the ARU

During these measurements the DIAL beam was kept at a fixed line of sight, in a similar configuration to the UV-DOAS, and not scanned to obtain concentration profiles. Therefore, benzene fluxes were not determined. The two measurement-paths for the DIAL and the UV-

DOAS were as close as was logistically possible. The DIAL data were processed to assess the total integrated concentration over the assigned path. The path length of the DOAS was stated by the EPA operators to be from 247m to 440m from the DIAL. The ARU unit was measured from the site map to be 100m long from 280 to 380 m from the DIAL. The DIAL and UV-DOAS results are plotted for comparison in Figures 2 and 3. The DIAL results are tabulated in Tables 1 and 2. The results plotted for the UV-DOAS are as supplied by Cary Secrest (US EPA). There is no difference between the UV-DOAS results in figures 2 and 3, only the DIAL pathlength has been varied, the UV-DOAS pathlength is a fixed parameter dependant on the instrument configuration. The DIAL results shown in the tables are the averages of a number of measurements taken during the periods indicated, and the standard deviations of the concentrations is also given. Where no standard deviation is given this is because the result is for a single measurement.

Scan ID	Start Time	End Time	Benzene Concentration	Standard deviation
			ppb	ppb
538	11:52	12:00	6.3	4.3
539	12:01	12:09	9.7	5.9
540	12:10	12:19	16.1	1.8
542	12:29	12:37	16.1	2.3
543	13:18	13:26	3.9	3.0
544	13:27	13:37	3.8	2.1
545	13:38	13:48	2.3	3.6
546	14:09	14:19	2.6	0.2
547	14:19	14:29	0.3	2.0
550	14:39	14:45	5.9	n/a
552	15:11	15:24	6.1	1.8
553	15:25	15:38	3.4	0.0
554	15:38	15:52	4.1	0.3
555	15:54	16:07	3.5	2.0
556	17:37	17:50	3.6	1.7
558	17:58	18:05	7.8	n/a
560	18:14	18:42	7.5	0.9

Table 3.1, DIAL results – ppb benzene determined over a 193m path comparable to the UV-DOAS.

Scan ID	Start Time	End Time	Benzene Concentration	Standard deviation
			ppb	ppb
538	11:52	12:00	4.6	4.1
539	12:01	12:09	16.7	9.4
540	12:10	12:19	15.3	7.1
542	12:29	12:37	26.3	7.2
543	13:18	13:26	11.3	5.6
544	13:27	13:37	5.4	7.0
545	13:38	13:48	1.9	10.2
546	14:09	14:19	5.3	5.7
547	14:19	14:29	1.6	2.8
550	14:39	14:45	11.5	n/a
552	15:11	15:24	8.9	1.6
553	15:25	15:38	3.8	0.4
554	15:38	15:52	7.0	2.5
555	15:54	16:07	5.9	2.4
556	17:37	17:50	4.5	3.2
558	17:58	18:05	12.7	n/a
560	18:14	18:42	13.5	1.8

Table 3.2, DIAL results – ppb benzene determined over a 100m path comparable to the extent of the ARU.

Air samples were taken in canisters and with pumped sorbent tubes, at the locations shown in Figure 1. Table 3 shows the results of the analyses of these canisters for benzene. The samples were taken between 17:29 and 18:29 for the EPA line of sight and 17:53 and 18:53 for the DIAL line of sight.

	Benzene		Toluene		Ethylbenzene		m/p-Xylene		o-Xylene	
	Tubes	Canisters	Tubes	Canisters	Tubes	Canisters	Tubes	Canisters	Tubes	Canisters
ARU	ppb	ppb	Ppb	ppb	ppb	Ppb	ppb	ppb	ppb	ppb
DIAL LOS	12.87	<2.00	18.79	12.26	2.33	2.04	9.36	5.51	3.05	<2.00
DOAS LOS	6.71	<1.88	9.79	20.52	1.90	2.46	5.29	8.49	1.44	2.59

Table 3.3, Air sample analyses for ARU measurements.

The concentrations of benzene measured using the pumped sorbent tubes are similar to the levels measured with both the UV-DOAS and the DIAL. The concentrations measured by the DIAL are close to the limit of detection for the DIAL system and the standard deviations of the results reflects this.

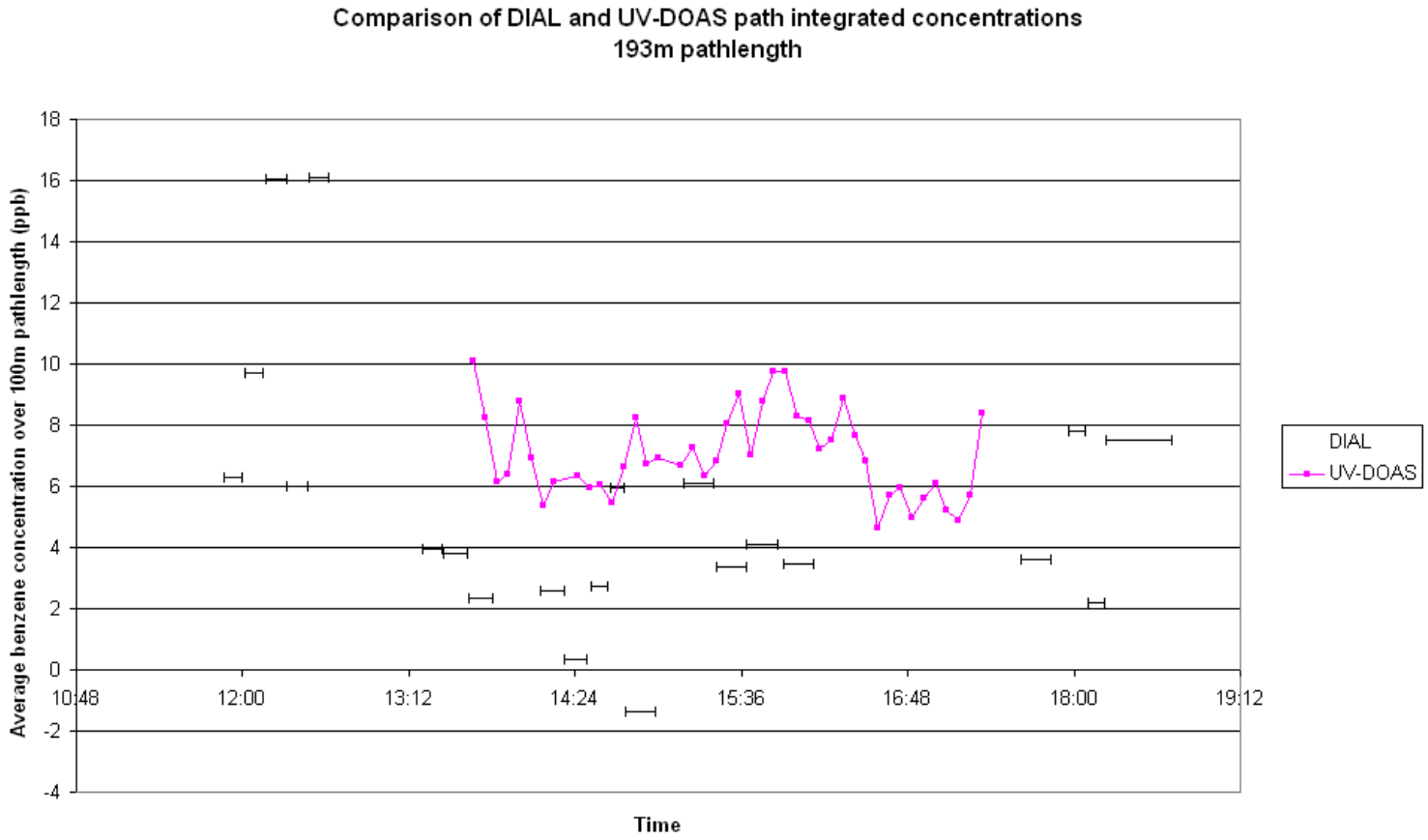

Figure 3.2, Comparison of DIAL and UV-DOAS benzene concentrations. DIAL integrated path corresponding to reported UV-DOAS 193m pathlength.

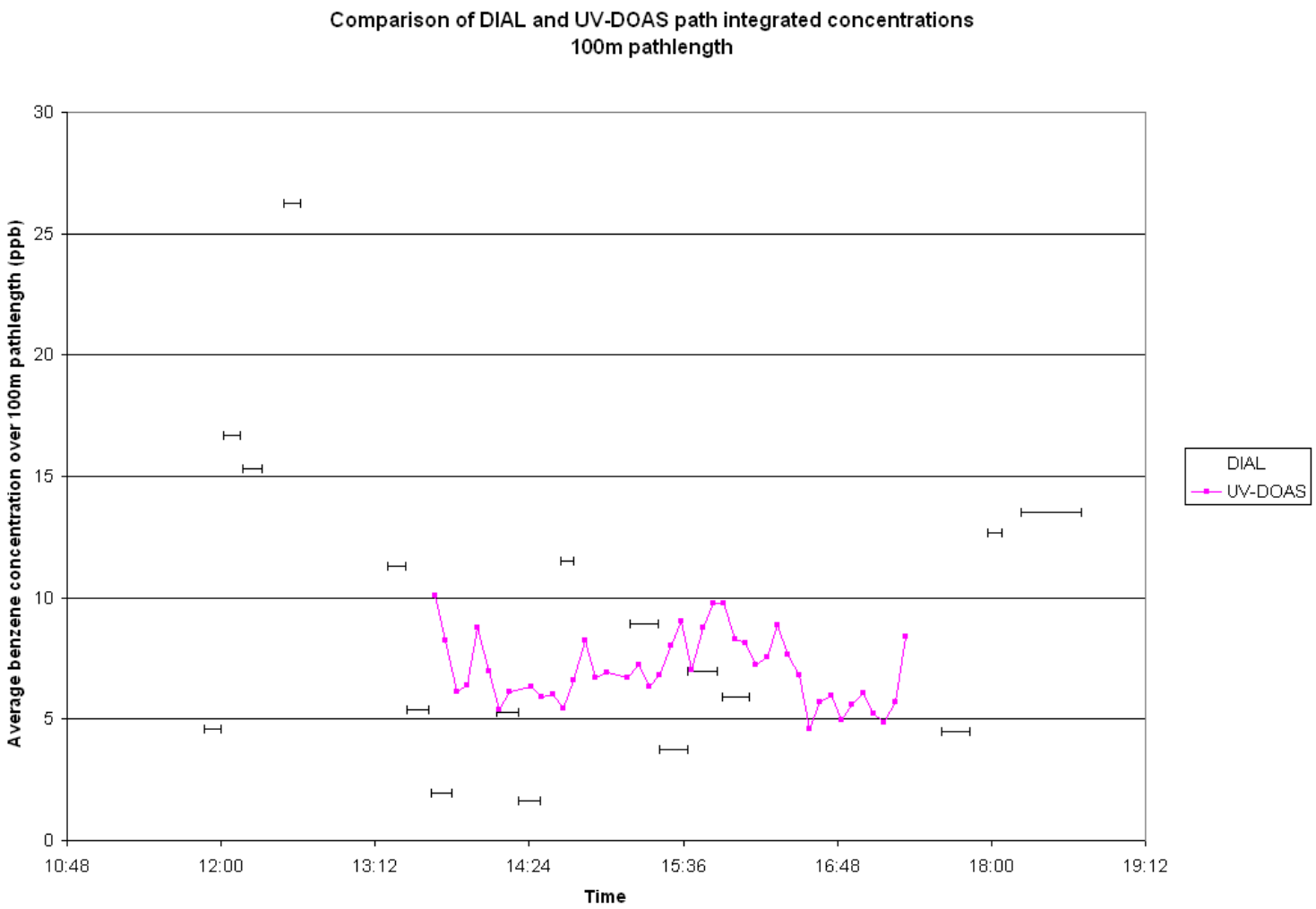

Figure 3.3, Comparison of DIAL and UV-DOAS benzene concentrations. DIAL results for 100m path corresponding to the location of the ARU unit.

Measurements of benzene fluxes from the coker

Measurements were made of the benzene concentrations downwind of coker, unit C, during the operation of this coker on the 18th August. The measurements were carried out from 17:20 to 20:45. The coker was cutting coke between 19:50 and 20:38.

The configuration of the measurements and location of the DIAL during these measurements is shown in Figure 4

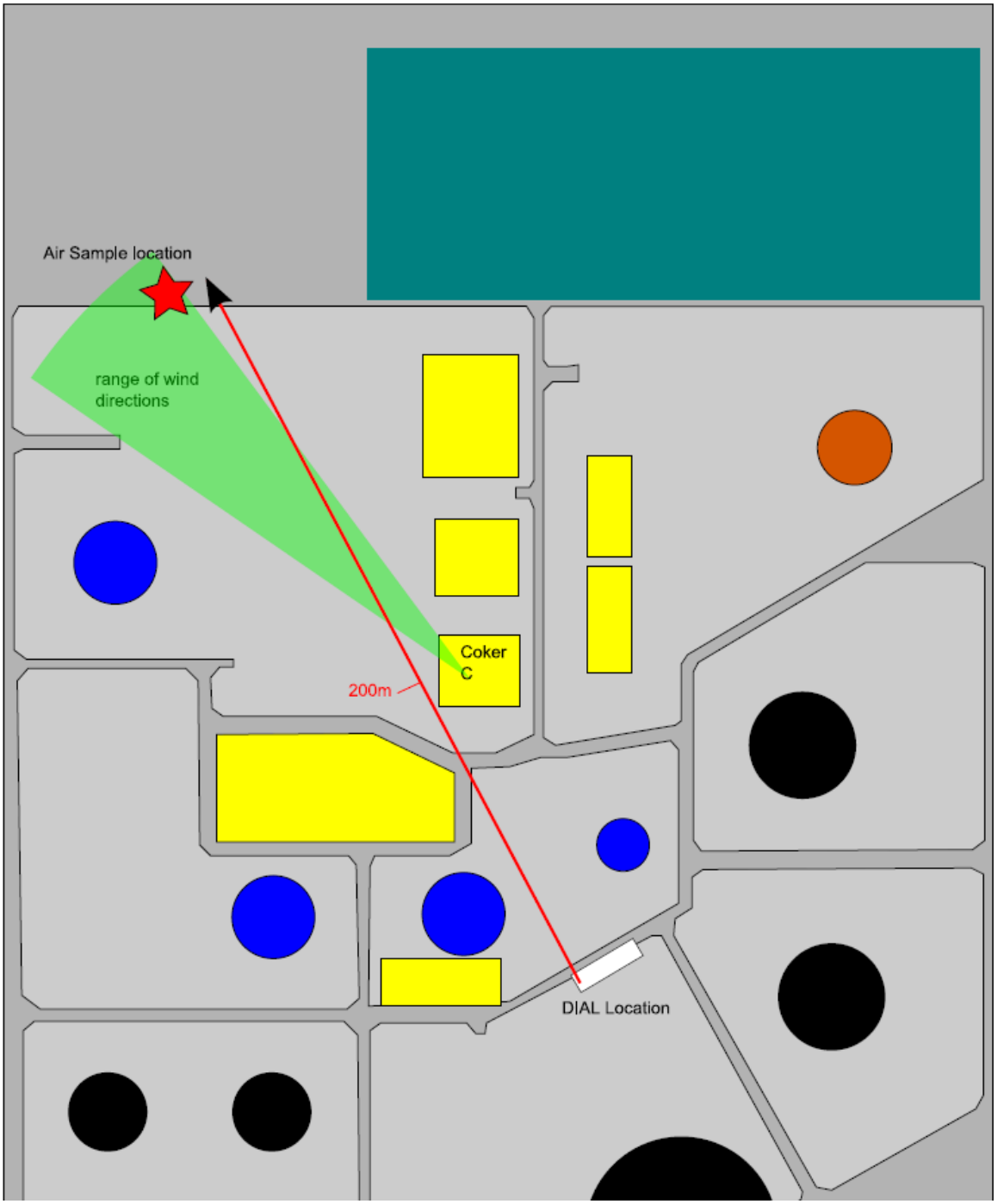

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Figure 3.4. Location of DIAL for measurements of benzene fluxes from coker Unit C.

The DIAL was located on Avenue J, to the west of Tank 1010, at GPS coordinates 29°22'10.98"N, 94°55'19.50"W. The wind during the measurements was from directions between 125° to 143° from N, with speeds between 6 mph to 9 mph. Vertical scans were made downwind of the coker; scans were also made upwind of the coker to check for any other sources of benzene. The results are given in Table 4. During most of the period of measurements the DIAL values are at or below the detection limits. For these measurements, the detection limits, in terms of lbs per hr flux, were of the order of 0.5 to 1 lbs per hr. During the period before the coker commenced cutting, the fluxes measured were often below the detection limit and have been reported as 0 lbs per hr. In some cases, a figure of less than a given flux is reported. In these cases, a detectable concentration was recorded, but the uncertainty in the results is such that only an upper limit is reported. Detected concentrations of benzene were in general around 0.1 ppm. During the coker cut, a small but observable flux of benzene was measured, the two results giving fluxes of 1.5 lbs per hr and 2.1 lbs per hr. Upwind scans showed no significant source of benzene.

The results of the analyses of the air sample taken downwind of the coker are shown in Table 5. This sample was taken during the period of the coker cut, and a low concentration of benzene ~ 1 to 2 ppb was measured.

		Met Data							
		DIAL Trailer		Mast					
				Upper		Lower			
		Average Wind Speed	Average Wind Direction	Wind Speed	Wind Direction	Wind Speed	Wind Direction	Emission rate	Concentration
Scan ID	**Time**	m/s	Degrees	m/s	Degrees	m/s	Degrees	lbs/hr	ppm
562	17:45	2.0	179.8092	3.3	129.6	2.6	148.6	0.9	0.2
563	18:04	2.4	197.3375	3.3	135.0	2.9	154.1	0.9	0.1
565	18:24	2.1	208.6307	3.2	127.1	2.7	154.7	1.3	0.1
566	18:41	1.9	186.855	3.6	129.3	2.9	152.3	0.0	0.1
567	18:57	1.9	191.1686	3.8	131.7	3.2	152.0	0.0	0.1
568	19:12	2.2	198.3785	2.7	135.5	2.4	156.5	0.0	0.1
569	19:23	1.7	179.4866	2.9	125.5	2.5	144.4	< 0.9	0.3
570	19:41	1.6	214.1907	3.0	136.9	2.6	156.9	0.0	0.2
571	19:56	1.2	122.1	2.7	137.0	2.4	157.3	< 0.7	0.2
572	20:11	1.8	139.7	2.8	143.1	2.4	162.1	1.5	0.1
573	20:26	1.7	135.1	3.2	136.8	2.7	156.7	2.1	0.2

Table 3.4. Measured fluxes during coker operation.

	Benzene		**Toluene**		**Ethylbenzene**		**m/p-Xylene**		**o-Xylene**	
	Tubes	**Canisters**	**Tubes**	**Canisters**	**Tubes**	**Canisters**	**Tubes**	**Canisters**	**Tubes**	**Canisters**
	ppb	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**	**ppb**
Downwind Coker	1.33	<2.00	0.61	2.11	0.44	<2.00	0.49	<2.00	<0.3	<2.00

Table 3.5, results of air sample analyses downwind of coker.

Section 4. Measurements of SO_2 from the Sulphur Recovery Unit

A series of measurements was carried out on the 14th August to measure the SO_2 flux from the Sulphur Recovery Unit wet gas scrubber plume. Close to the stack this appeared as a visible plume, mainly consisting of water vapour. The measurements were made through the plume, roughly at the point at which it became invisible to the unaided eye. The enhanced backscatter from the plume was used to check that the scans did intercept the plume. The aim of the measurements was to compare the measured flux with an emission rate determined from the stack flow rate and measurements of the stack gas SO_2 concentration determined from an installed continuous emissions monitor. However, prior calculations indicated that the likely concentration within the plume would be at or below the DIAL detection limit, and this was found to be the case. The average flux measured by the DIAL was 0.003 lbs/hr, with a standard deviation of 0.008 lbs/hr. Table 4.1 lists the measured SO_2 fluxes.

		Wind Speed	Wind Direction	Emission rate	Concentration	Notes
Scan ID	Time	m/s	Degrees	lbs/hr	ppm	
502	09:52	3.1	19.6	<0.01	0.001	SRU unit plume
503	10:02	3.3	6.6	<0.01	0.001	SRU unit plume
507	10:47	3.3	8.9	0.02	0.001	SRU unit plume
508	11:14	4.0	0.1	0.01	0.001	SRU unit plume
509	11:43	3.6	6.2	<0.01	0.001	SRU unit plume
510	12:02	4.1	4.5	<0.01	0.001	SRU unit plume
511	12:22	2.5	29.1	0.01	0.005	SRU unit plume
512	12:34	2.7	7.7	<0.01	0.001	SRU unit plume
518	13:51	3.5	71.4	<0.01	0.001	SRU unit plume
519	14:10	4.6	96.4	<0.01	0.003	SRU unit plume
525	15:14	4.2	124.7	0.02	0.001	SRU unit plume
529	16:19	4.0	121.9	<0.01	0.001	SRU unit plume

Table 4.1. Measurements of SO_2 flux from SRU.

The DIAL location was:

Refinery Location 13
Avenue F, north of flare 5.
29°22'28.42"N
94°54'54.56"W

Annex 1. Description of the DIAL technique.

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.

Description of the theory of Dial measurements

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

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

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 at wavelength x.

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.

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 normalisation for 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).

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

where C(r) is the point concentration at range r along the line-of-sight.

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 lidar 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 high speed digitisers. The digitisers are clocked using a clock generator triggered by an optical detector in the transmission chain. 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 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. 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 by multiplying the log of the ratio of the returned normalised signals by the differential absorption.

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.
In order to better visualise the data the integrated concentration profiles are piecewise differentiated to give the range-resolved concentration along the line-of-sight.

v) Calculation of emission fluxes
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 flux is then determined using the concentration profile together with meteorological data.

The emitted flux 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.

(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 flux.

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large and complex 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. In such cases, a more complex procedure is used which employs a further software package to combine the data from the set of anemometers with that of an additional meteorological model, to generate the complete wind field over the concentration profile. This model calculates the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain). 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.
- Since the backscattered lidar signal varies with range, generally following a (range)-2 function, the sensitivity is a function of range. The sensitivity values given in the table 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 NPL DIAL has a theoretical range resolution of 7 metres along the measurement beam, and a vertical or 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 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 2a and 2b. 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 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 common to all hydrocarbons with three or more carbon atoms, linked to the stretch frequency of the carbon-hydrogen bond. 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.

Species	Sensitivity[1]	Maximum range[2]
Nitric oxide	5 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 A1.1 Ultraviolet 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

Table A1.2 Infrared capability of NPL DIAL Facility

Note 1. The concentration sensitivities apply for measurements of a 50 metre wide plume at a range of 200 metres, under typical meteorological conditions.

Note 2. The range value represents the typical working maximum range for the NPL DIAL system.

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, 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 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 system also employs a wavemeter to monitor the wavelengths transmitted during operation. 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 detailed below:

i) Intercomparisons have been carried out in the vicinity of chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL radiation 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 fluxes 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 fluxes to within ± 15%.

Measurements of gas cell concentrations during the Texas measurement campaign.

A series of measurements was made of a 10 cm gas cell filled with a pentane standard gas mixture provided by TCEQ/REFINERY. The measurements were made by placing the gas cell in the output transmitted beam. This introduces an absorption into the DIAL signal at zero range, which has the effect of introducing an offset in the signals, equivalent to the total concentration-pathlength of the gas in the cell. The differential absorption for pentane at the wavelengths used for the VOC DIAL measurements was determined from the NPL quantified spectral database, and this was used to calculate the concentration of pentane in the gas cell. In addition a number of other gas cell measurements were made of propane and benzene.

The results of these measurements are given in Table A1.3 below. These present the means of a series of measurements made of the gas cells on different days.

Date	Scans	Cell	Measured column	Concentration (ppm)	
				Predicted	Actual
27/07/2007	110-112	10 cm propane	0.57 ± 0.04	8180 ± 530	8413
27/07/2007	117-123	10 cm pentane	1.16 ± 0.12	7100 ± 700	7500
30/07/2007	222-223	10cm pentane	1.34 ± 0.20	8200 ± 1200	7500
07/08/2007	371-372	10cm pentane	1.24 ± 0.01	7600 ± 100	7500
17/08/2007	557-558	20cm benzene	0.09	900 ± 70	1000

Table A1.3, Measurements of gas cell concentrations.
The uncertainty figures are based on the standard deviation of the individual measurements.

NPL open-path calibration facility

NPL has also developed and operate a full-scale facility for the calibration of open path monitors, including DIAL. This consists of a 10 m long windowless cell able to maintain a uniform, independently-monitored concentration of a gaseous species along its length. This provides a known controlled section of the atmosphere with traceable concentration over a defined range (10m). The absence of windows removes reflections and other artefacts from measurements made using optical techniques, providing a direct way to validate and assess the calibration of DIAL instruments.

The calibration facility is windowless with a 1 m diameter, to minimise any beam reflections from the cell walls and ends. At each end of the cell is an annular calibration-gas feed ring with multiple outlets injecting the calibration gas mixture into the cell. A ring of tangential fans around the centre of the cell extract gas and entrained air pulled in through the open ends of the cell. This ensures the backscatter in the cell approximates to the ambient air conditions. Each fan has a long exhaust tube to avoid recirculation of the gas into the cell.

This facility has been employed to directly validate VOC measurements by the NPL DIAL facility [2].

Figure A1.1 The NPL 10m calibration cell.

The facility provides the ability to generate a defined concentration path and so it also provides range-resolution validation for DIAL and lidar instruments. The system was used to validate the DIAL with a number of measurements of propane and methane, as a part of its acceptance tests for Siemens, Shell and British Gas.

[1] Measurements of the Emissions to Atmosphere of Volatile Organic Compounds from the Hellenic Aspropyrgos Oil Refinery; T D Gardiner, M.J.T. Milton, R.A. Robinson, P.T.Woods, A.S.Andrews, H. D'Souza, D Alfonso, N.R Swann; NPL Report QM S99, Sept 1996

[2] Calibration of DIAL and Open Path Systems Using External Gas Cells; M.J.T. Milton, P.T. Woods, R.H. Partridge, B.A Goody; Proc. Europto, Munich 1995.

Annex 2 Speciated VOC measurements and Flux Correction Factors

The DIAL measures 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 C3 and above. The sensitivity of the DIAL is slightly different to 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 was calibrated to give a mass emission rate for a gasoline vapour. A different 'cocktail' of hydrocarbons would 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 by determining the absorption of each constituent it is possible to determine a correction factor which will provide the true 'mass value' assuming the emissions measured have a similar relative composition to the sampled air.

Flux Correction Factors

The multi-component analysis of the ambient air sample results was used to determine the differential absorption coefficient (in m^2g-1) for the particular cocktail of hydrocarbons in each sample. This was done by taking the differential absorption coefficient for each species from the NPL quantified database of the infrared absorption of industrial organic species, and scaling it by the mass-fraction of that species in the sample. The standard DIAL differential absorption coefficient for VOC measurements is 0.49 m2g-1, based on the infrared absorption of gasoline vapour.

These results are summarised in Table A2.1, which show the differential absorption coefficients, and the factor by which the standard DIAL VOC flux results need to be multiplied by to take into account the particular VOC mix present.

Sample	Tube	
	diff abs	flux factor
DTTS1	0.62	0.8
DTTS2	0.39	1.3
DTTS3	0.55	0.9
DTTS4	0.31	1.6
DTTS5	0.29	1.7
DTTS6	0.41	1.2
DTTS7	0.37	1.3
DTTS8	0.41	1.2
DTTS9	0.44	1.1
DTTS10	0.46	1.1
DTTS11	0.24	2.0
DTTS12	0.43	1.1
DTTS13	0.24	2.1
DTTS14	0.50	1.0
DTTS15	0.44	1.1
DTTS16	0.47	1.0

Table A2.1. Flux correction factors determined from each of the air samples.

Air samples were taken at a number of locations around the plants. Figures A2.1, A2.2, A2.3 and A2.4 show the locations of the samples. The Air samples were taken using SUMO canisters and pumped Perkin Elmer Automatic Thermal Desorption (ATD) tubes.

The ATD tubes were sampled at a flow rate of 40ml/min, to enable a comparison between the SUMO canisters and the ATD tubes; a flow restrictor was fitted to canister, so each sample was taken over the same time period.

The sampler tubes are approximately 6mm OD and length 90mm long. The sampler tubes contained approximately 200milligrams to 300 milligrams of sorbent. Two sorbent tubes were used in series containing two sorbent materials used, 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.

The SUMO canister analysis gave results in the Carbon number range of C_2-C_{10}, whilst the linked ATD tubes containing Tenax TA and Carbopack-X gave a Carbon number range of C_4-C_{22}

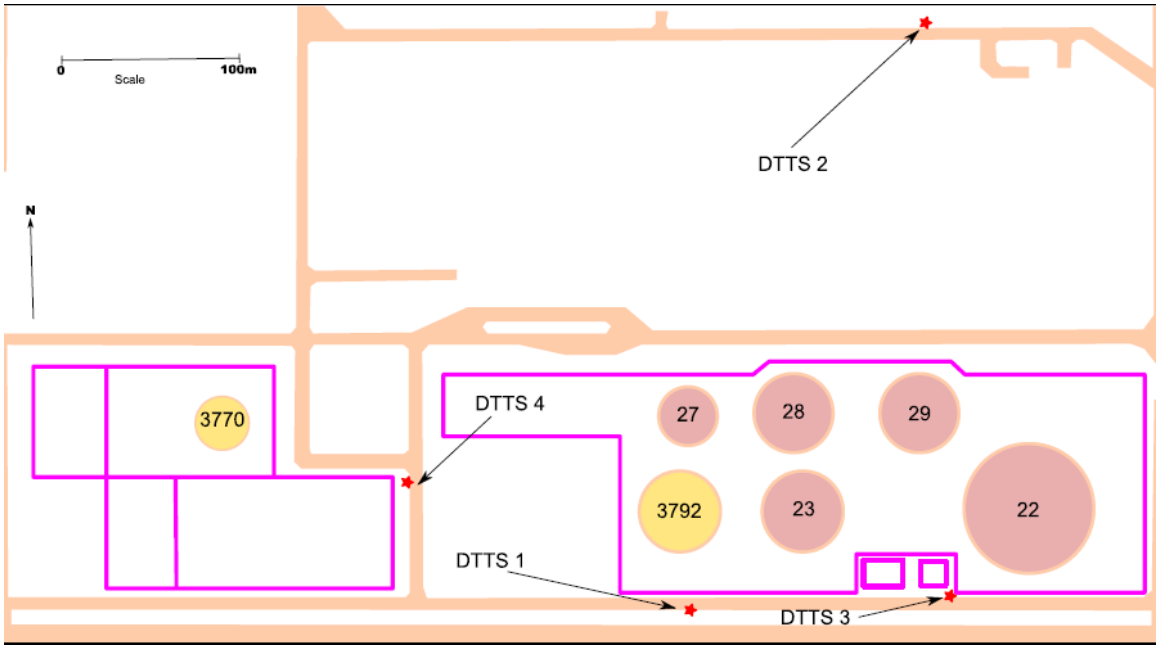

Figure A2.1 Location of air samples around the naphtha tanks at the Bulk Terminal

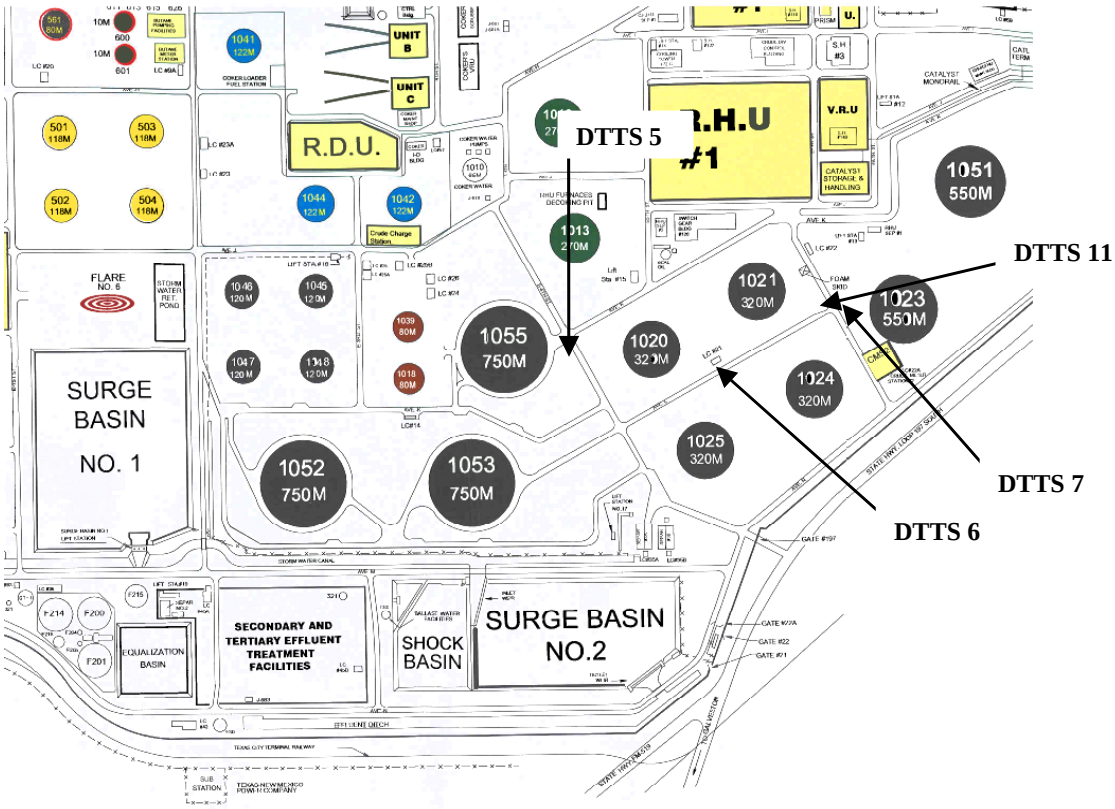

Figure A2.2 Location of air samples in the crude oil storage areas at the Refinery.

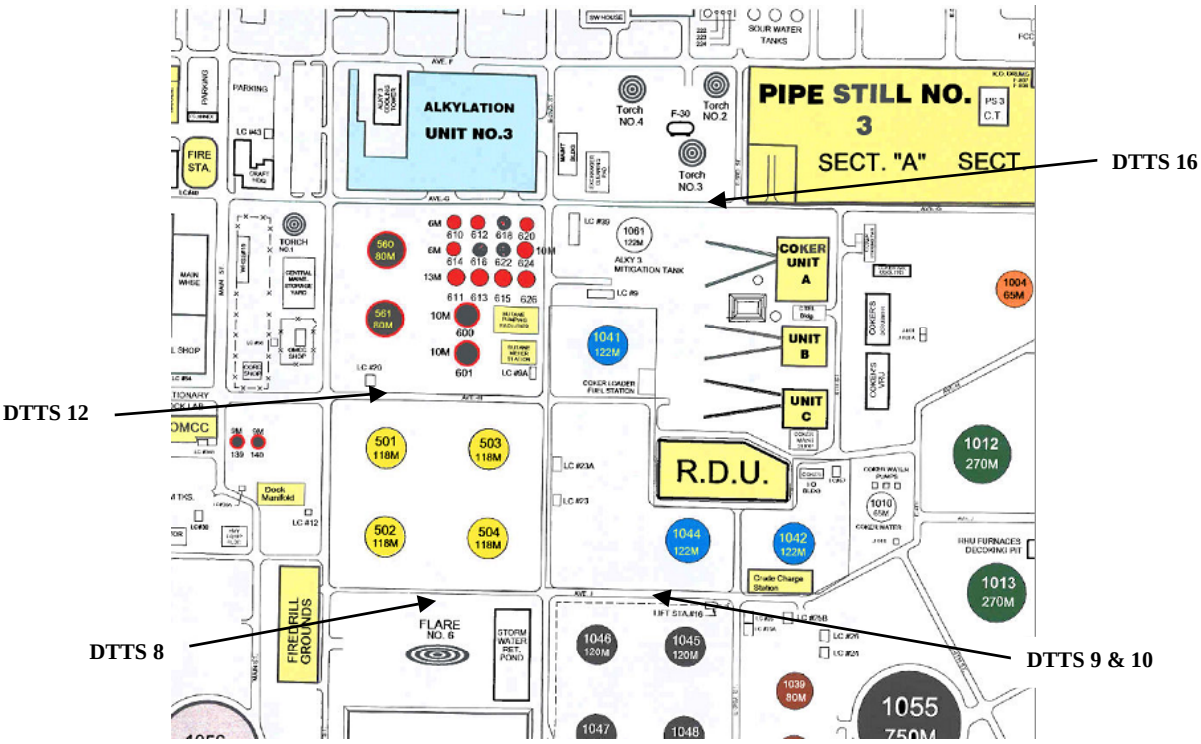

Figure A2.3 Location of air samples in the gasoline tanks and coker areas at the Refinery.

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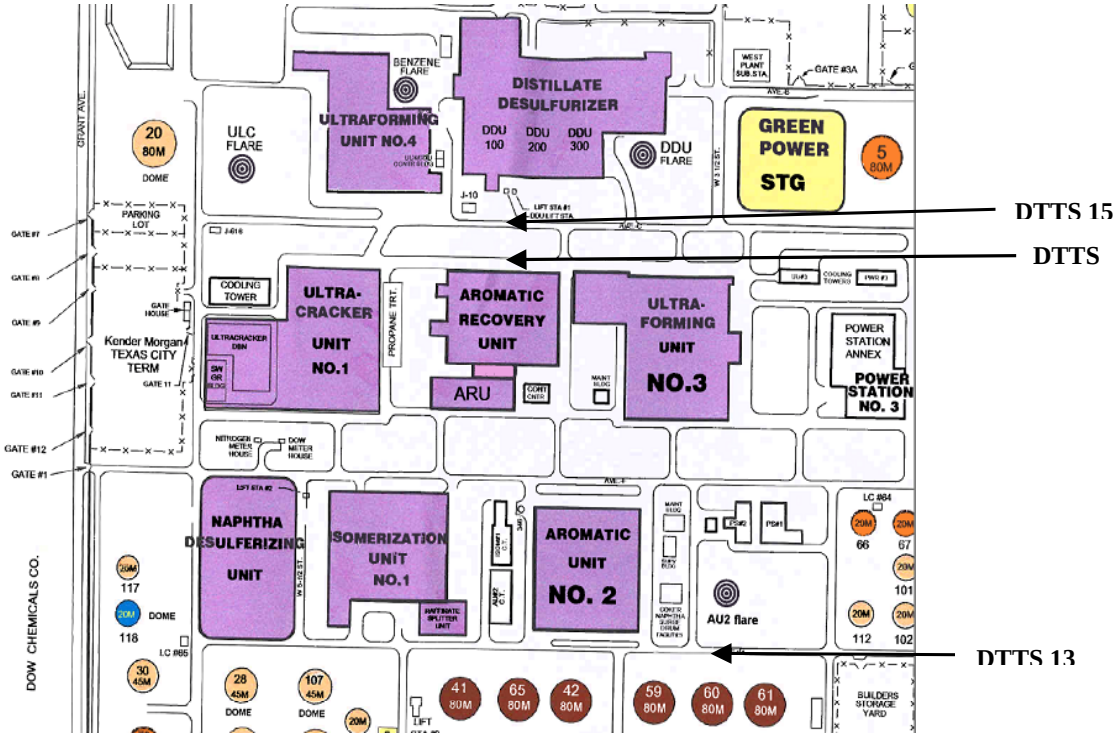

Figure A2.4 Location of air samples in the gasoline tanks and coker areas at the Refinery.

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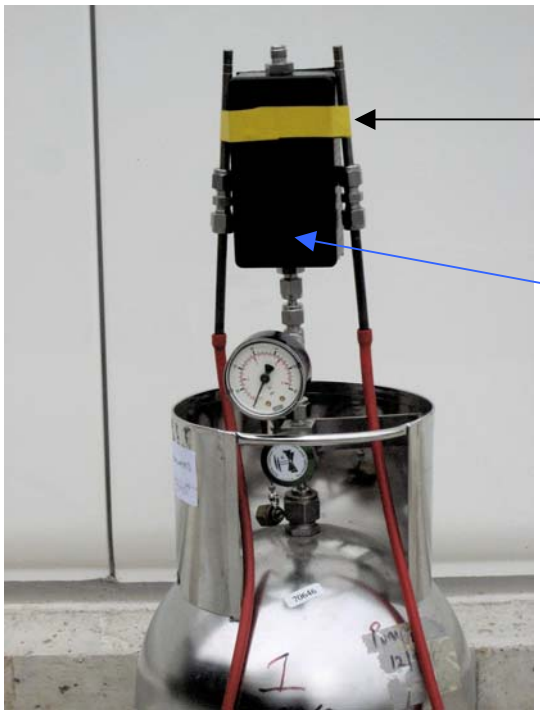
Sampling Procedure

The ATD tubes were attached to the flow restrictor so as the tubes were at the same height as the top of flow restrictors sample entry point.



The samples were taken at a height of approximately 2m by mounting the sampling array on a Tripod. The samples were taken by opening the valve on the SUMO canister and starting the sampling pumps. The flow restrictors had been set so as they sampled over a period of 1.25 hours.

Analysis of the ATD tubes

The method of analysis was based on EN ISO 16017-2 [1] and was carried out using UKAS (United Kingdom Accreditation Service) accredited method QPDQM/B/526. This method combines Automatic Thermal Desorption with Gas Chromatography, with a Flame Ionisation Detector [1]

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.

Tables A2.2 and A2.3 present the results from the canister and tube analyses respectively. The tube analyses were carried out by NPL's in house accredited analysis laboratory, the canister samples were analysed by EAS Environmental Analytical Service, Inc, California.

Table A2.2 Full results of the speciation analyses on the Canister Samples.

Sample No.	**DTTS1**	**DTTS2**	**DTTS3**	**DTTS4**	**DTTS5**	**DTTS6**	**DTTS7**	**DTTS8**
Date	17-Jul-07	18-Jul-07	19-Jul-07	21-Jul-07	28-Jul-07	28-Jul-07	29-Jul-07	30-Jul-07
Start time	17:17	16:20	12:31	03:57	14:25	14:40	16:56	16:39
End time	18:09	17:27	13:44	05:06	15:47	16:00	18:12	17:51
Average Wind Direction/deg	164	128	322	95	170	174	149	159
Average Wind Speed/mph	4.5	2.4	4.6	2.3	4.3	4.3	3.9	4.2
Cannister Number	169	610	708	881	190	996	762	606
Species	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V
Ethene	<1.93	<1.91	4.76	<1.91	<1.96	<1.94	<2.00	20.24
Acetylene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Ethane	<1.93	1.98	15.93	3.14	2.83	10.86	7.01	223.95
Propene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Propane	<1.93	6.32	10.65	2.15	<1.96	5.45	12.16	23.61
I-Butane	3.73	5.17	12.74	8.22	6.02	16.72	8.00	72.47
Methanol	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1-Butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,3-Butadiene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	4.88
n-Butane	<1.93	<1.91	24.44	2.43	<1.96	3.97	6.69	11.16
t-2-Butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	4.70
c-2-Butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Ethanol	<1.93	<1.91	<2.09	7.52	<1.96	<1.94	<2.00	2402.7
3-Methyl-1-butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Acetone	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
i-Pentane	323.89	5.67	63.51	17.78	4.80	26.94	8.13	36.51
1-Pentene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Isopropanol	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methyl-1-butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Pentane	<1.93	<1.91	38.65	<1.91	<1.96	2.65	2.35	39.77
Isoprene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
t-2-Pentene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
c-2-Pentene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Tert butyl alcohol	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methyl-2-butene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,2-Dimethylbutane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Cyclopentene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Propanol	<1.93	<1.91	2.78	<1.91	<1.96	<1.94	<2.00	4.66
Cyclopentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Methyl tert butyl ether	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,3-Dimethylbutane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methylpentane	<1.93	<1.91	8.13	<1.91	<1.96	<1.94	<2.00	<2.06
3-Methylpentane	<1.93	<1.91	5.33	<1.91	<1.96	<1.94	<2.00	<2.06
1-Hexene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Hexane	<1.93	<1.91	10.26	<1.91	<1.96	<1.94	<2.00	12.04
Diisopropyl ether	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
3-Methylcyclopentene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Ethyl tert butyl ether	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Methylcyclopentane	<1.93	<1.91	3.77	<1.91	<1.96	<1.94	<2.00	<2.06
2,4-Dimethylpentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Benzene	<1.93	<1.91	3.17	<1.91	<1.96	<1.94	5.19	<2.06
Cyclohexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methylhexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,3-Dimethylpentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
3-Methylhexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methyl-1-hexene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06

Checked by:

Sample No.	DTTS1	DTTS2	DTTS3	DTTS4	DTTS5	DTTS6	DTTS7	DTTS8
Date	17-Jul-07	18-Jul-07	19-Jul-07	21-Jul-07	28-Jul-07	28-Jul-07	29-Jul-07	30-Jul-07
Start time	17:17	16:20	12:31	03:57	14:25	14:40	16:56	16:39
End time	18:09	17:27	13:44	05:06	15:47	16:00	18:12	17:51
Average Wind Direction/deg	164	128	322	95	170	174	149	159
Average Wind Speed/mph	4.5	2.4	4.6	2.3	4.3	4.3	3.9	4.2
Cannister Number	169	610	708	881	190	996	762	606
Tert amyl methyl ether	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,2,4-Trimethylpentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Heptane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Methylcyclohexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,5-Dimethylhexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,4-Dimethylhexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2,3,4-Trimethylpentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Toluene	<1.93	<1.91	3.03	<1.91	1.99	<1.94	3.35	28.65
2,3-Dimethylhexane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methylheptane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
4-Methylheptane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Ethyl-3-methylpentane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
3-Methylheptane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Methyl-1-heptane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Octane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	2.12
Ethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
m,p-xylene	<1.93	2.74	<2.09	<1.91	<1.96	<1.94	<2.00	2.84
Styrene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
o-xylene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1-Nonene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Nonane	<1.93	4.09	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
i-Propylbenzerne	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Propylbenzerne	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
a-Pinene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
3-Ethyltoluene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
4-Ethyltoluene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,3,5-Trimethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
2-Ethyltoluene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
b-Pinene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,2,4-Trimethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	2.07	<2.06
n-Decane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,2,3-Trimethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	2.28
Indan	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
d-Limonene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,3-Diethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,4-Diethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
n-Butylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,4-Dimethyl-2-ethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,3-Dimethyl-4-ethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,2-Dimethyl-4-ethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Undecane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,2,4,5-Tetramethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
1,2,3,5-Tetramethylbenzene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Napthalene	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06
Dodecane	<1.93	<1.91	<2.09	<1.91	<1.96	<1.94	<2.00	<2.06

Checked by: RA Robinson

Sample No.	DTTS9	DTTS10	DTTS11	DTTS12	DTTS13	DTTS14	DTTS15	DTTS16
Date	3-Aug-07	3-Aug-07	5-Aug-07	6-Aug-07	7-Aug-07	17-Aug-07	17-Aug-07	18-Aug-07
Start time	13:30	15:37	04:48	04:30	04:55	17:53	17:29	20:05
End time	14:47	17:28	06:03	05:54	06:19	18:58	18:30	20:57
Average Wind Direction/deg	84	113	183	140	201	131	131	128
Average Wind Speed/mph	4.3	5	3.4	2.6	2	4.4	4.7	2.4
Cannister Number	2968	711	782	2962	2970	758	732	656
Species	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V	ppb V
Ethene	9.65	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Acetylene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Ethane	24.58	27.98	5.36	117.36	3.35	9.17	6.96	15.92
Propene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Propane	28.92	14.99	8.47	48.25	80.36	13.33	16.46	10.30
I-Butane	15.23	9.19	7.12	39.59	5.26	20.06	15.94	5.97
Methanol	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1-Butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,3-Butadiene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	3.09	<2.00
n-Butane	16.33	9.88	4.99	64.73	<1.93	11.47	29.96	5.95
t-2-Butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
c-2-Butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Ethanol	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
3-Methyl-1-butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Acetone	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
i-Pentane	19.88	<1.97	<1.94	<1.96	8.87	53.05	110.80	16.86
1-Pentene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Isopropanol	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methyl-1-butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Pentane	<1.94	<1.97	<1.94	<1.96	<1.93	4.64	39.57	11.68
Isoprene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
t-2-Pentene	<1.94	<1.97	<1.94	2.85	<1.93	<2.00	<1.88	<2.00
c-2-Pentene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Tert butyl alcohol	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methyl-2-butene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,2-Dimethylbutane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	5.39	<2.00
Cyclopentene	<1.94	2.91	<1.94	9.48	<1.93	<2.00	<1.88	<2.00
n-Propanol	<1.94	2.11	<1.94	2.86	<1.93	<2.00	<1.88	<2.00
Cyclopentane	<1.94	<1.97	<1.94	<1.96	<1.93	2.25	<1.88	<2.00
Methyl tert butyl ether	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,3-Dimethylbutane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	5.21	<1.88	10.70
3-Methylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	5.76
1-Hexene	2.88	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Hexane	<1.94	<1.97	<1.94	<1.96	6.72	<2.00	<1.88	<2.00
Diisopropyl ether	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
3-Methylcyclopentene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Ethyl tert butyl ether	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Methylcyclopentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,4-Dimethylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Benzene	<1.94	<1.97	<1.94	<1.96	4.58	<2.00	<1.88	<2.00
Cyclohexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methylhexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,3-Dimethylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	7.20
3-Methylhexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methyl-1-hexene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00

Checked by: RA Robinson

Sample No.	DTTS9	DTTS10	DTTS11	DTTS12	DTTS13	DTTS14	DTTS15	DTTS16
Date	3-Aug-07	3-Aug-07	5-Aug-07	6-Aug-07	7-Aug-07	17-Aug-07	17-Aug-07	18-Aug-07
Start time	13:30	15:37	04:48	04:30	04:55	17:53	17:29	20:05
End time	14:47	17:28	06:03	05:54	06:19	18:58	18:30	20:57
Average Wind Direction/deg	84	113	183	140	201	131	131	128
Average Wind Speed/mph	4.3	5	3.4	2.6	2	4.4	4.7	2.4
Cannister Number	2968	711	782	2962	2970	758	732	656
Tert amyl methyl ether	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,2,4-Trimethylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Heptane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	5.54	<2.00
Methylcyclohexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,5-Dimethylhexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,4-Dimethylhexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2,3,4-Trimethylpentane	3.92	<1.97	2.58	<1.96	<1.93	<2.00	<1.88	<2.00
Toluene	<1.94	<1.97	<1.94	<1.96	1.96	12.26	20.52	2.11
2,3-Dimethylhexane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methylheptane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
4-Methylheptane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Ethyl-3-methylpentane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
3-Methylheptane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Methyl-1-heptane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Octane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	2.09	<2.00
Ethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	2.04	2.46	<2.00
m,p-xylene	<1.94	<1.97	<1.94	<1.96	<1.93	5.51	8.49	<2.00
Styrene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
o-xylene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	2.59	<2.00
1-Nonene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Nonane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
i-Propylbenzerne	<1.94	2.13	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Propylbenzerne	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
a-Pinene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
3-Ethyltoluene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
4-Ethyltoluene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,3,5-Trimethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
2-Ethyltoluene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
b-Pinene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,2,4-Trimethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	2.06	<2.00
n-Decane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,2,3-Trimethylbenzene	2.54	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Indan	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
d-Limonene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,3-Diethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,4-Diethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
n-Butylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,4-Dimethyl-2-ethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,3-Dimethyl-4-ethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,2-Dimethyl-4-ethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Undecane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,2,4,5-Tetramethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
1,2,3,5-Tetramethylbenzene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Napthalene	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00
Dodecane	<1.94	<1.97	<1.94	<1.96	<1.93	<2.00	<1.88	<2.00

Checked by: RA Robinson

Table A2.3 Full results of the speciation analyses on the Sorbent Tube Samples.

Sample No.	TRV BLK A	TRV BLK B	DTTS1	DTTS2	DTTS3	DTTS4	DTTS5
Date			17-Jul-07	18-Jul-07	19-Jul-07	21-Jul-07	28-Jul-07
Start time			17:17	16:20	12:31	03:57	14:25
End time			18:09	17:27	13:44	05:06	15:47
Sample Volume/ml			2500.5	3230.8	2970.4	3297.5	3948.6
Average Wind Direction/deg			164	128	322	95	170
Average Wind Speed/mph			4.5	2.4	4.6	2.3	4.3
	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
i-Butane	0.8	0.7	4.4	1.6	13.1	7.5	2.4
n-Butane	<0.6	<0.6	<0.6	0.6	19.3	1.0	<0.6
trans-2-Butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1-Butene	<0.6	<0.6	<0.6	<0.6	0.8	<0.6	<0.6
2-methylpropene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cis-2-butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,3 Butadiene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
i-pentane	<0.6	<0.6	60.8	0.9	13.7	1.9	0.6
1-pentene	<0.6	<0.6	2.8	<0.6	0.9	<0.6	<0.6
2 me-1-butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
isoprene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentane	<0.6	<0.6	<0.6	1.4	34.6	1.1	<0.6
cis-2-pentene (Z)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-2-pentene (E)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2 dime cyclopropane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2-di me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclo pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-me-1-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,3-di me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclo pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-me pentane	<0.6	<0.6	<0.6	<0.6	7.1	<0.6	<0.6
4-me-cis-2-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-me-trans-2-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3-me pentane	<0.6	<0.6	<0.6	<0.6	3.6	<0.6	<0.6
1-hexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-hexane	<0.6	<0.6	6.5	<0.6	11.8	<0.6	<0.6
cis-2-hexene (Z)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-3-hexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-2-hexene (E)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
methylcyclopentane	<0.6	<0.6	<0.6	<0.6	3.0	<0.6	<0.6
2,4 di me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2,3-trimethyl-1-butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2,3-tri-me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
benzene	<0.2	<0.2	0.2	0.2	5.0	1.8	0.2
cyclohexane	<0.6	<0.6	<0.6	<0.6	1.5	<0.6	<0.6
2-methyl hexane	<0.6	<0.6	<0.6	<0.6	1.2	<0.6	<0.6
2,3 di me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3-me hexane	<0.6	<0.6	<0.6	<0.6	1.6	<0.6	<0.6
cyclohexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1-heptene	<0.6	<0.6	<0.6	<0.6	0.9	<0.6	<0.6
2,2,4 tri me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-heptane	<0.6	<0.6	<0.6	<0.6	2.3	<0.6	<0.6
methylcyclohexane	<0.6	<0.6	<0.6	<0.6	2.0	<0.6	<0.6
2,3,4 tri me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,3,3-tri me pentane	<0.6	<0.6	<0.6	<0.6	2.7	2.4	<0.6

Checked by:

Sample No.	TRV BLK A	TRV BLK B	DTTS1	DTTS2	DTTS3	DTTS4	DTTS5
Date			17-Jul-07	18-Jul-07	19-Jul-07	21-Jul-07	28-Jul-07
Start time			17:17	16:20	12:31	03:57	14:25
End time			18:09	17:27	13:44	05:06	15:47
Sample Volume/ml			2500.5	3230.8	2970.4	3297.5	3948.6
Average Wind Direction/deg			164	128	322	95	170
Average Wind Speed/mph			4.5	2.4	4.6	2.3	4.3
	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-methyl heptane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-methyl heptane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cycloheptene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cycloheptane	<0.6	<0.6	<0.6	<0.6	1.0	<0.6	<0.6
n-octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
ethylbenzene	<0.6	<0.6	<0.6	<0.6	1.5	<0.6	<0.6
m/p-xylene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2 me octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3 me octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
styrene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
o-xylene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
nonane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cis-cyclooctene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
isopropylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclooctane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-propylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	1.0	<0.6
3-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,3,5 tri me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-me nonene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,4 tri me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-decane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,3-Trimethylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,3,5-tetra me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-butyl benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-undecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-dodecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
naphthalene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-tridecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-tetradecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-hexadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-heptadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-octadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-nonadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-cosane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-docosane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6

Checked by: RA Robson

Sample No.	**DTTS6**	**DTTS7**	**DTTS8**	**DTTS9**	**DTTS10**	**DTTS11**	**DTTS12**
Date	28-Jul-07	29-Jul-07	30-Jul-07	3-Aug-07	3-Aug-07	5-Aug-07	6-Aug-07
Start time	14:40	16:56	16:39	13:30	15:37	04:48	04:30
End time	16:00	18:12	17:51	14:47	17:28	06:03	05:54
Sample Volume/ml	3927.9	3637.8	3409.8		5289	3600.9	3980.4
Average Wind Direction/deg	174	149	159	84	113	183	140
Average Wind Speed/mph	4.3	3.9	4.2	4.3	5	3.4	2.6
	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
i-Butane	7.5	9.6	24.8	6.5	9.4	3.2	11.8
n-Butane	8.7	4.2	9.8	<0.6	13.8	3.4	21.6
trans-2-Butene	<0.6	<0.6	1.3	<0.6	<0.6	<0.6	1.1
1-Butene	<0.6	<0.6	1.4	<0.6	<0.6	<0.6	1.0
2-methylpropene	<0.6	<0.6	1.4	<0.6	<0.6	<0.6	0.9
cis-2-butene	<0.6	<0.6	1.0	<0.6	<0.6	<0.6	<0.6
1,3 Butadiene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
i-pentane	5.4	2.6	16.5	0.7	7.3	2.2	21.4
1-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2 me-1-butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
isoprene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentane	3.6	1.5	1.6	<0.6	6.4	0.8	4.0
cis-2-pentene (Z)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-2-pentene (E)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2 dime cyclopropane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2-di me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclo pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-me-1-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,3-di me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclo pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-me pentane	0.7	<0.6	<0.6	<0.6	0.8	<0.6	1.7
4-me-cis-2-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-me-trans-2-pentene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3-me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	1.0
1-hexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-hexane	0.9	<0.6	<0.6	<0.6	1.7	<0.6	1.9
cis-2-hexene (Z)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-3-hexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
trans-2-hexene (E)-	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
methylcyclopentane	0.6	<0.6	<0.6	<0.6	0.7	<0.6	1.1
2,4 di me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2,3-trimethyl-1-butene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2,2,3-tri-me butane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
benzene	0.9	4.4	0.5	0.2	0.7	0.3	1.6
cyclohexane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-methyl hexane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	0.7
2,3 di me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3-me hexane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	0.7
cyclohexene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1-heptene	<0.6	<0.6	0.9	<0.6	<0.6	<0.6	1.1
2,2,4 tri me pentane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-heptane	<0.6	<0.6	<0.6	<0.6	0.9	<0.6	<0.6
methylcyclohexane	0.6	4.8	<0.6	<0.6	0.8	<0.6	0.8
2,3,4 tri me pentane	<0.6	1.7	<0.6	<0.6	<0.6	<0.6	<0.6
2,3,3-tri me pentane	1.6	0.9	1.4	<0.6	0.8	1.5	2.1

Checked by:

Sample No.	**DTTS6**	**DTTS7**	**DTTS8**	**DTTS9**	**DTTS10**	**DTTS11**	**DTTS12**
Date	28-Jul-07	29-Jul-07	30-Jul-07	3-Aug-07	3-Aug-07	5-Aug-07	6-Aug-07
Start time	14:40	16:56	16:39	13:30	15:37	04:48	04:30
End time	16:00	18:12	17:51	14:47	17:28	06:03	05:54
Sample Volume/ml	3927.9	3637.8	3409.8		5289	3600.9	3980.4
Average Wind Direction/deg	174	149	159	84	113	183	140
Average Wind Speed/mph	4.3	3.9	4.2	4.3	5	3.4	2.6
	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v	ppb v/v
toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-methyl heptane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-methyl heptane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cycloheptene	<0.6	<0.6	<0.6	<0.6	<0.6	10.0	<0.6
cycloheptane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
ethylbenzene	<0.6	<0.6	1.5	<0.6	<0.6	<0.6	1.4
m/p-xylene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2 me octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3 me octane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
styrene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
o-xylene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
nonane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cis-cyclooctene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
isopropylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
cyclooctane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-propylbenzene	0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
3-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
4-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,3,5 tri me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
2-ethyl toluene	<0.6	<0.6	<0.6	<0.6	<0.6	1.3	<0.6
2-me nonene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,4 tri me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-decane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,3-Trimethylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
1,2,3,5-tetra me benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-butyl benzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-undecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentylbenzene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-dodecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
naphthalene	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-tridecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-tetradecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-pentadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-hexadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-heptadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-octadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-nonadecane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-cosane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
n-docosane	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6

Checked by:

Sample No.	**DTTS13**	**DTTS14**	**DTTS15**	**DTTS16**
Date	7-Aug-07	17-Aug-07	17-Aug-07	18-Aug-07
Start time	04:55	17:53	17:29	20:05
End time	06:19	18:58	18:30	20:57
Sample Volume/ml	4000.8	3217.6	2833.9	2532.6
Average Wind Direction/deg	201	131	131	128
Average Wind Speed/mph	2	4.4	4.7	2.4
	ppb v/v	ppb v/v	ppb v/v	ppb v/v
i-Butane	2.1	10.7	4.0	4.0
n-Butane	0.6	22.8	9.0	7.3
trans-2-Butene	<0.6	5.2	2.7	<0.6
1-Butene	<0.6	1.6	1.0	<0.6
2-methylpropene	<0.6	1.5	0.6	<0.6
cis-2-butene	<0.6	3.7	1.9	<0.6
1,3 Butadiene	<0.6	<0.6	<0.6	<0.6
i-pentane	1.0	82.2	37.6	8.1
1-pentene	1.1	0.8	0.6	<0.6
2 me-1-butene	<0.6	<0.6	<0.6	<0.6
isoprene	<0.6	7.7	2.8	4.2
n-pentane	<0.6	23.7	8.2	4.2
cis-2-pentene (Z)-	<0.6	3.1	1.3	<0.6
trans-2-pentene (E)-	<0.6	<0.6	<0.6	<0.6
1,2 dime cyclopropane	<0.6	3.8	1.5	<0.6
2,2-di me butane	<0.6	<0.6	<0.6	<0.6
cyclo pentene	<0.6	<0.6	<0.6	<0.6
4-me-1-pentene	<0.6	<0.6	<0.6	<0.6
2,3-di me butane	<0.6	2.0	0.7	<0.6
cyclo pentane	<0.6	<0.6	<0.6	<0.6
2-me pentane	2.7	11.4	4.2	1.6
4-me-cis-2-pentene	<0.6	<0.6	<0.6	<0.6
4-me-trans-2-pentene	0.8	<0.6	<0.6	<0.6
3-me pentane	<0.6	6.1	2.4	0.8
1-hexene	<0.6	<0.6	<0.6	<0.6
n-hexane	5.3	13.0	4.0	1.6
cis-2-hexene (Z)-	<0.6	<0.6	<0.6	<0.6
trans-3-hexene	<0.6	0.6	<0.6	<0.6
trans-2-hexene (E)-	<0.6	<0.6	<0.6	<0.6
methylcyclopentane	<0.6	7.5	2.0	<0.6
2,4 di me pentane	<0.6	<0.6	<0.6	<0.6
2,2,3-trimethyl-1-butene	<0.6	<0.6	<0.6	<0.6
2,2,3-tri-me butane	<0.6	<0.6	<0.6	<0.6
benzene	5.1	12.9	6.7	1.3
cyclohexane	<0.6	4.0	2.0	1.5
2-methyl hexane	<0.6	3.8	1.3	<0.6
2,3 di me pentane	<0.6	0.7	<0.6	<0.6
3-me hexane	0.7	4.1	1.6	<0.6
cyclohexene	<0.6	<0.6	<0.6	<0.6
1-heptene	<0.6	1.3	<0.6	<0.6
2,2,4 tri me pentane	<0.6	<0.6	<0.6	<0.6
n-heptane	<0.6	5.7	1.6	<0.6
methylcyclohexane	0.6	6.6	1.7	0.6
2,3,4 tri me pentane	<0.6	<0.6	<0.6	<0.6
2,3,3-tri me pentane	0.7	15.2	7.9	<0.6

Checked by: RA Robinson

Sample No.	**DTTS13**	**DTTS14**	**DTTS15**	**DTTS16**
Date	7-Aug-07	17-Aug-07	17-Aug-07	18-Aug-07
Start time	04:55	17:53	17:29	20:05
End time	06:19	18:58	18:30	20:57
Sample Volume/ml	4000.8	3217.6	2833.9	2532.6
Average Wind Direction/deg	201	131	131	128
Average Wind Speed/mph	2	4.4	4.7	2.4
	ppb v/v	ppb v/v	ppb v/v	ppb v/v
toluene	<0.6	<0.6	<0.6	<0.6
2-methyl heptane	<0.6	<0.6	<0.6	<0.6
4-methyl heptane	<0.6	1.3	<0.6	<0.6
cycloheptene	<0.6	3.3	<0.6	<0.6
cycloheptane	<0.6	<0.6	0.9	<0.6
n-octane	<0.6	2.2	1.8	<0.6
ethylbenzene	0.9	9.4	5.3	<0.6
m/p-xylene	<0.6	<0.6	<0.6	<0.6
2 me octane	<0.6	0.6	<0.6	<0.6
3 me octane	<0.6	<0.6	<0.6	<0.6
styrene	<0.6	3.1	1.5	<0.6
o-xylene	<0.6	1.6	<0.6	<0.6
nonane	<0.6	<0.6	<0.6	<0.6
cis-cyclooctene	<0.6	<0.6	<0.6	<0.6
isopropylbenzene	<0.6	<0.6	<0.6	<0.6
cyclooctane	<0.6	<0.6	<0.6	<0.6
n-propylbenzene	<0.6	0.6	<0.6	0.6
3-ethyl toluene	<0.6	<0.6	<0.6	<0.6
4-ethyl toluene	<0.6	0.7	<0.6	<0.6
1,3,5 tri me benzene	<0.6	<0.6	<0.6	<0.6
2-ethyl toluene	<0.6	0.6	<0.6	<0.6
2-me nonene	<0.6	1.3	<0.6	<0.6
1,2,4 tri me benzene	<0.6	0.9	<0.6	<0.6
n-decane	<0.6	0.7	<0.6	<0.6
1,2,3-Trimethylbenzene	<0.6	<0.6	<0.6	<0.6
1,2,3,5-tetra me benzene	<0.6	<0.6	<0.6	<0.6
n-butyl benzene	<0.6	0.8	<0.6	<0.6
n-undecane	<0.6	<0.6	<0.6	<0.6
n-pentylbenzene	<0.6	<0.6	<0.6	<0.6
n-dodecane	<0.6	<0.6	<0.6	<0.6
naphthalene	<0.6	<0.6	<0.6	<0.6
n-tridecane	<0.6	<0.6	0.6	<0.6
n-tetradecane	<0.6	<0.6	0.6	<0.6
n-pentadecane	<0.6	<0.6	<0.6	<0.6
n-hexadecane	<0.6	<0.6	<0.6	<0.6
n-heptadecane	<0.6	<0.6	<0.6	<0.6
n-octadecane	<0.6	<0.6	<0.6	<0.6
n-nonadecane	<0.6	<0.6	<0.6	<0.6
n-cosane	<0.6	<0.6	<0.6	<0.6
n-docosane	<0.6	<0.6	<0.6	<0.6

Checked by:

Annex 3. Meteorological Measurements

Wind direction and speed were recorded during the DIAL measurements at one fixed location, at the north east of the Bulk Terminal site, and using a mast located on the DIAL facility itself. Two further meteorological stations were operated by TCEQ, located to the north and south of the REFINERY site (one of these stations was located at the southern side of Bulk Terminal during the period measurements were being made at Bulk Terminal). The NPL fixed mast provided wind speed and direction at two heights, ~ 3m and 11m. In general the fixed mast data have been used to derive the wind field for the DIAL flux measurements, though in some cases the DIAL wind has been used where it was observed to be more representative of local conditions.

The following series of plots present the wind roses, taken from the 11m wind vane mounted on the fixed meteorological mast.

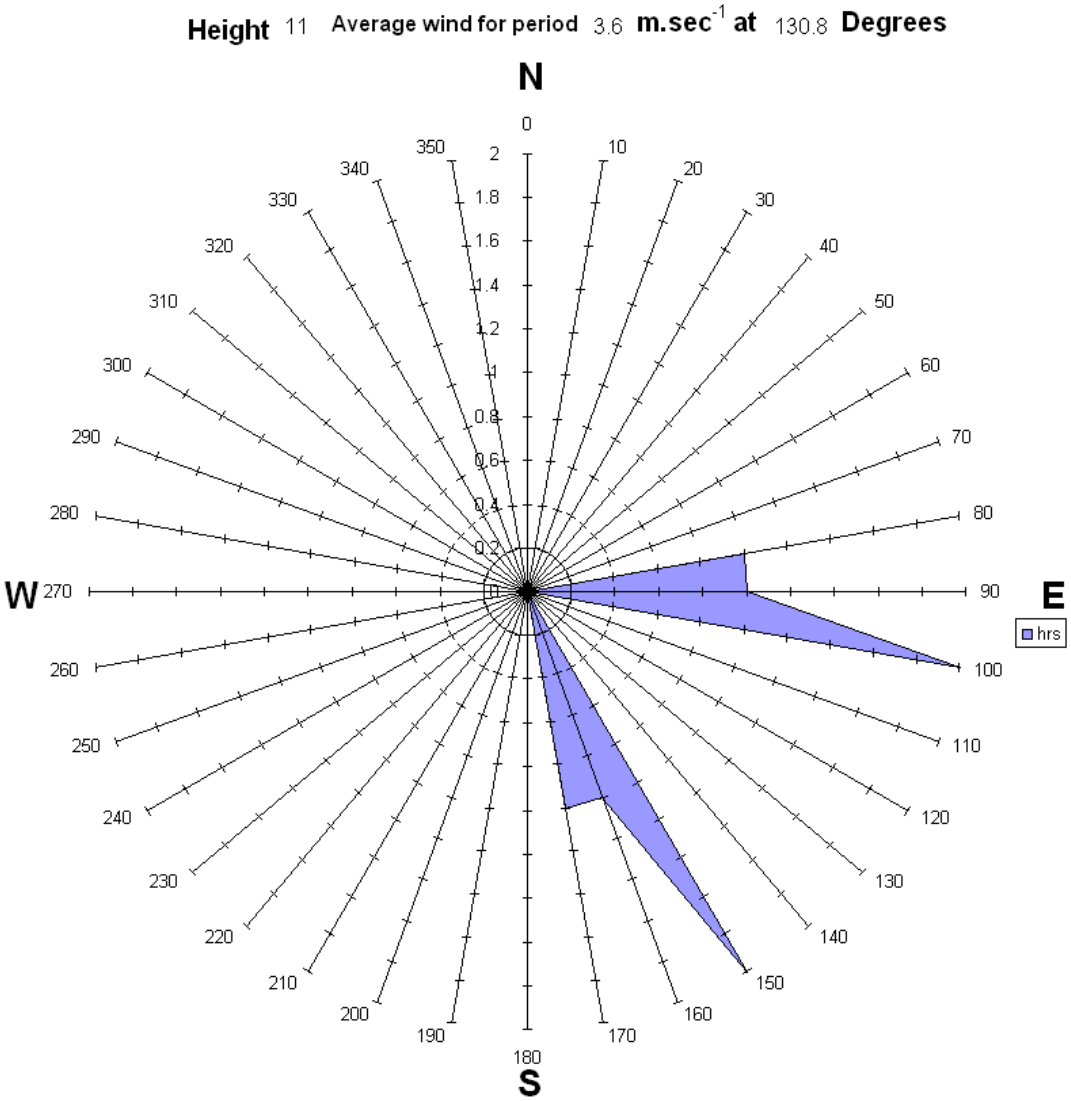


Figure 3.1 Wind rose diagram – top mast – 16 July 2007

Checked by:

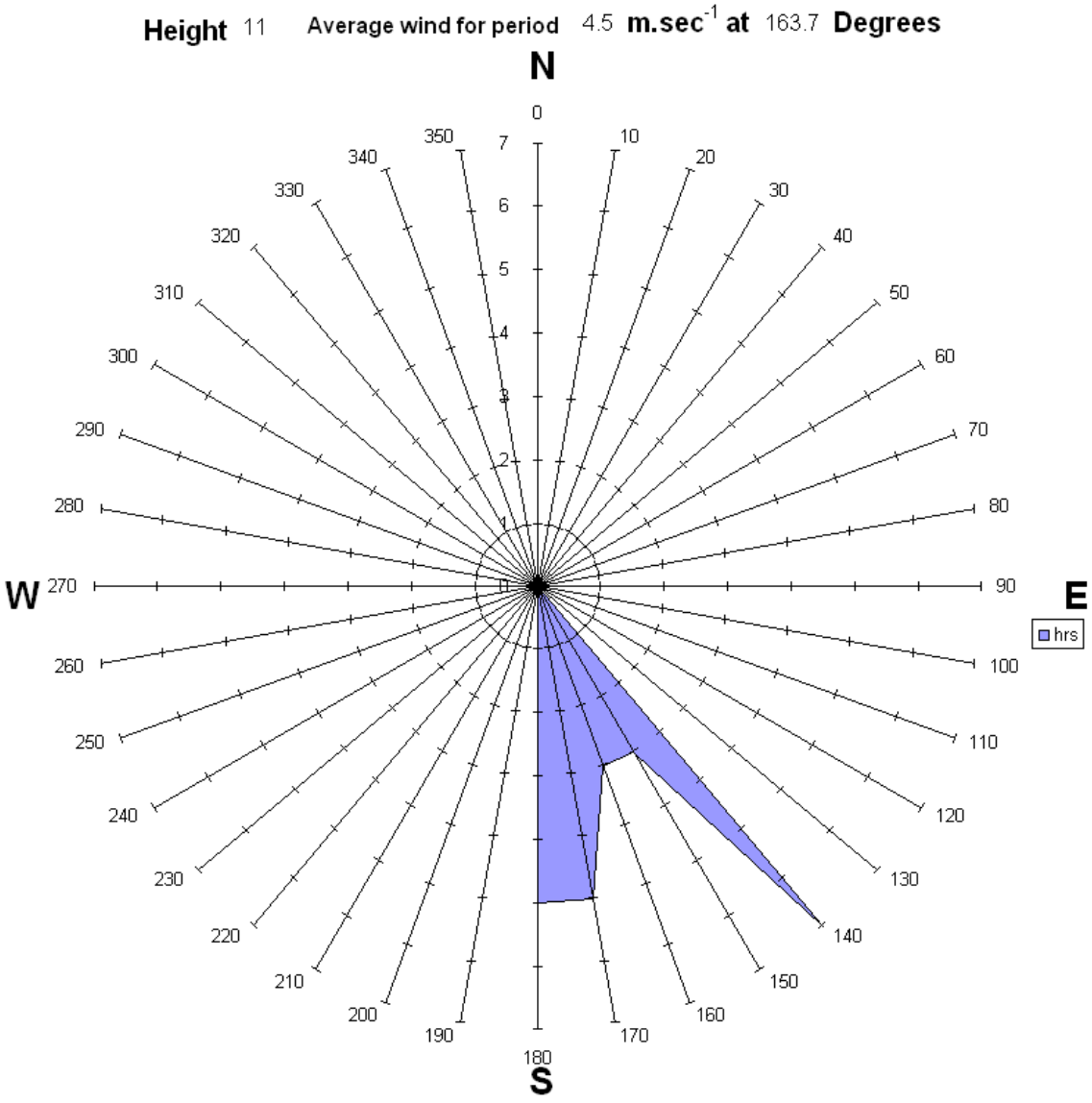


Figure 3.2 Wind rose diagram – top mast – 17 July 2007

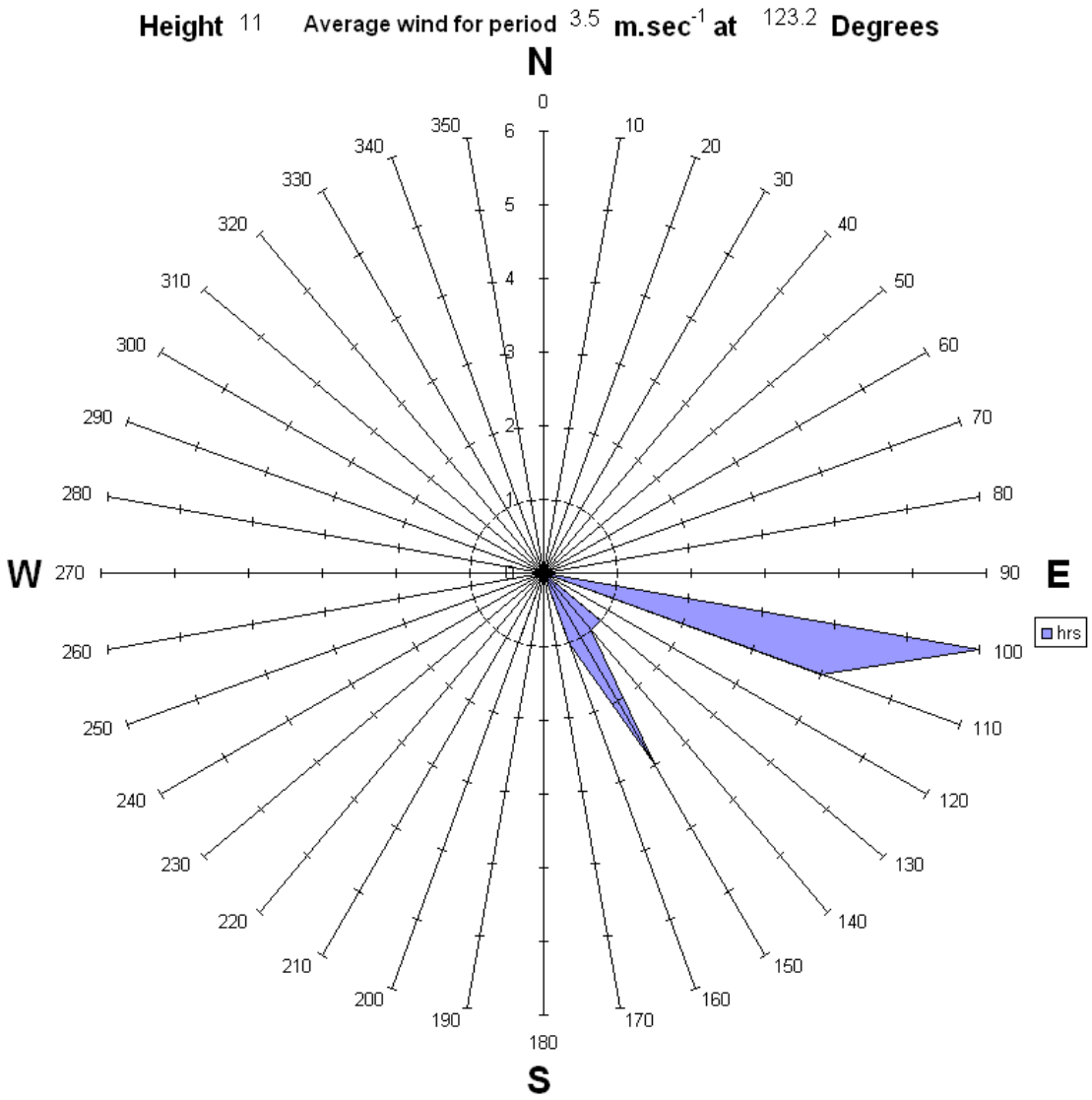


Figure 3.3 Wind rose diagram – top mast – 18 July 2007

Checked by:

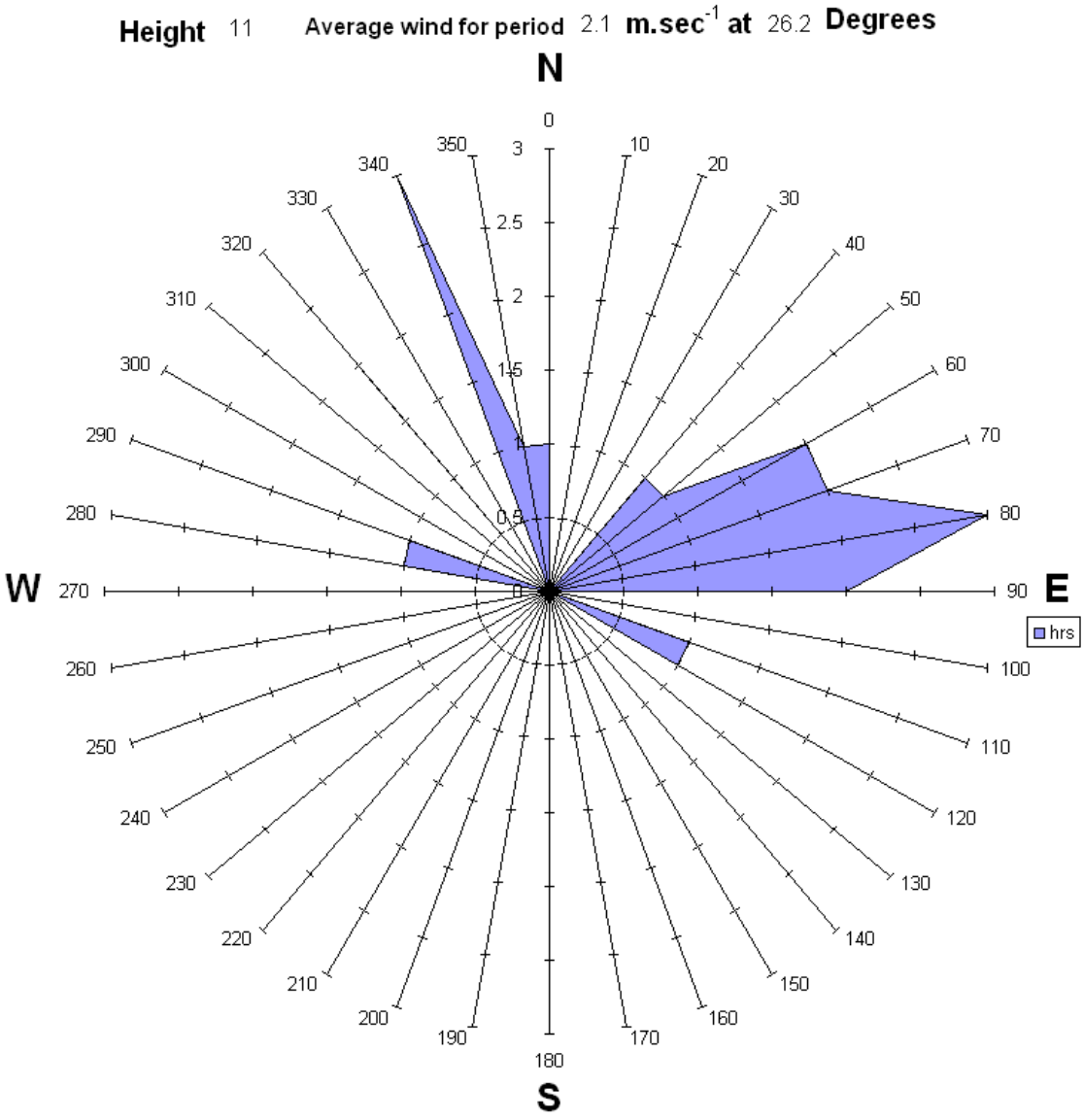


Figure 3.4 Wind rose diagram – top mast – 19 July 2007

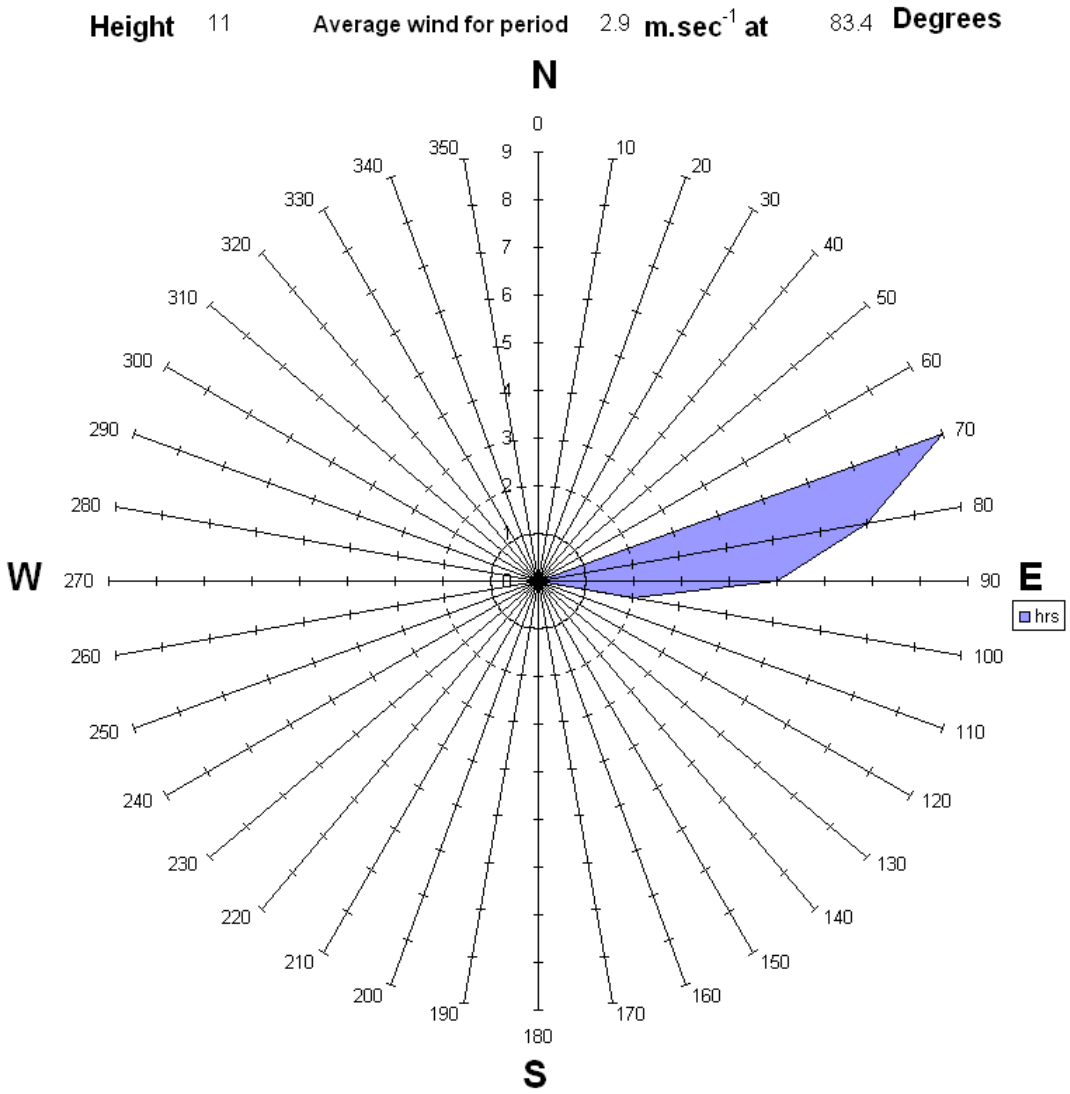


Figure 3.5 Wind rose diagram – top mast – 20 & 21 July 2007

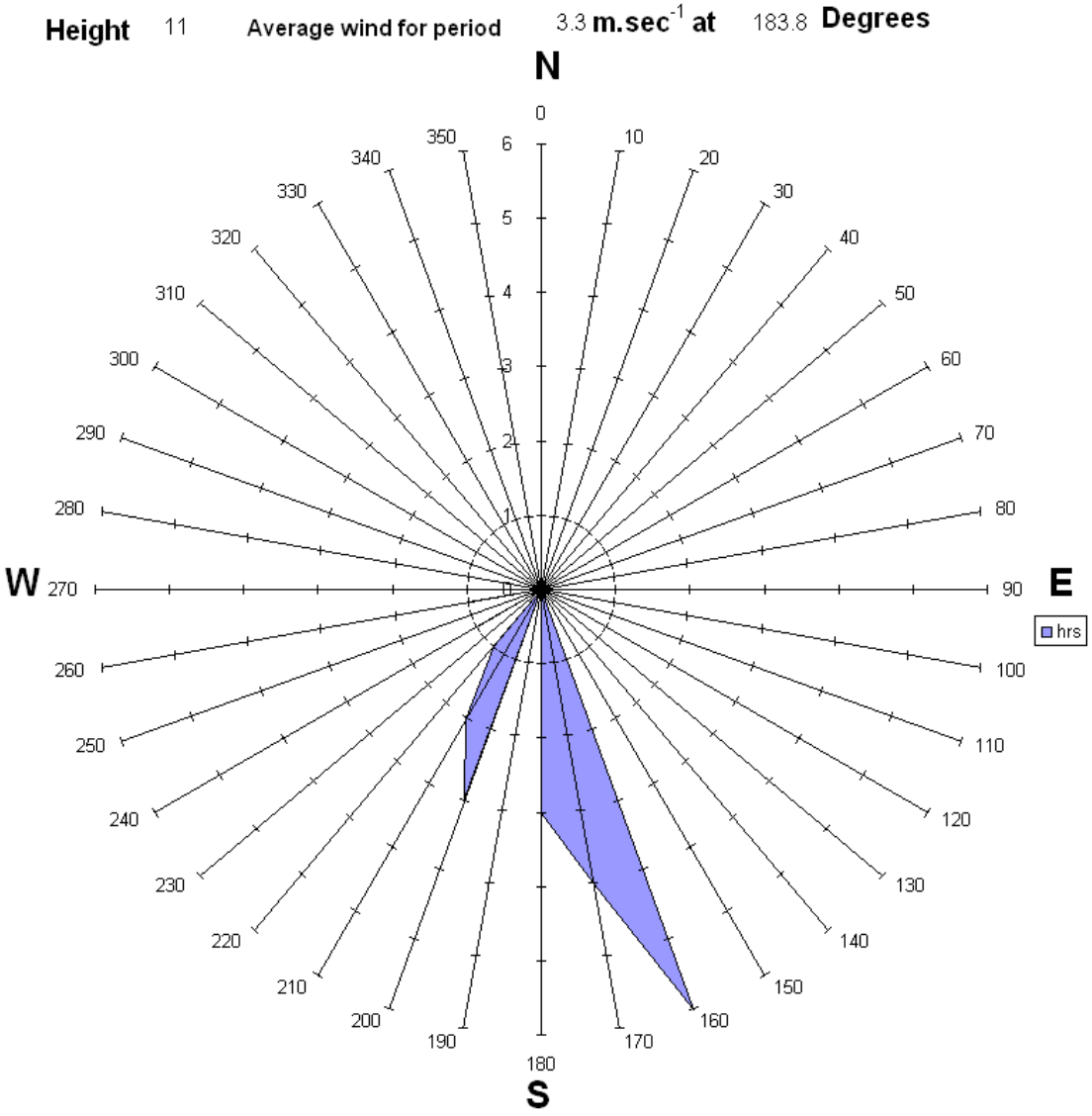


Figure 3.6 Wind rose diagram – top mast – 28 July 2007

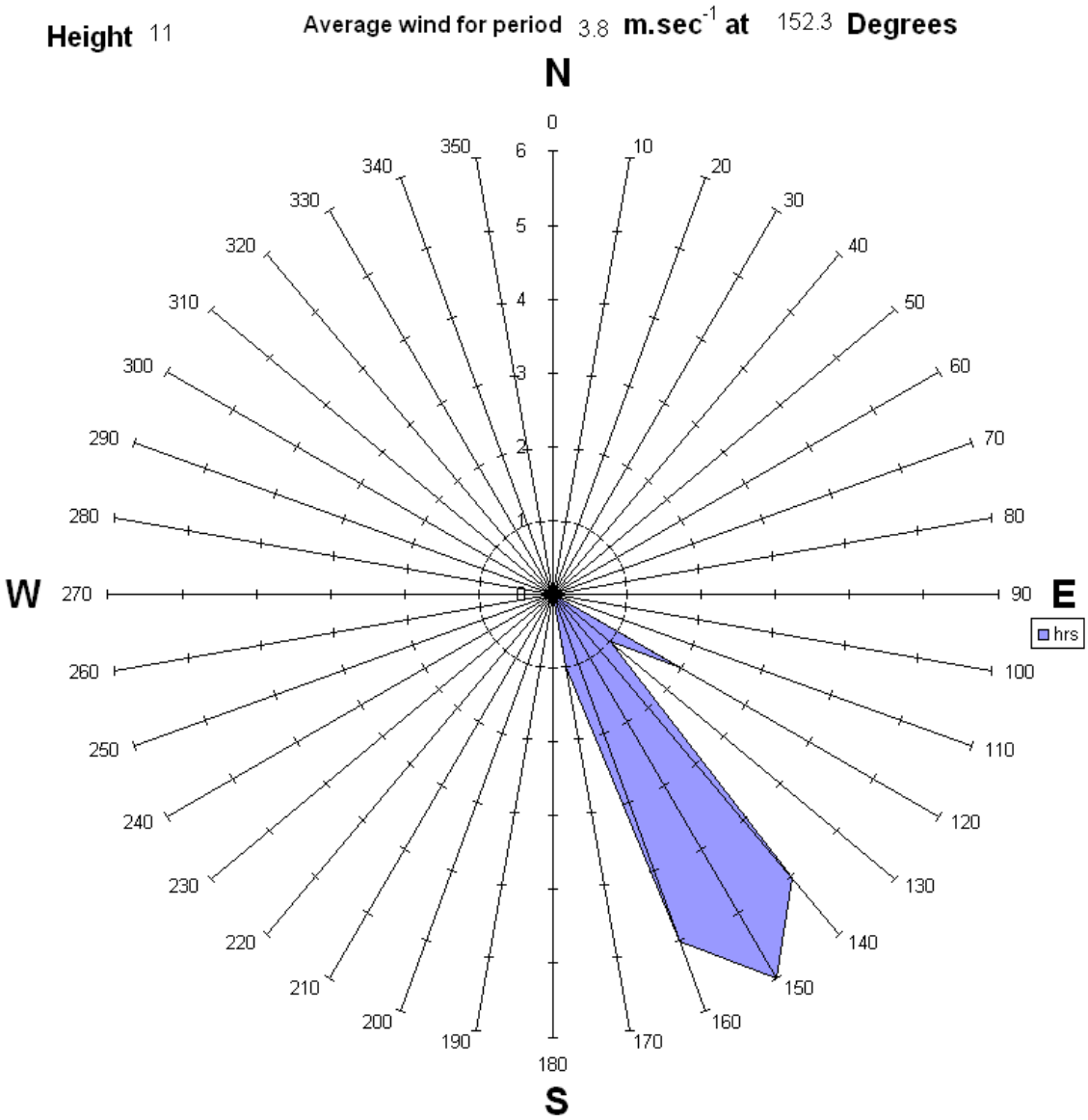


Figure 3.7 Wind rose diagram – top mast – 29 July 2007

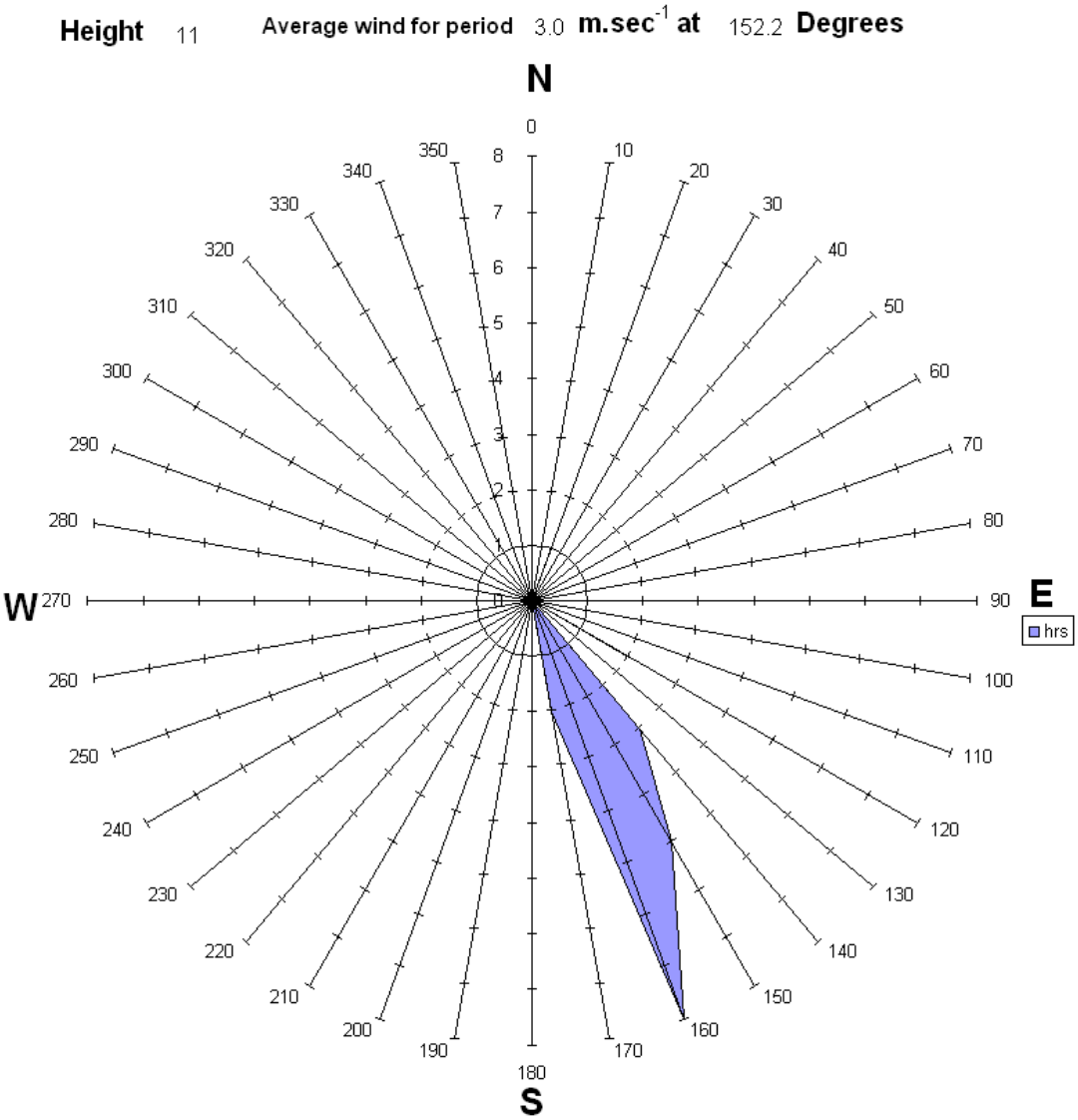


Figure 3.8 Wind rose diagram – top mast – 30 July 2007

Checked by:

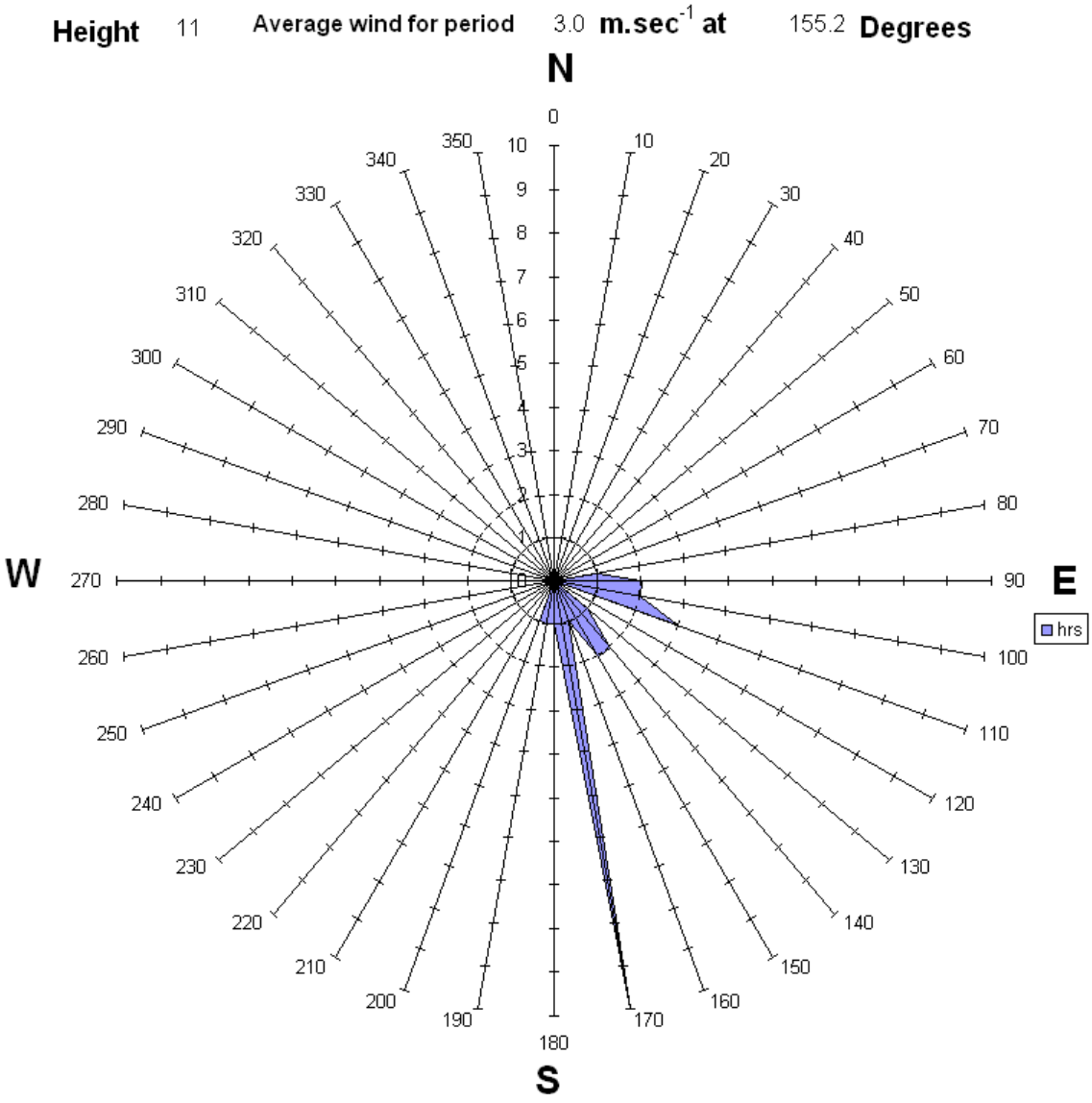


Figure 3.9 Wind rose diagram – top mast – 31 July 2007

Checked by:

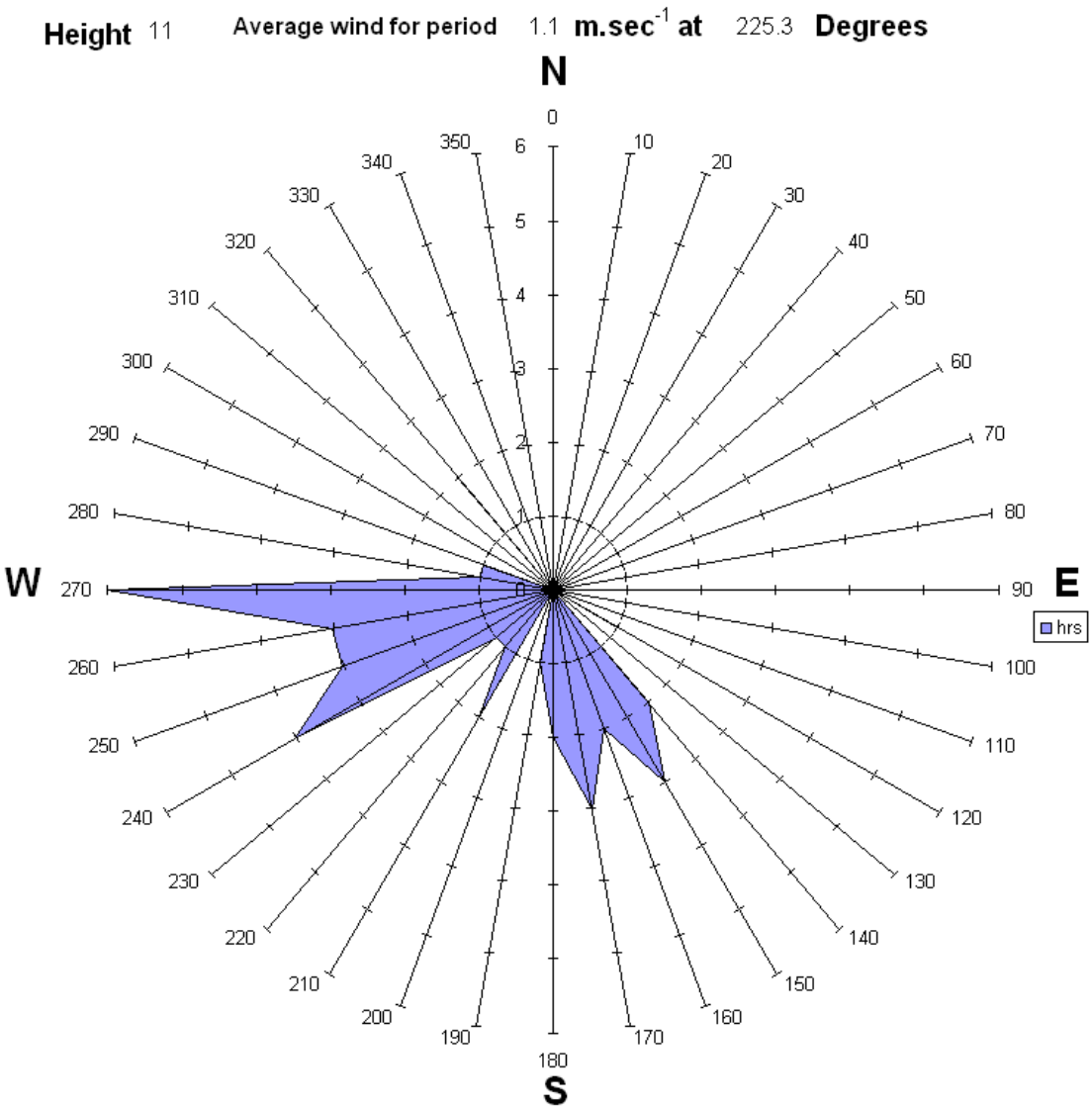


Figure 3.10 Wind rose diagram – top mast – 1 August 2007

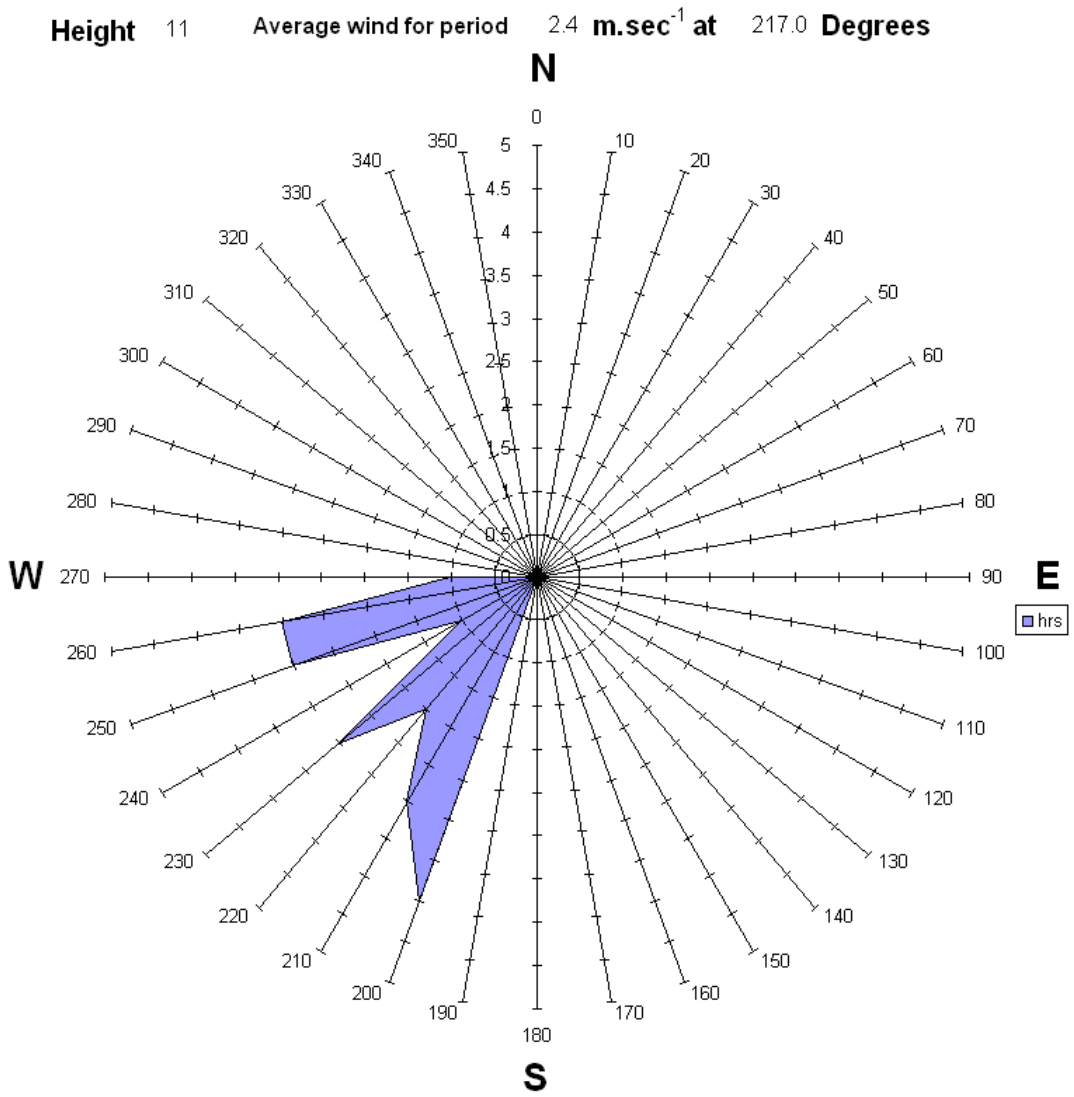


Figure 3.11 Wind rose diagram – top mast – 2 August 2007

Checked by:

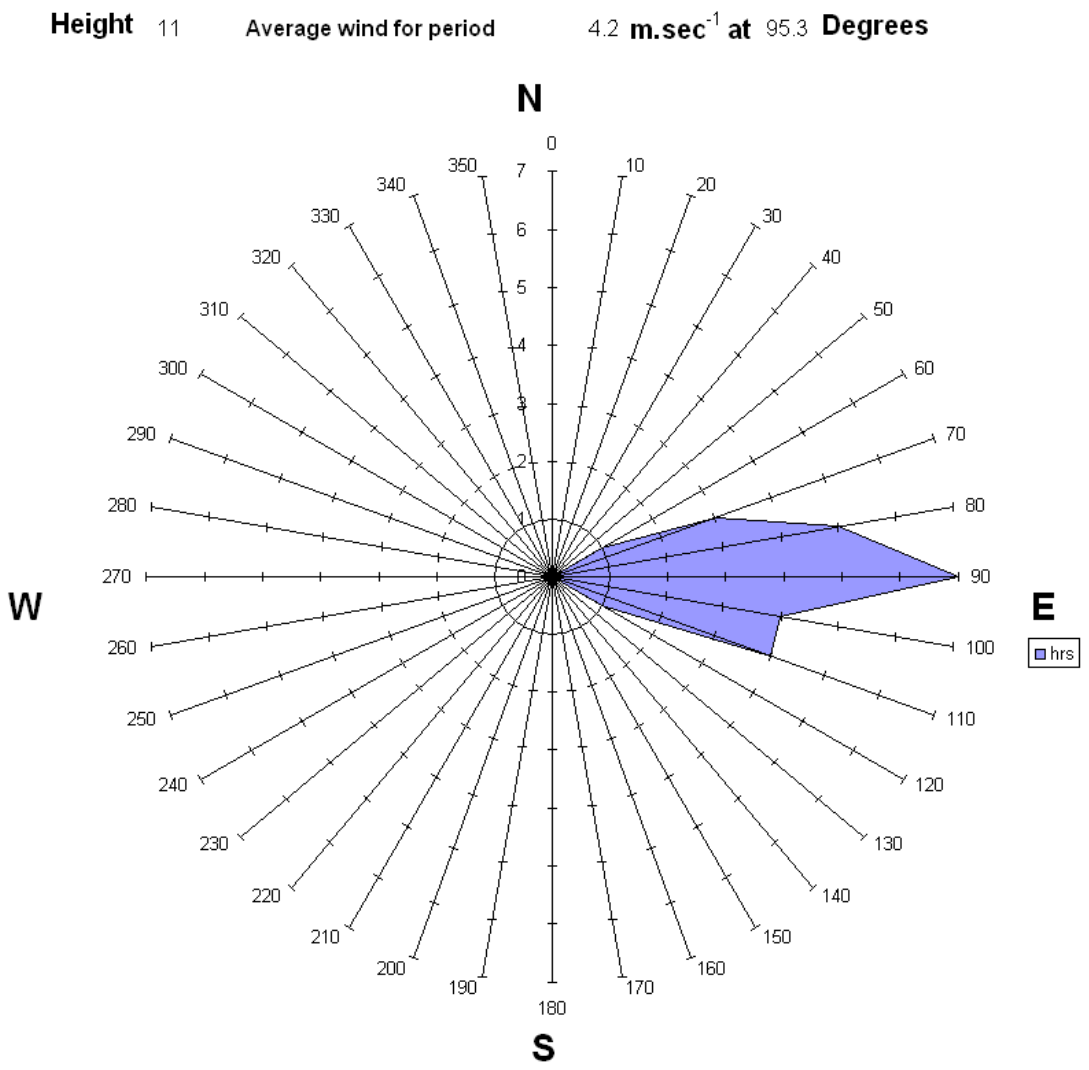


Figure 3.12 Wind rose diagram – top mast – 3 August 2007

Checked by:

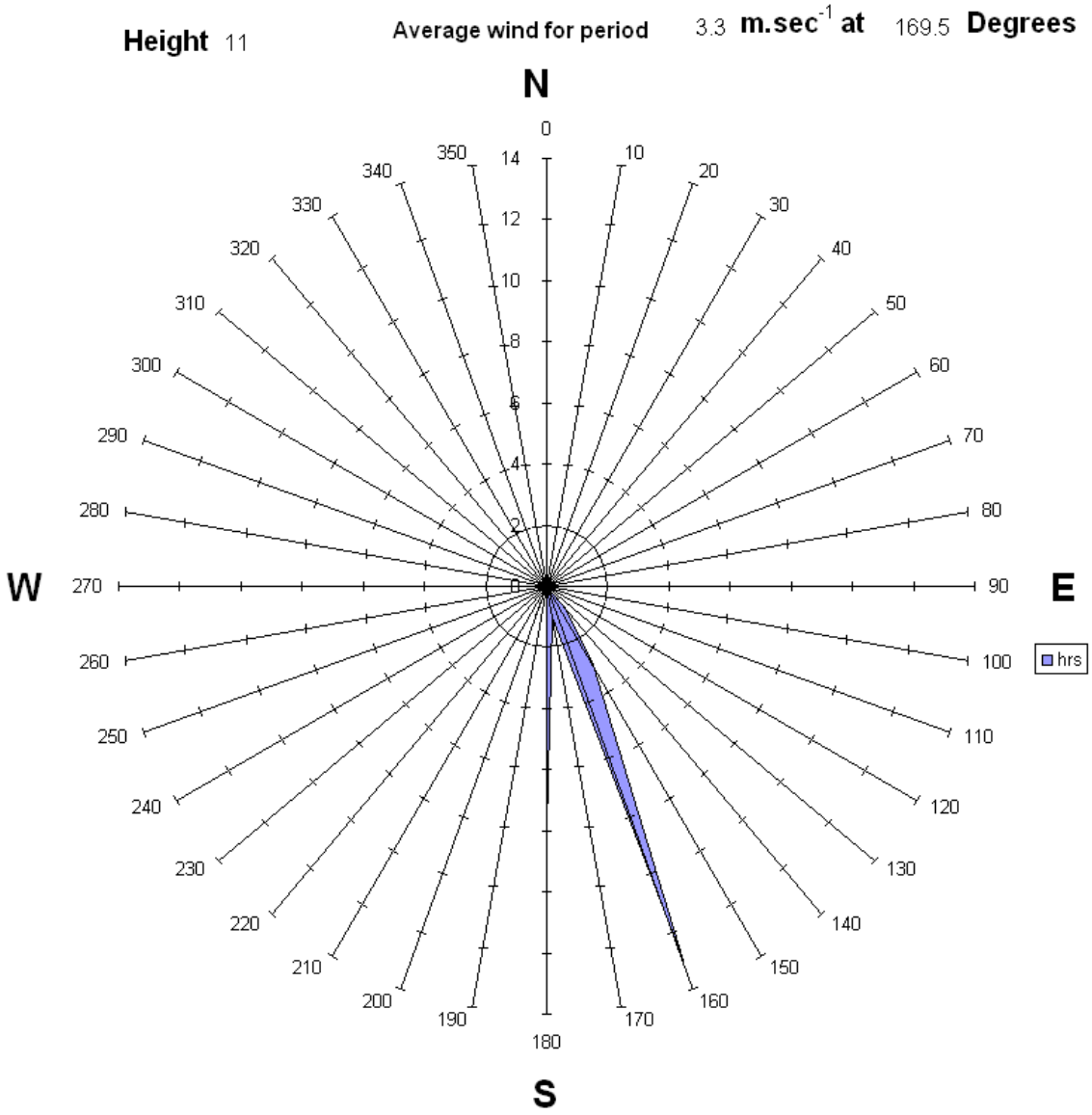


Figure 3.13 Wind rose diagram – top mast – 5 & 6 August 2007

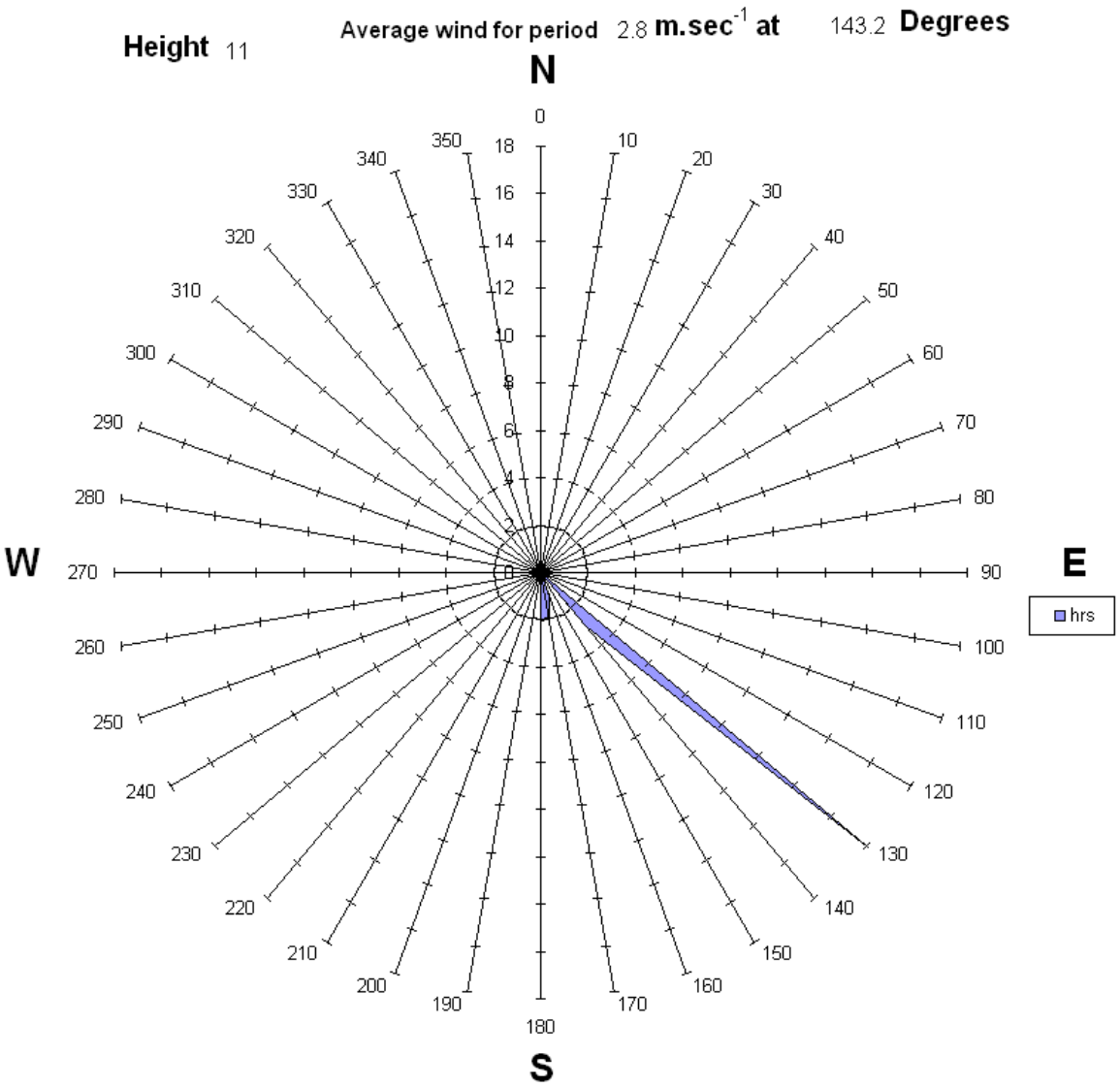


Figure 3.14 Wind rose diagram – top mast – 6 & 7 August 2007

Checked by:

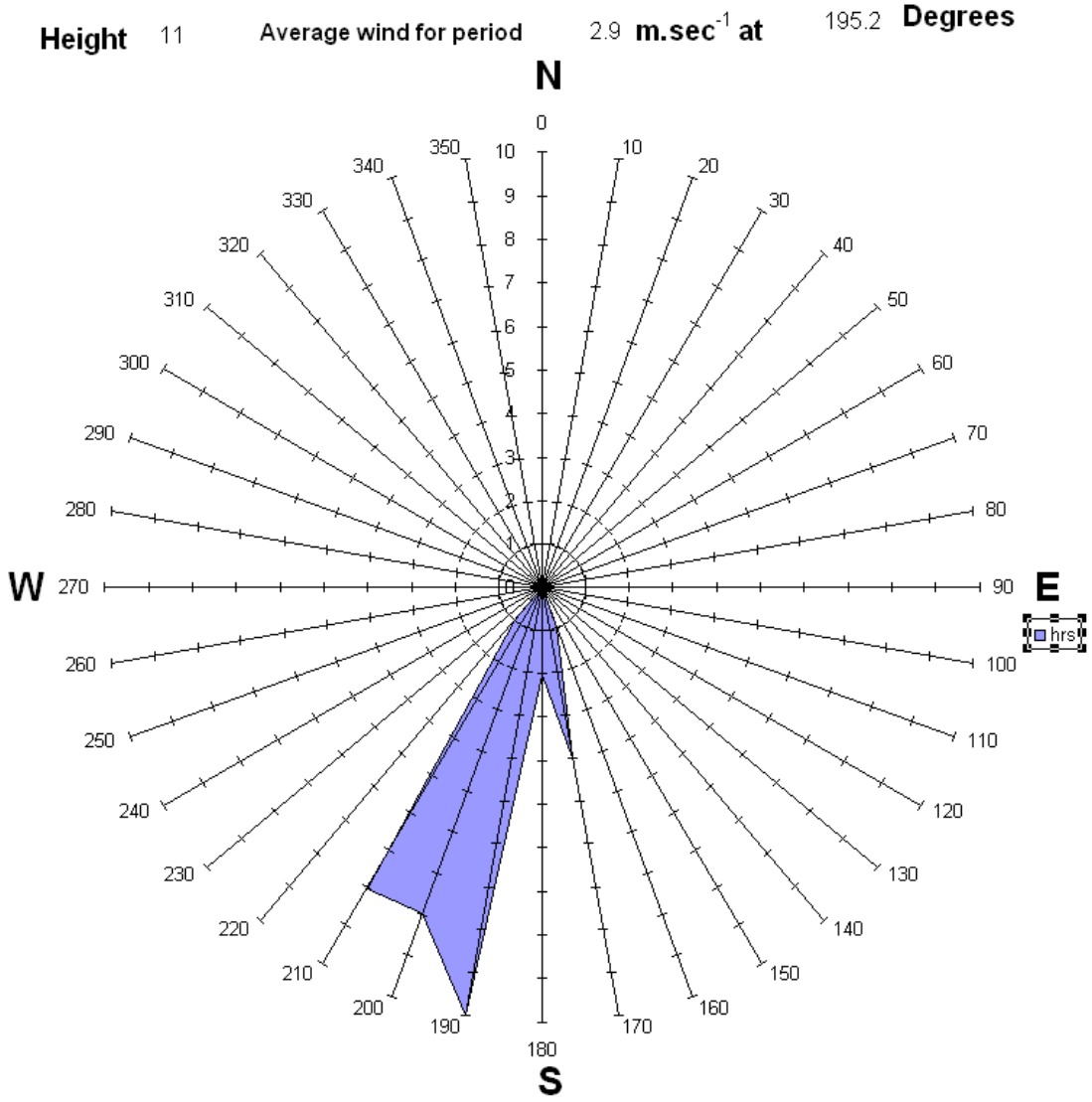


Figure 3.15 Wind rose diagram – top mast – 7 & 8 August 2007

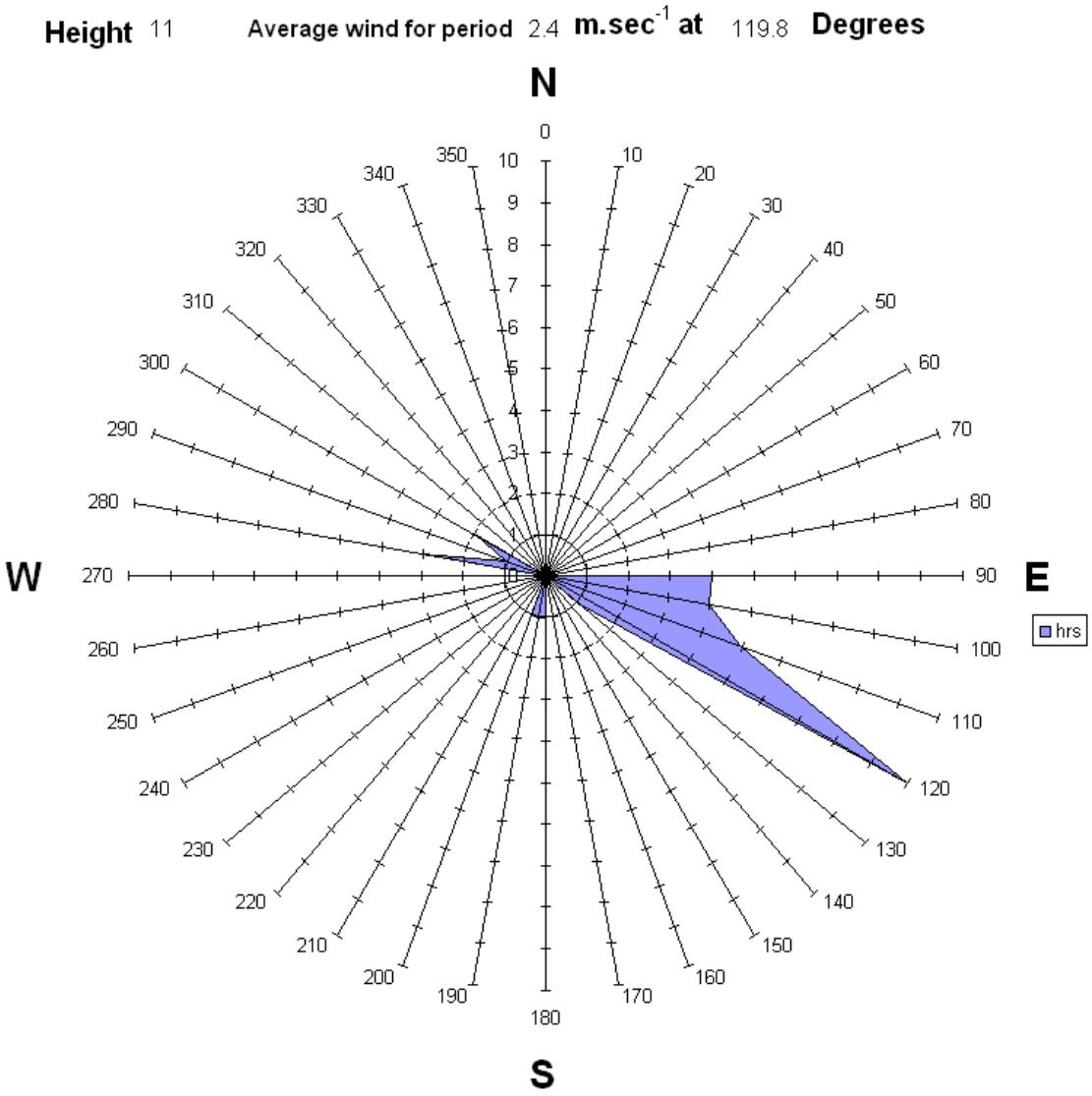


Figure 3.16 Wind rose diagram – top mast – 9 August 2007

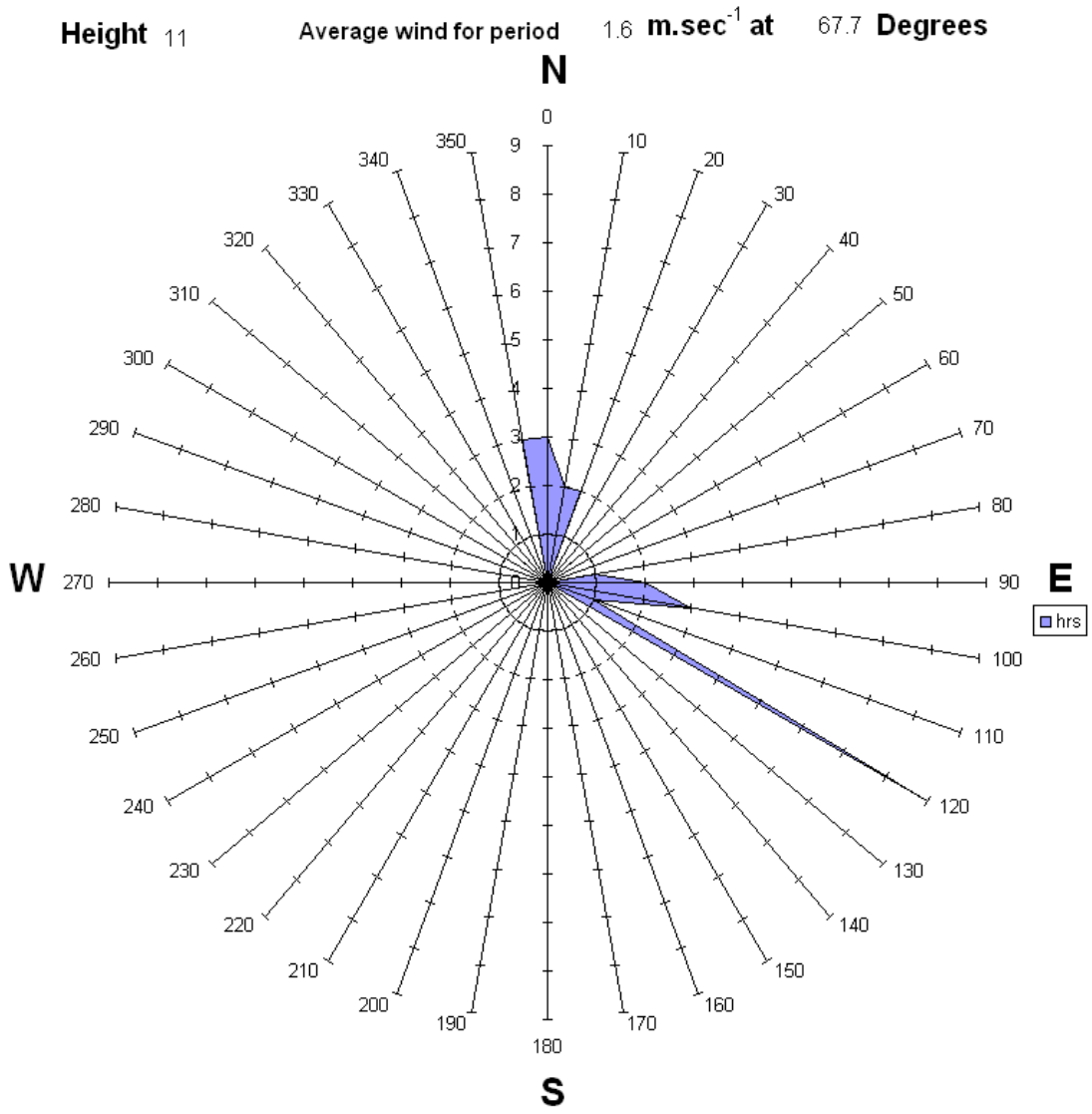


Figure 3.17 Wind rose diagram – top mast – 10 August 2007

Checked by:

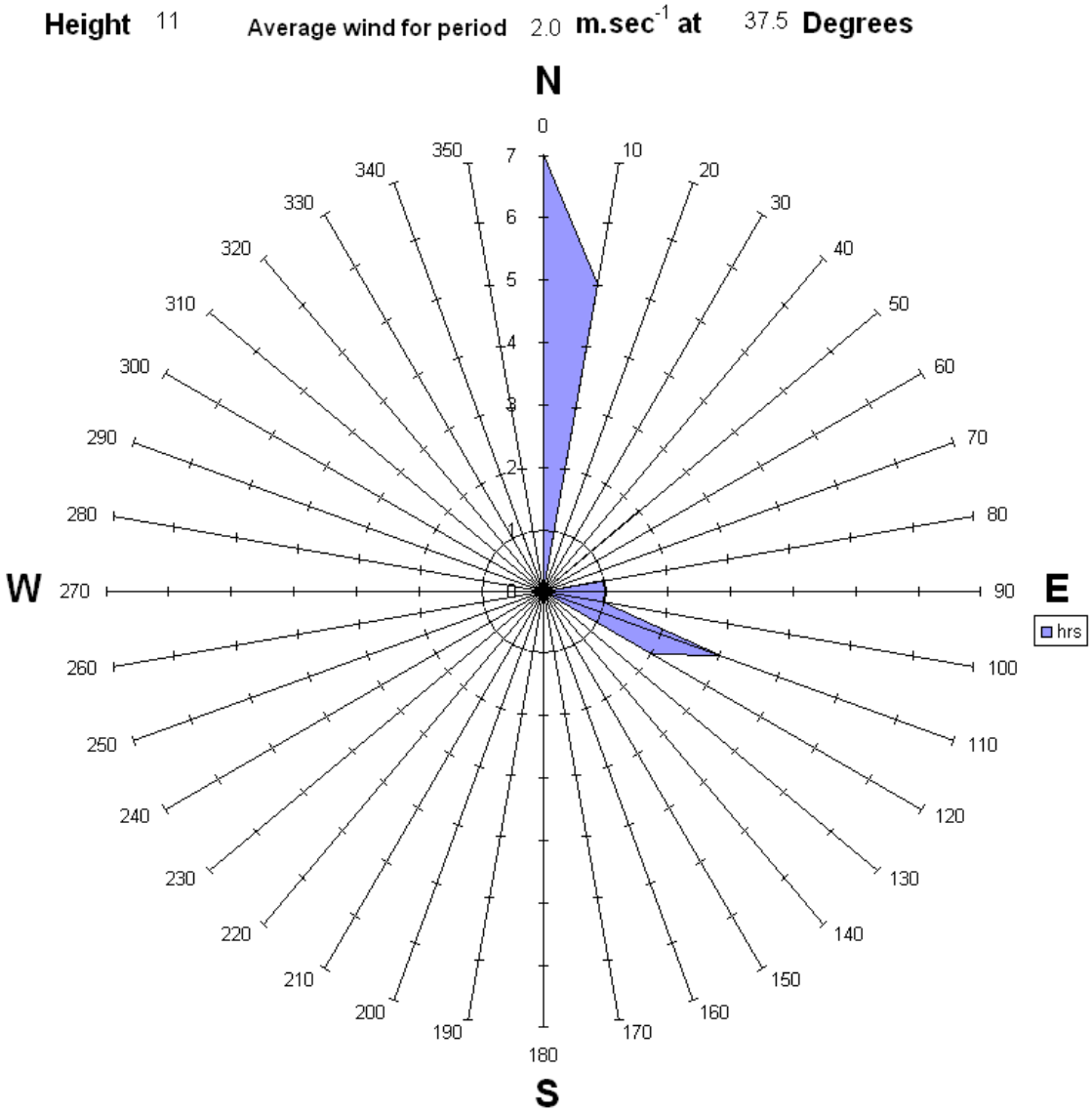


Figure 3.18 Wind rose diagram – top mast – 11 August 2007

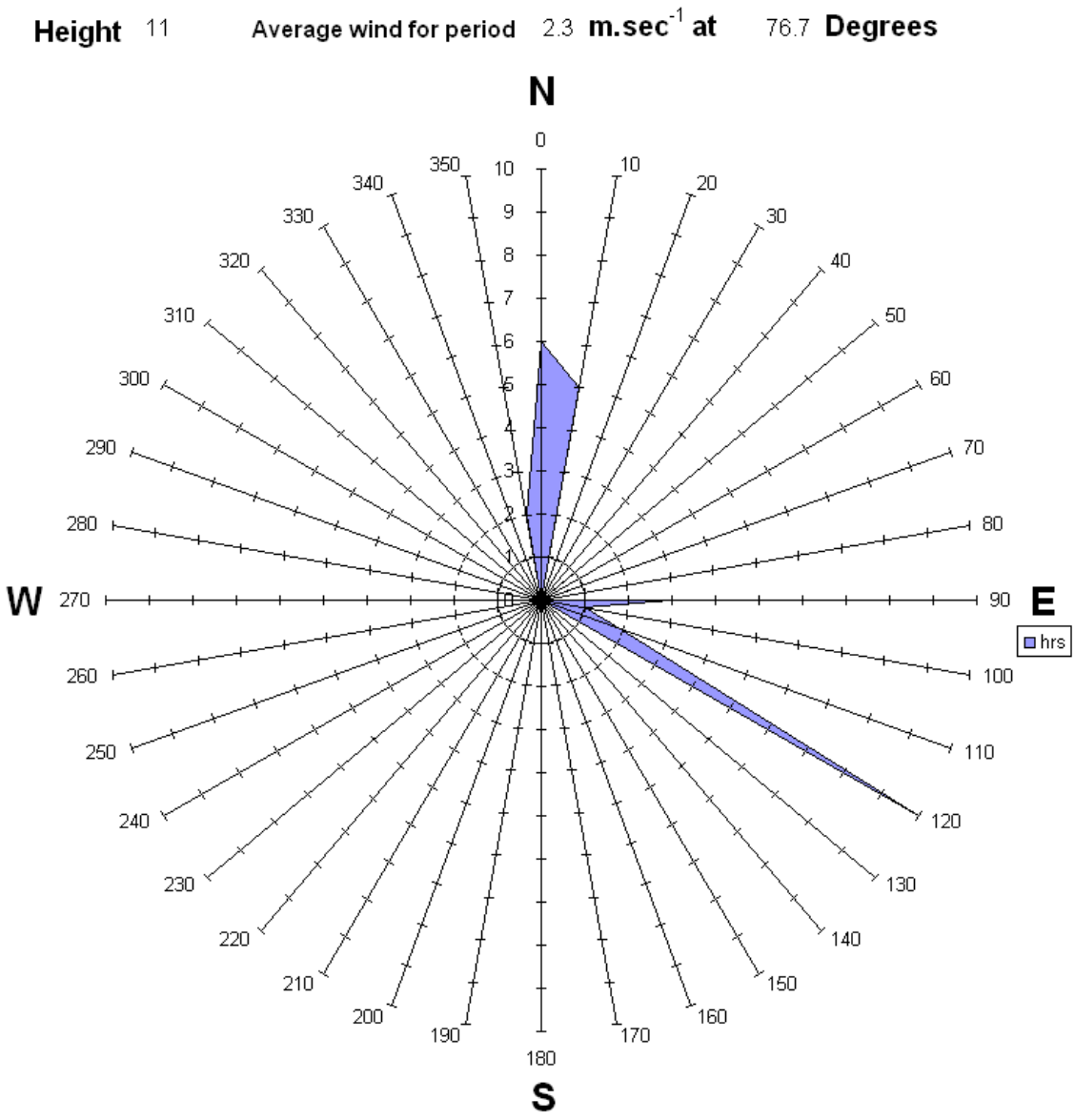


Figure 3.19 Wind rose diagram – top mast – 14 August 2007

Checked by:

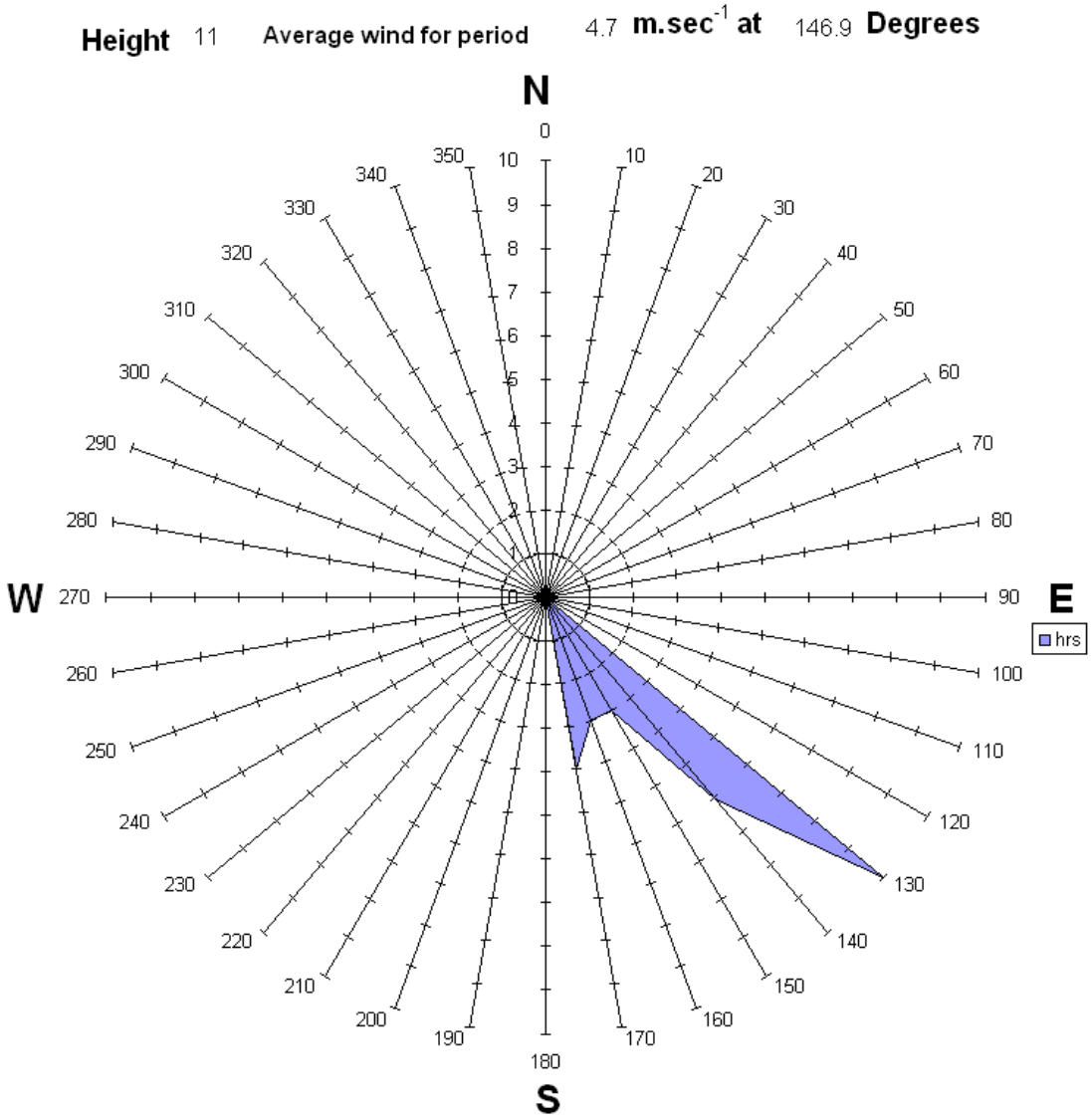


Figure 3.20 Wind rose diagram – top mast – 17 August 2007

Checked by:

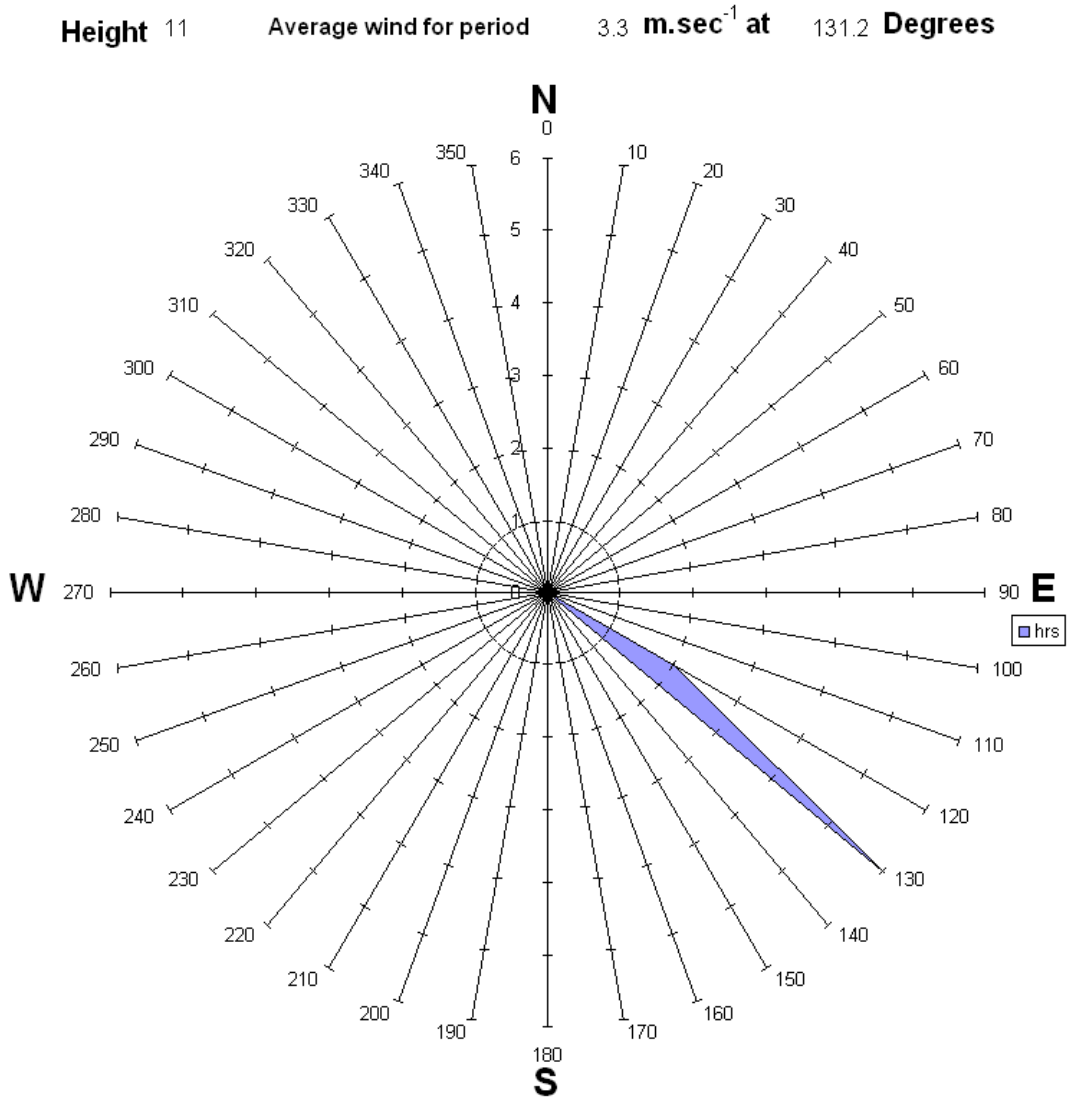


Figure 3.21 Wind rose diagram – top mast – 18 August 2007

Checked by: