APPENDIX A

NPL DIAL REPORT

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Differential Absorption Lidar (DIAL) Measurements of Benzene Emissions from a Coke Oven in Tonawanda, US, May 2010

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Analytical Science Division

ABSTRACT
This report presents the results of measurements of the emissions of benzene from a coke oven in Tonawanda, US, carried out using the NPL Differential Absorption Lidar (DIAL). The measurements were conducted between 25th and 28th May 2010.

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Approved on behalf of NPLML by Martyn Sene, Director, Operations Division

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INTRODUCTION

This report presents the results of a measurement campaign carried out using the NPL differential absorption lidar (DIAL) system to monitor emission fluxes of benzene from Tonawanda Coke site in Tonawanda, US, from the 25^{th} to the 28^{th} May 2010. Measurements of benzene emission fluxes were made using downwind and upwind scans in a vertical plane.

The primary objective of the study was to assess emission fluxes of benzene from the areas identified as potential sources.

A brief overview of the measurements approach and the DIAL locations used during the campaign is given below. Section 2 presents the results of the benzene flux measurements. 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 using sorption tubes. Annex 3 shows a summary of the daily benzene cell scans measurements for the data quality check. Annex 4 presents a series of wind roses to provide a summary of the meteorological conditions present during the campaign.

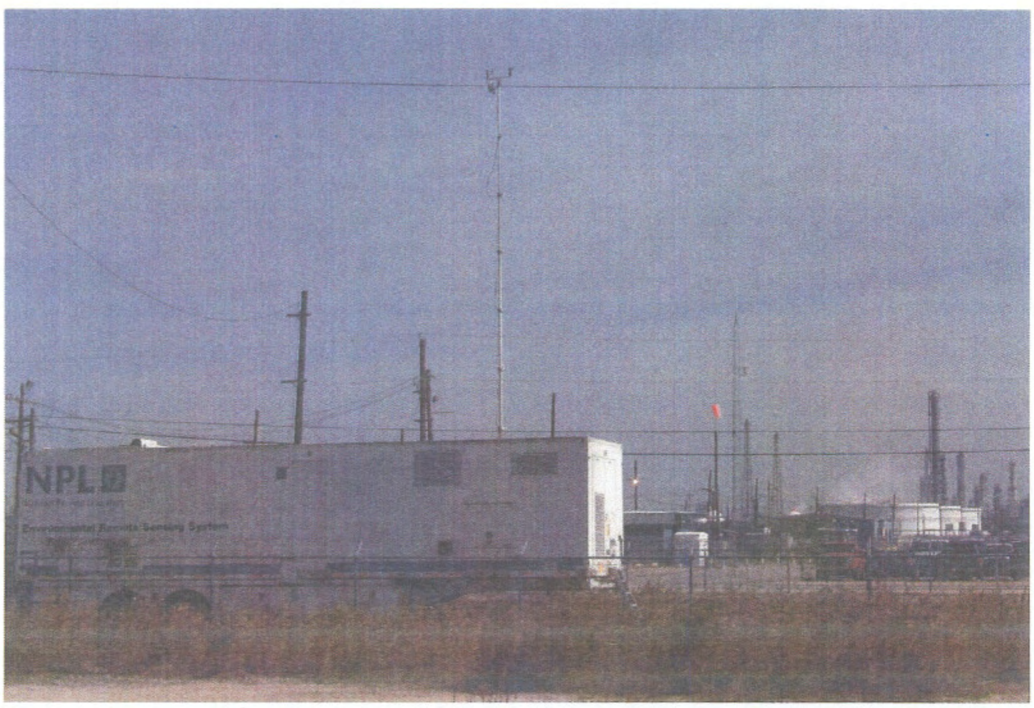

Figure 1.1 The NPL DIAL on a site.

1.1 OVERVIEW OF MEASUREMENTS APPROACH

The NPL DIAL was used to measure benzene emission fluxes from different areas of the site. Table 1.1 lists the DIAL measurement locations, and provides the GPS locations for each position. These locations are shown in the map in Figure 1.2 where the Coke Ovens and Process areas are highlighted.

Table 1.1 Summary of DIAL measurement locations.

DIAL Location	Description	GPS Position
Loc1	SE of Battery	42° 58' 57.37" N - 78° 55' 31.89" W
Loc2	NE of Loc1	42° 58' 58.81" N - 78° 55' 31.07" W
Loc3	NW of Main Stacks	42° 59' 5.72" N - 78° 55' 28.11" W
Loc4	Further East from Loc3	42° 59' 5.99" N - 78° 55' 23.53" W
Loc5	East of Ovens	42° 59' 1.61" N - 78° 55' 26.39" W
Loc6	East End of Battery Road	42° 59' 2.46" N - 78° 55' 29.80" W
Loc7	NE of Loc2	42° 58' 59.19" N - 78° 55' 30.70" W

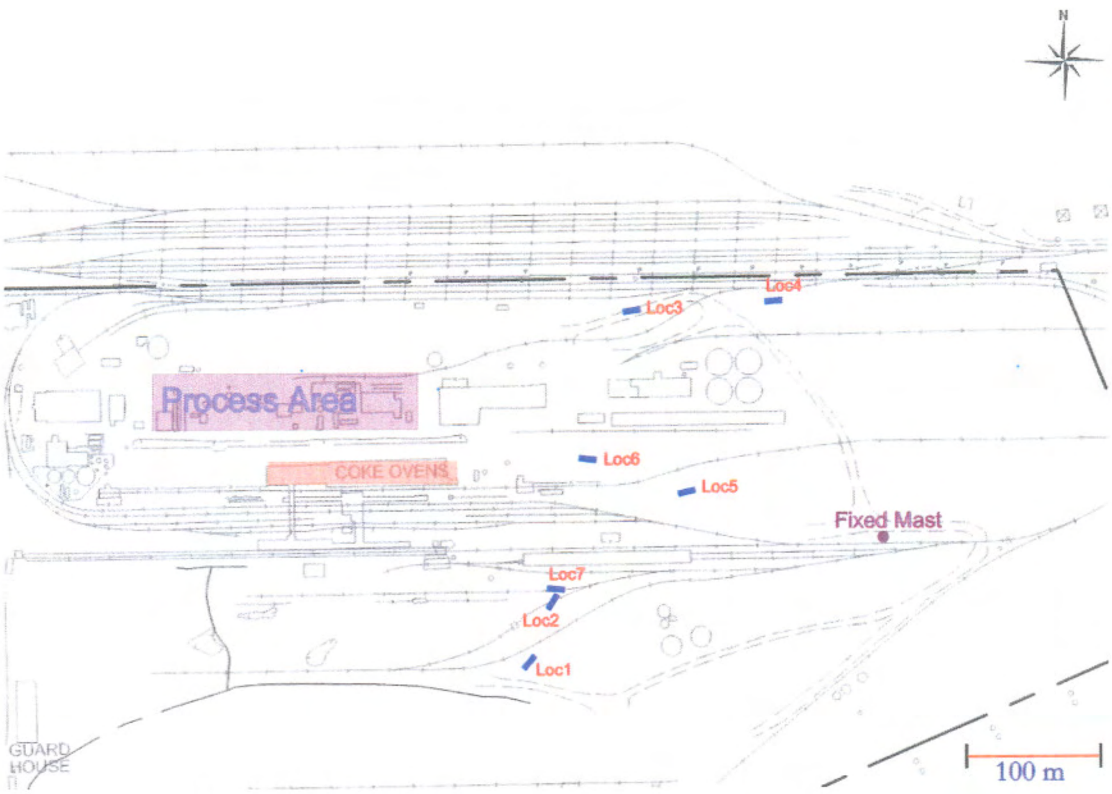

Figure 1.2 DIAL measurement locations and location of fixed meteorological mast. (Note: Process area and Coke Oven extent are only indicative)

Emission fluxes were measured as described in Annex 1, by scanning the DIAL measurement beam in a vertical plane downwind of the target sources, and determining the total concentration of benzene in that plane. The wind field used to determine the flux was measured using the fixed mast (located on the east part of the site at the position identified on Figure 1.2), the 12 m DIAL mounted meteorological mast, and when appropriate a 2 m portable meteorological sensor. The fixed mast supported two wind sensor packages, at 11m and 3m local elevation. The wind field used for the flux calculations (see Annex 1) was determined from the speed on the fixed mast (11m and 3m) for all the flux measurements. The portable wind sensor was used to check the wind speed in different areas of the site. The direction measured from the fixed mast upper height sensor was used to define the wind direction for most flux measurements. The DIAL wind vane sensor was used for the wind direction for Loc1. The wind covered most directions over the course of the campaign, as summarized in Annex 3.

1.2 TABLES AND FIGURES

The measurement lines-of-sight (LOS) used at each location for the benzene measurements are shown from Figures 2.1 to 2.8. These figures also show the position of the portable wind sensor and the average wind direction measured over the full time frame during which the measurements from a given location took place. Figures 2.4 and 2.7 also show the position where the tube air samples were taken. Figures 2.1a to 2.8a show contour plots and visual representations of the emissions observed in the downwind DIAL measurements. The DIAL maximum scan range depends on the atmospheric conditions, it varies from day to day and it can also change during the same day. Therefore, some figures show emission beyond 400 m range from the DIAL while in other scans the maximum DIAL measurement range is less than 350 m from the DIAL location.

Tables 2.1 to 2.8 report the benzene fluxes determined for each scan made during the measurement campaign. The scan numbers are not sequential because some scans are recorded for the daily benzene cell scans measurements for the data quality check, reported in Annex 3, also some scans may have been aborted by the operator. No scan was eliminated from the report. The tables also list the locations and the lines-of-sight used for each measurement. The wind directions reported in the tables are from the sensor used for the flux calculations. The wind speeds reported in the tables are from the higher of the two sensors used to determine the wind profile. The Notes in each table are only indicative of the area measured in a specific LOS to aid the reader in visualising the general location from where the plumes are coming. Refer to the results discussion for more detailed explanations of why the emission is believed to arise from that specific area of the site. Sometimes the Notes refer to the intended target of the measurement even if the measurement may not have been completely successful for different reasons such as an unexpected change in wind direction. Refer to the results discussion for more detailed explanations.

Emissions from other areas of the site may have been upwind of the measured sources. However, generally these sources have been excluded in two ways. If the upwind sources to be excluded are close to the measured sources, and produce localised plumes, these have been discriminated spatially from the measured fluxes by selecting the regions of the scanned region to integrate, in order to calculate the flux. Conversely, if the upwind sources are further away and the emissions from them have dispersed to produce a broad background, this has been removed as a background from the measured, spatially localised emissions of interest.

Table 2.9 reports the mean and standard deviation of the benzene fluxes measured in each location for each LOS. The standard deviation given in the tables is the standard deviation of the individual flux measure from which each mean flux value has been determined. The standard deviation will include the effects of the source variability, DIAL measurement uncertainty and the influence of other variable factors such as the wind speed and direction.

MEASUREMENTS OF BENZENE EMISSIONS.

Table 2.1 Flux measurements from Loc1 on 25th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
1	Loc1/LOS1	10:53	10:58	2.1	228.9	3.56	Coke Ovens & East of Process
2	Loc1/LOS1	10:59	11:09	2.1	188.4	2.18	Coke Ovens & East of Process
3	Loc1/LOS1	11:12	11:26	1.5	230.0	4.88	Coke Ovens & East of Process
4	Loc1/LOS1	11:26	11:39	0.9	279.2	2.01	Coke Ovens & Process
5	Loc1/LOS1	11:41	12:01	2.1	282.4	3.55	Coke Ovens & Process
7	Loc1/LOS1	12:14	12:34	0.7	222.6	2.99	Coke Ovens & East of Process
8	Loc1/LOS1	12:36	13:01	1.0	206.3	3.05	Coke Ovens & East of Process
9	Loc1/LOS2	13:07	13:25	1.6	278.8	0.18	Upwind
10	Loc1/LOS2	13:26	13:44	1.8	54.0	3.74	Mainly Coke Ovens

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

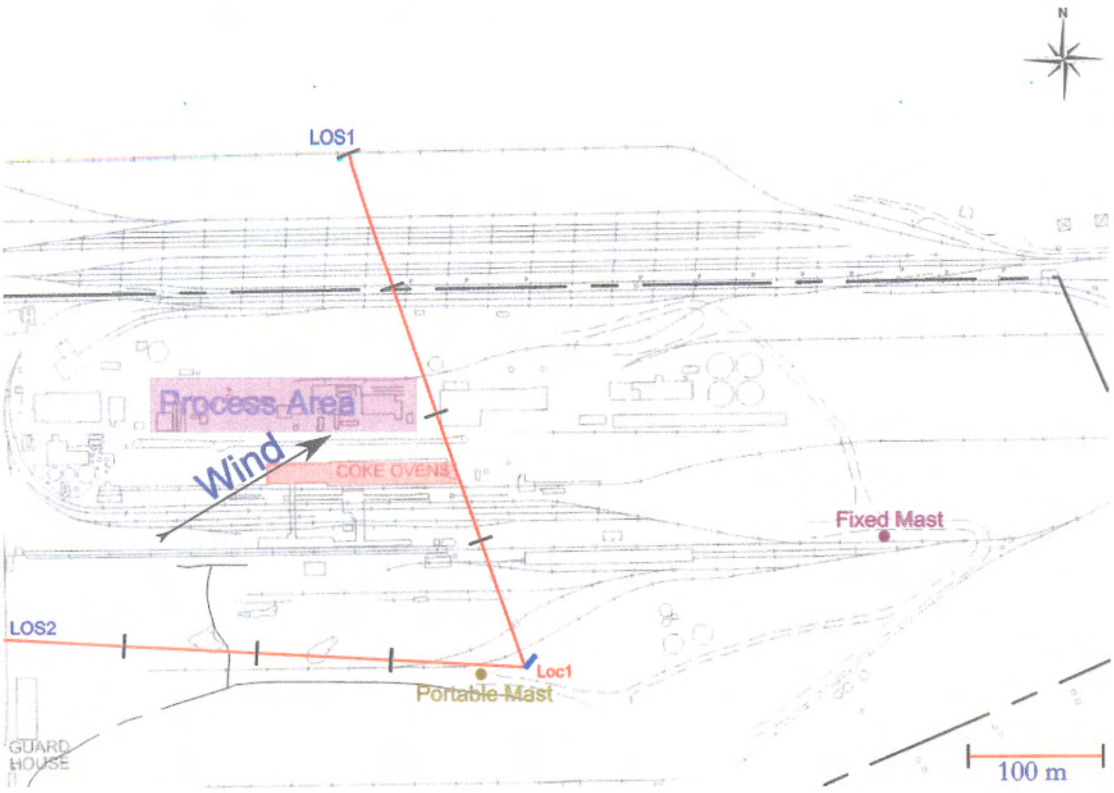

Figure 2.1 Measurement configuration for location Loc1 on 25th of May.

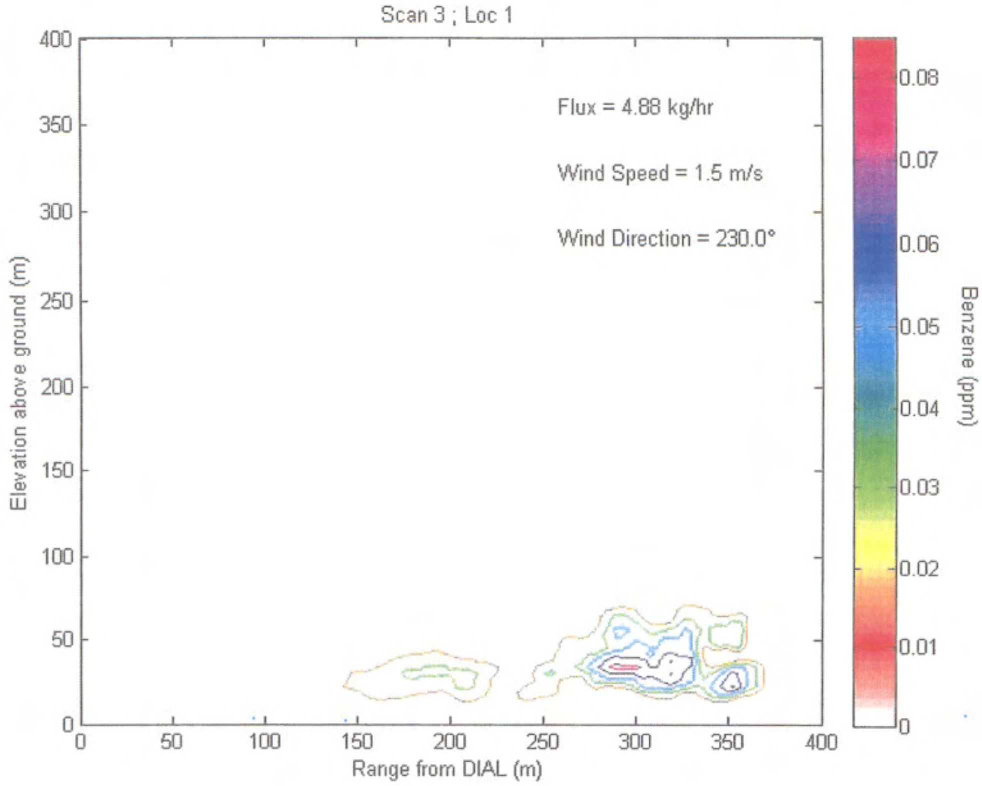

Figure 2.1a1 Contour plot of concentration profile for Scan 3 representing LOS1.

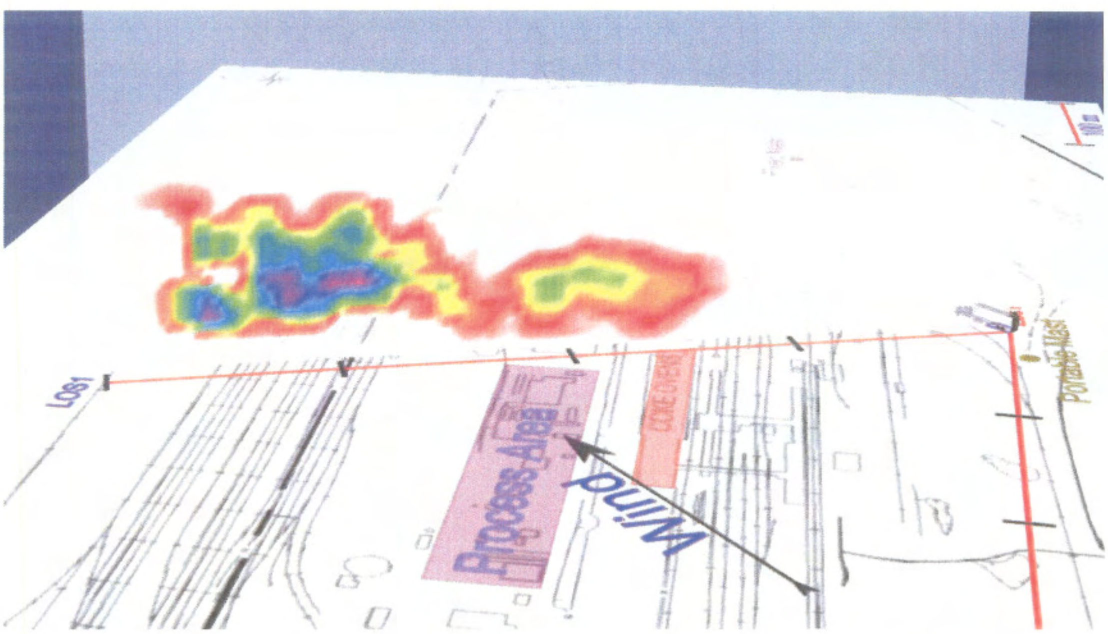

Figure 2.1a2 Visualisation of flux measurement for Scan 3 representing LOS1.

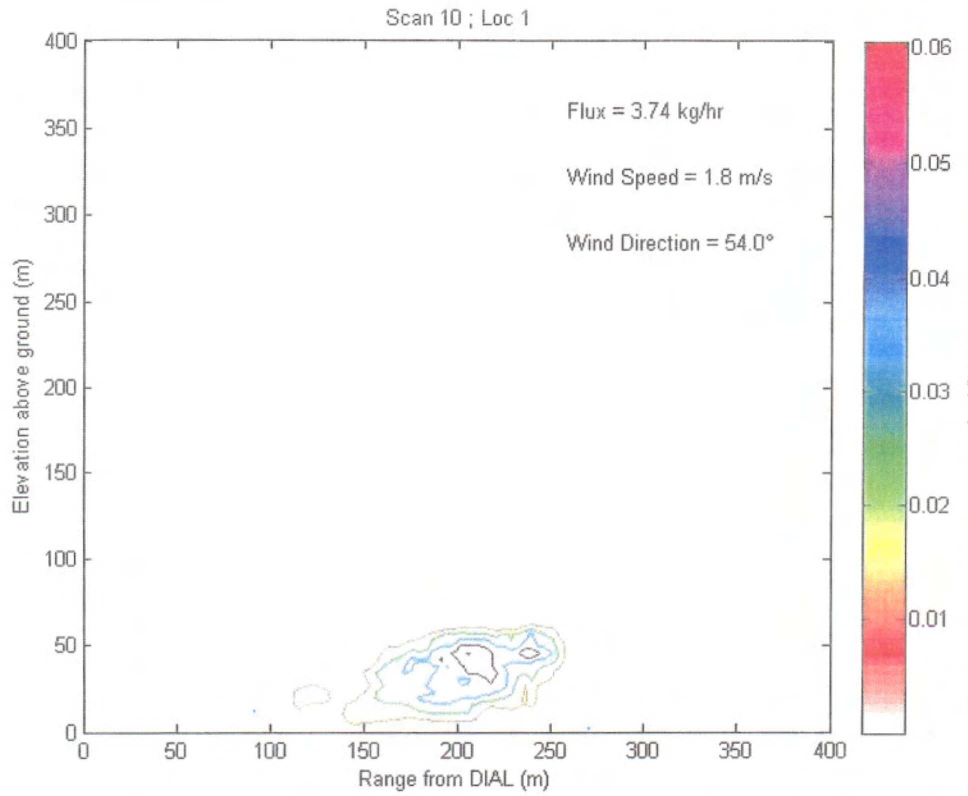

Figure 2.1b1 Contour plot of concentration profile for Scan 10 representing LOS2.

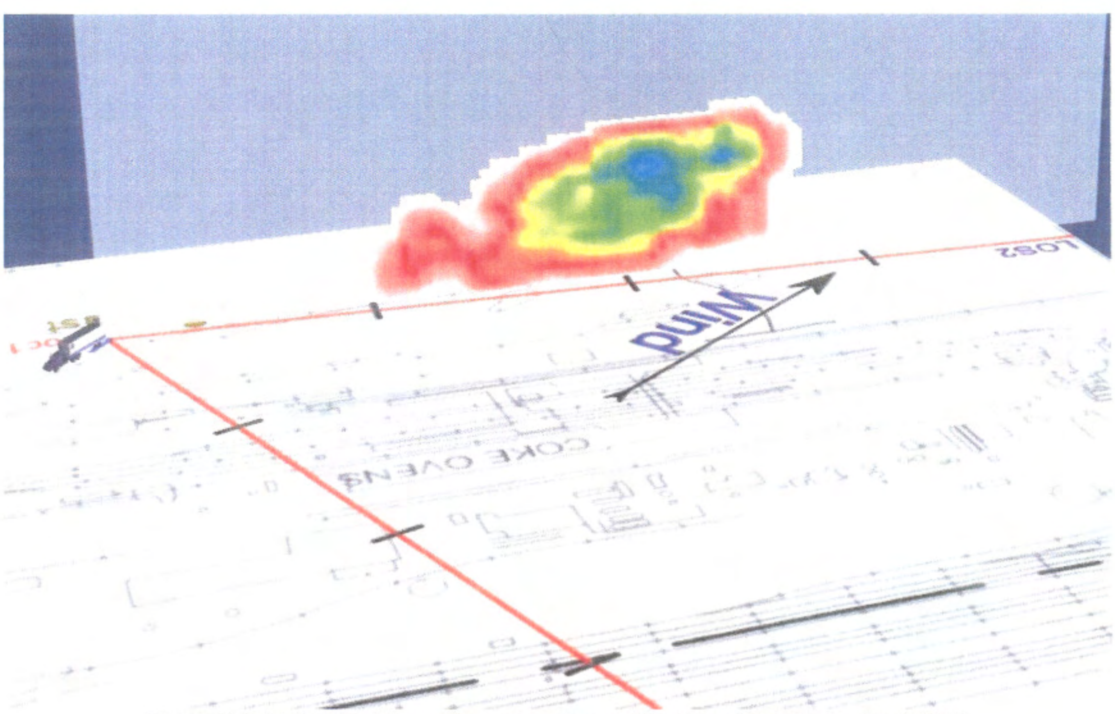

Figure 2.1b2 Visualisation of flux measurement for Scan 10 representing LOS2.

Table 2.2 Flux measurements from Loc2 on 25th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
12	Loc2/LOS1	14:32	14:47	0.6	192.5	0.98	West Part of Coke Ovens
13	Loc2/LOS2	14:51	15:09	2.3	262.3	6.41	Coke Ovens & Process
15	Loc2/LOS1	15:49	16:13	2.0	332.3	1.53	East Part of Coke Ovens
16	Loc2/LOS1	16:13	16:36	2.2	344.0	3.31	East Part of Coke Ovens
17	Loc2/LOS1	16:37	17:01	2.1	359.4	3.44	East Part of Coke Ovens
18	Loc2/LOS3	17:06	17:24	2.9	355.6	3.51	Coke Ovens & East of Process
19	Loc2/LOS3	17:24	17:43	3.4	8.1	3.90	Coke Ovens & East of Process
20	Loc2/LOS3	17:44	18:05	3.6	8.2	4.09	Coke Ovens & East of Process
21	Loc2/LOS3	18:13	18:25	3.5	5.7	0.94	Coke Ovens Localised Emission
22	Loc2/LOS3	18:25	18:37	3.5	12.4	0.96	Coke Ovens Localised Emission
23	Loc2/LOS3	18:37	18:41	3.3	12.8	0.95	Coke Ovens Localised Emission
24	Loc2/LOS3	18:42	19:04	3.0	7.0	3.54	Coke Ovens& East of Process

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

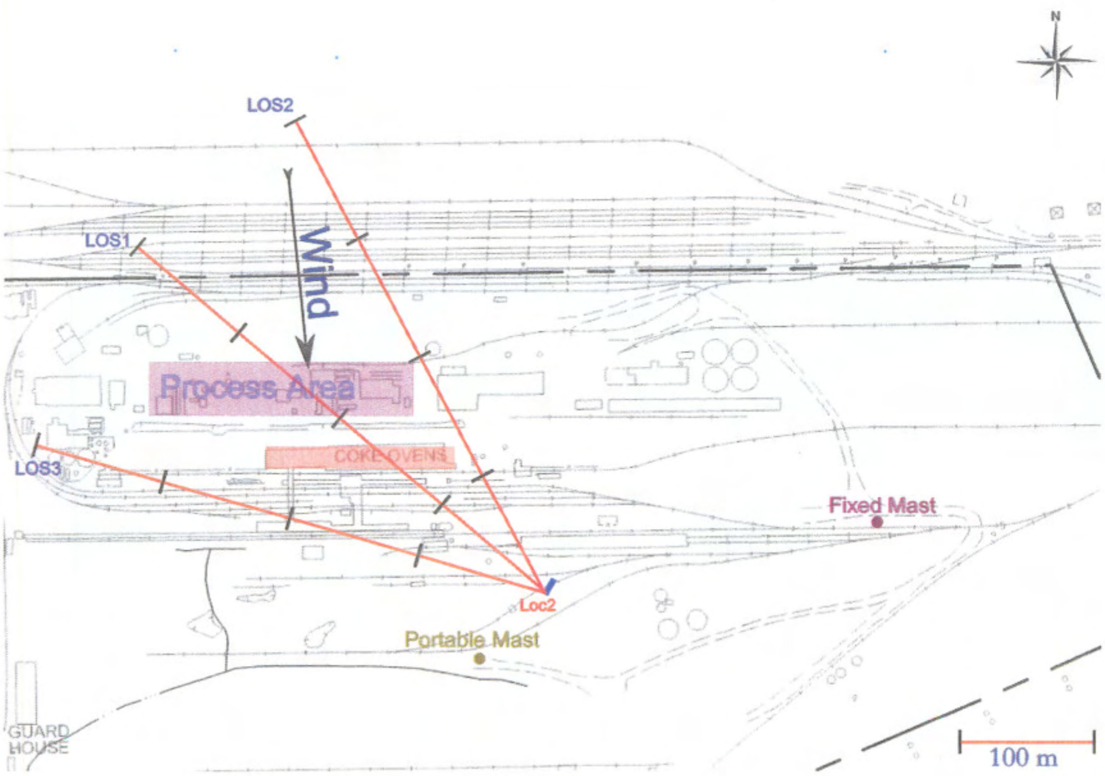

Figure 2.2 Measurement configuration for location Loc2 on 25th of May.

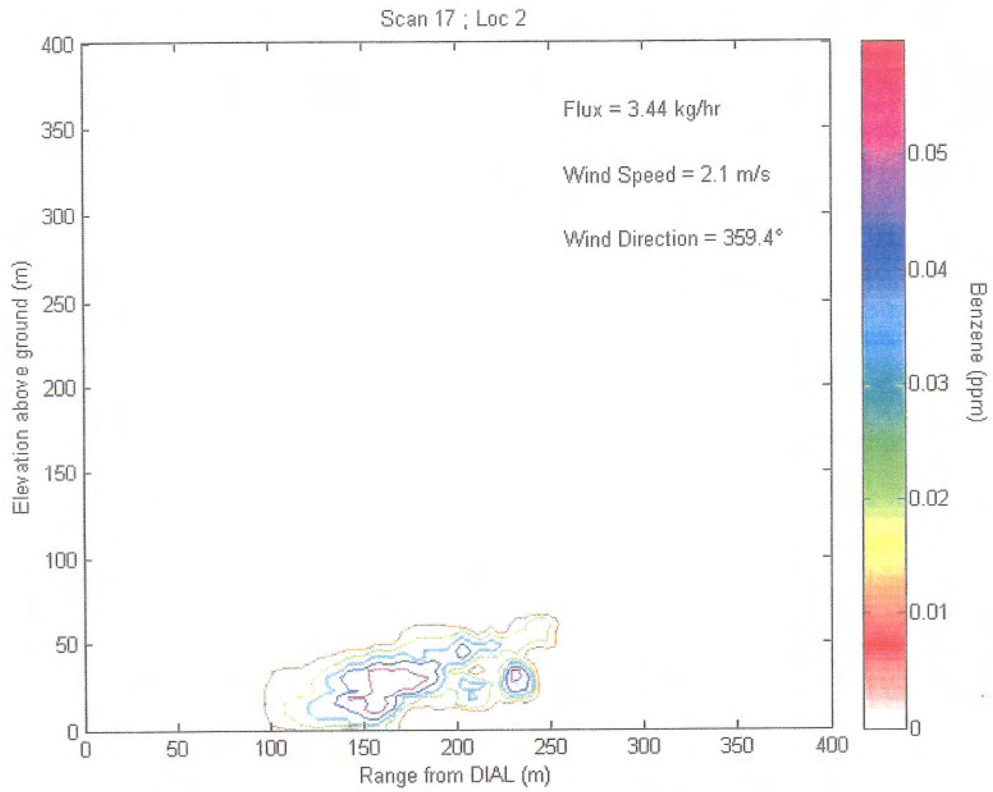

Figure 2.2a1 Contour plot of concentration profile for Scan 17 representing LOS1.

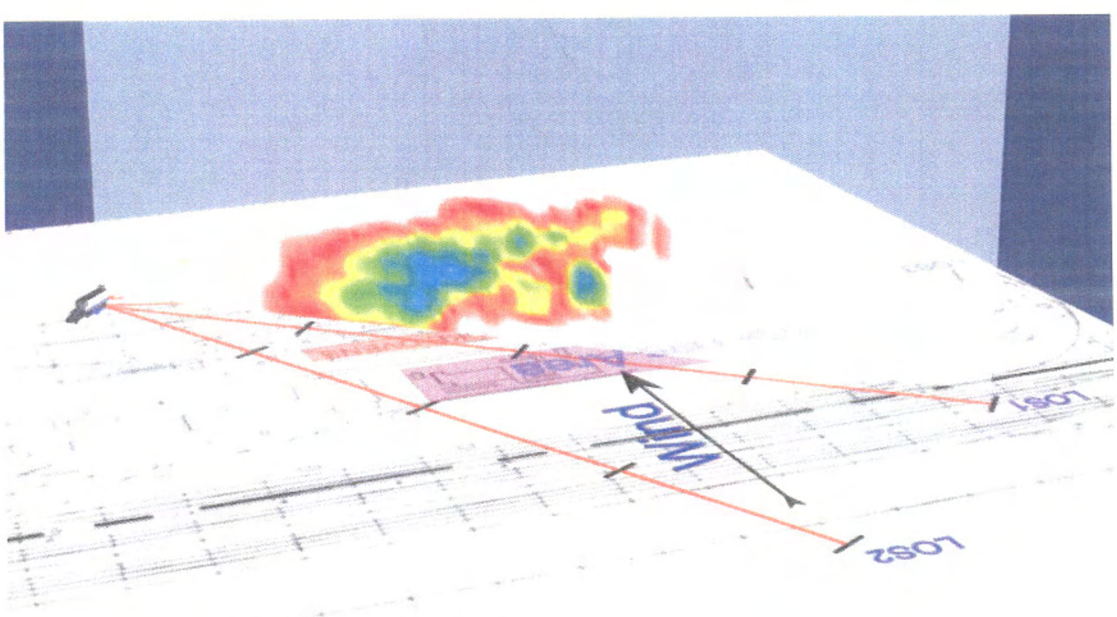

Figure 2.2a2 Visualisation of flux measurement for Scan 17 representing LOS1.

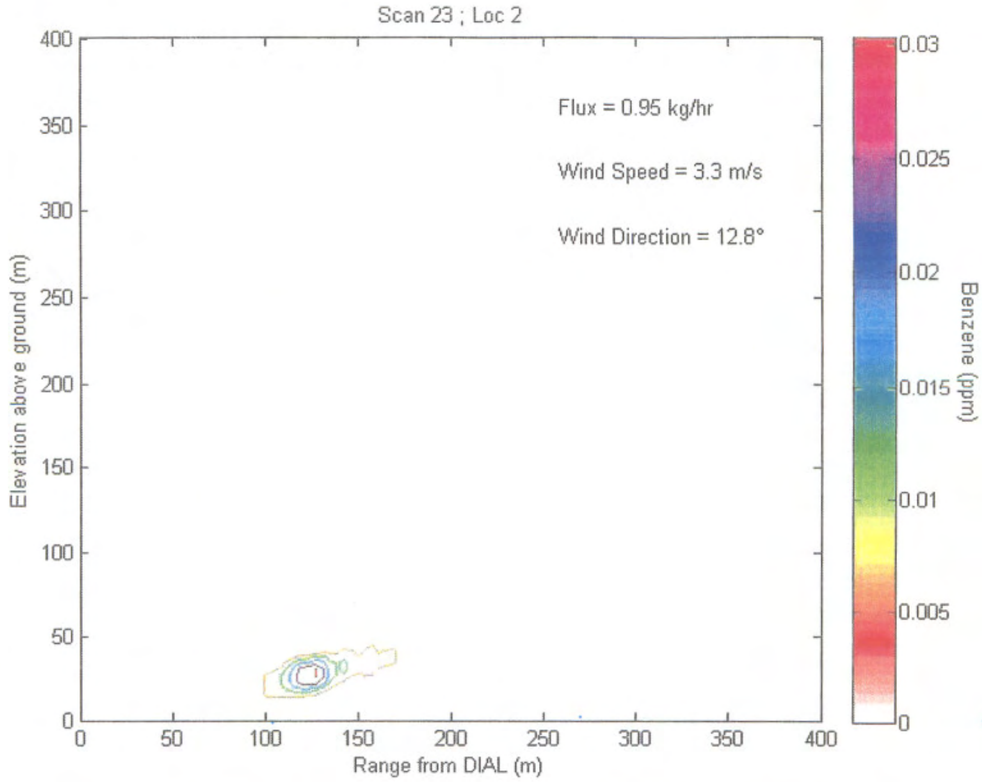

Figure 2.2b1 Contour plot of concentration profile for Scan 23 representing LOS3.

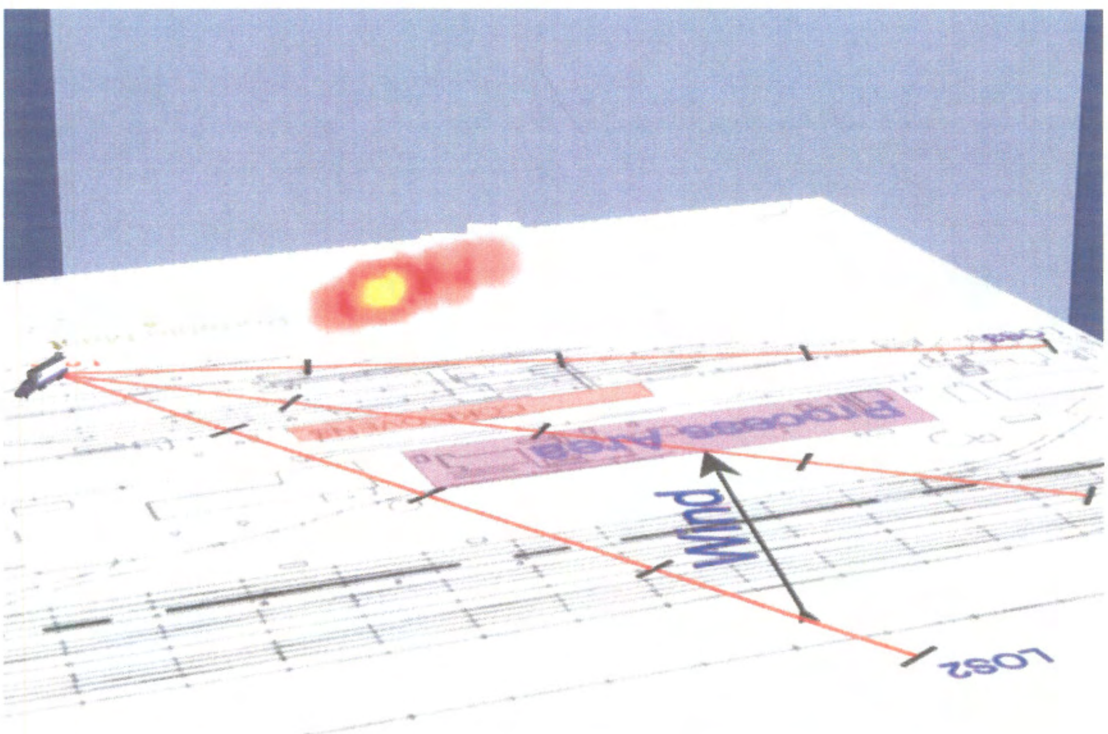

Figure 2.2b2 Visualisation of flux measurement for Scan 23 representing LOS3.

Table 2.3 Flux measurements from Loc3 on 26th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
27	Loc3/LOS1	11:12	11:22	2.0	210.4	8.95	Coke Ovens & Process (1)
28	Loc3/LOS1	11:22	11:32	2.5	193.3	10.96	Coke Ovens & Process (1)
29	Loc3/LOS1	11:34	11:44	2.6	196.6	11.05	Coke Ovens & Process (1)
30	Loc3/LOS1	11:48	11:54	2.6	215.4	0.69	Ovens & Process High El. Angles
35	Loc3/LOS2	13:02	13:11	3.1	241.5	0.06	Stack Plume
36	Loc3/LOS2	13:16	13:24	2.8	226.2	0.00	Stack Plume
37	Loc3/LOS2	13:25	13:40	3.9	209.9	0.22	Stack Plume
40	Loc3/LOS1	13:59	14:15	3.7	203.4	14.04	Coke Ovens & Process (2)
41	Loc3/LOS1	14:17	14:33	3.6	204.5	12.71	Coke Ovens & Process (2)
42	Loc3/LOS1	14:34	14:51	3.8	212.7	15.82	Coke Ovens & Process (2)
43	Loc3/LOS3	14:59	15:19	4.2	218.1	1.74	Upwind or Near Field Plume
45	Loc3/LOS3	15:35	15:55	4.2	214.4	1.89	Upwind or Near Field Plume

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

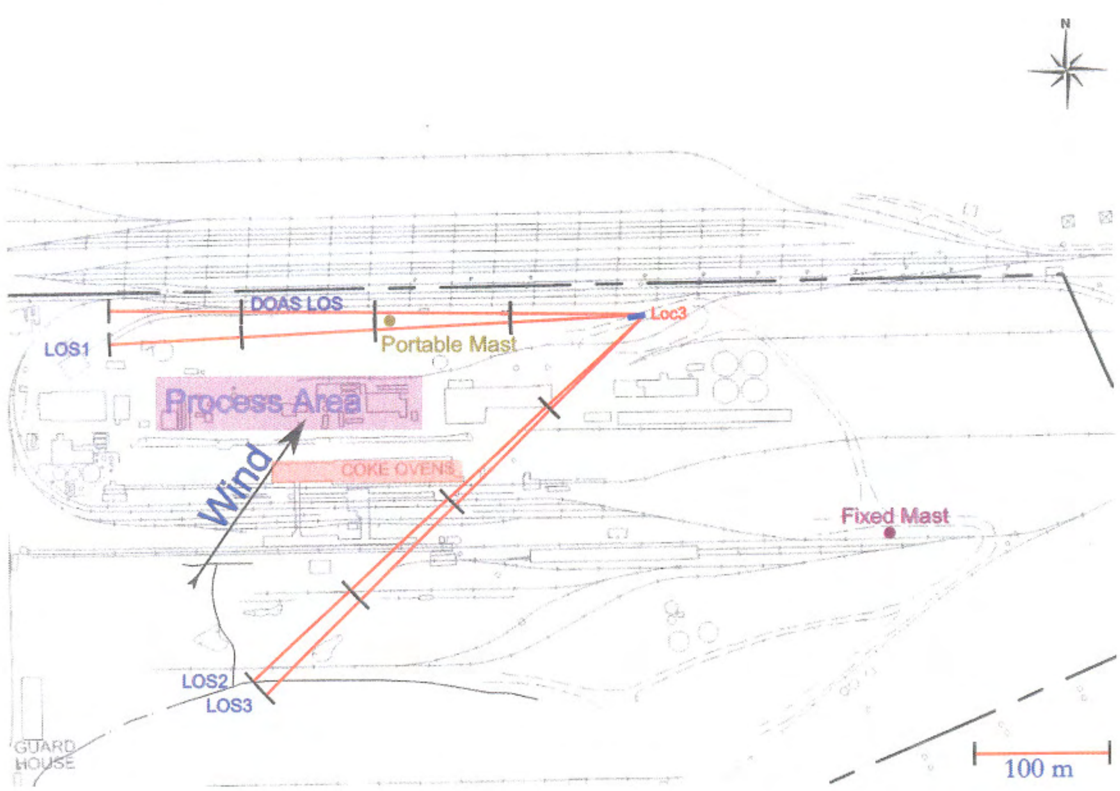

Figure 2.3 Measurement configuration for location Loc3 on 26th of May.

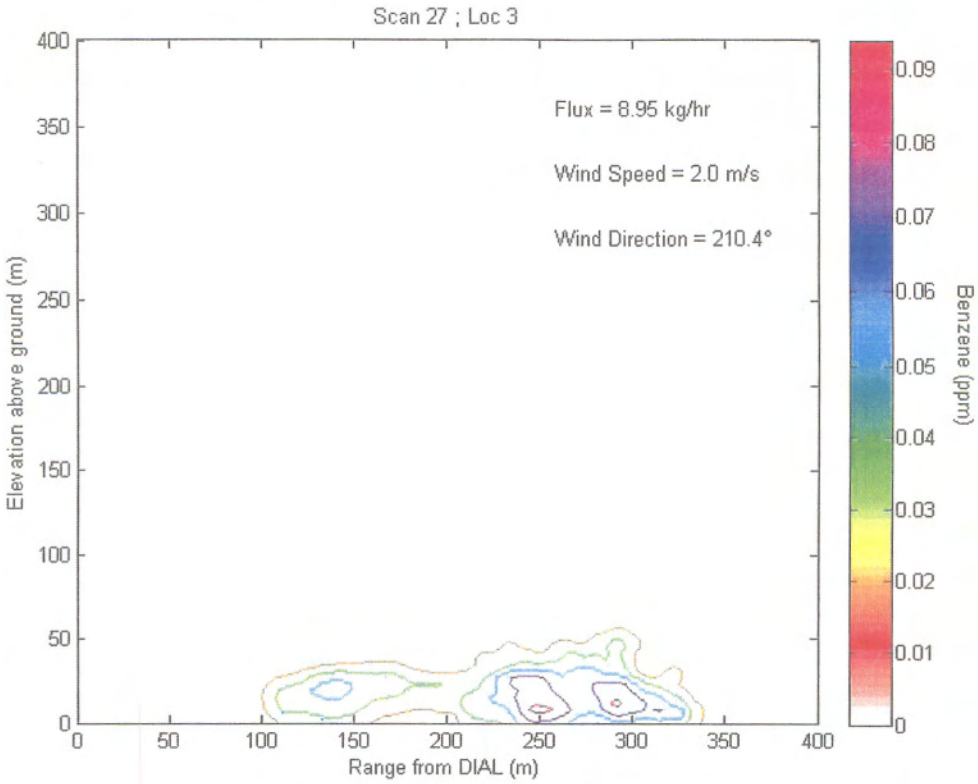

Figure 2.3a1 Contour plot of concentration profile for Scan 27 representing LOS1.

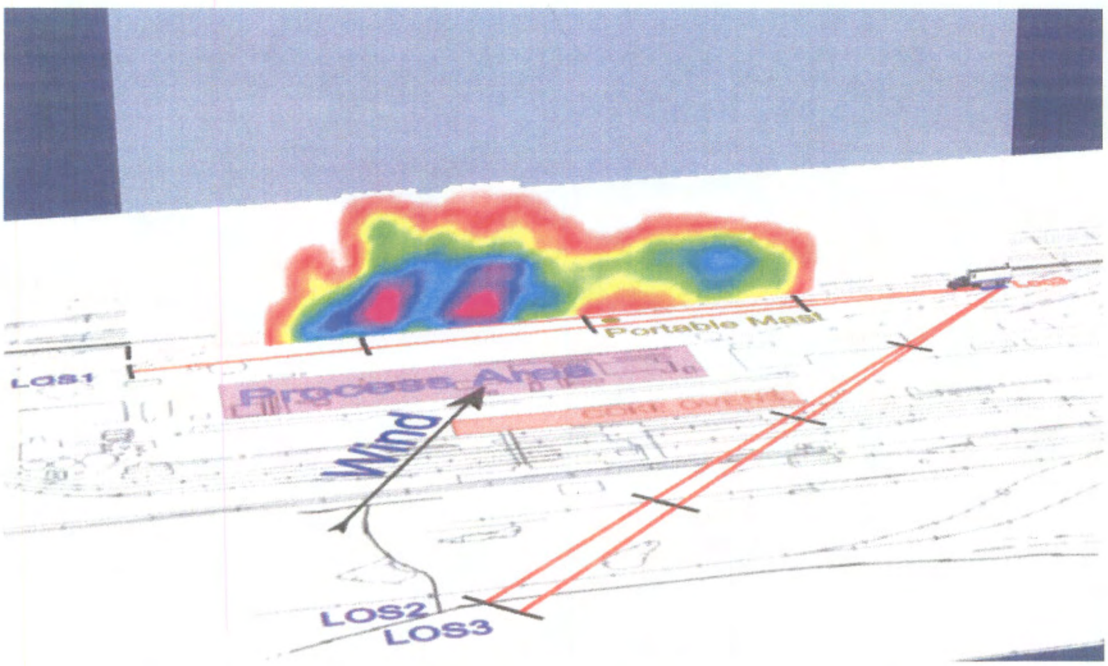

Figure 2.3a2 Visualisation of flux measurement for Scan 27 representing LOS1.

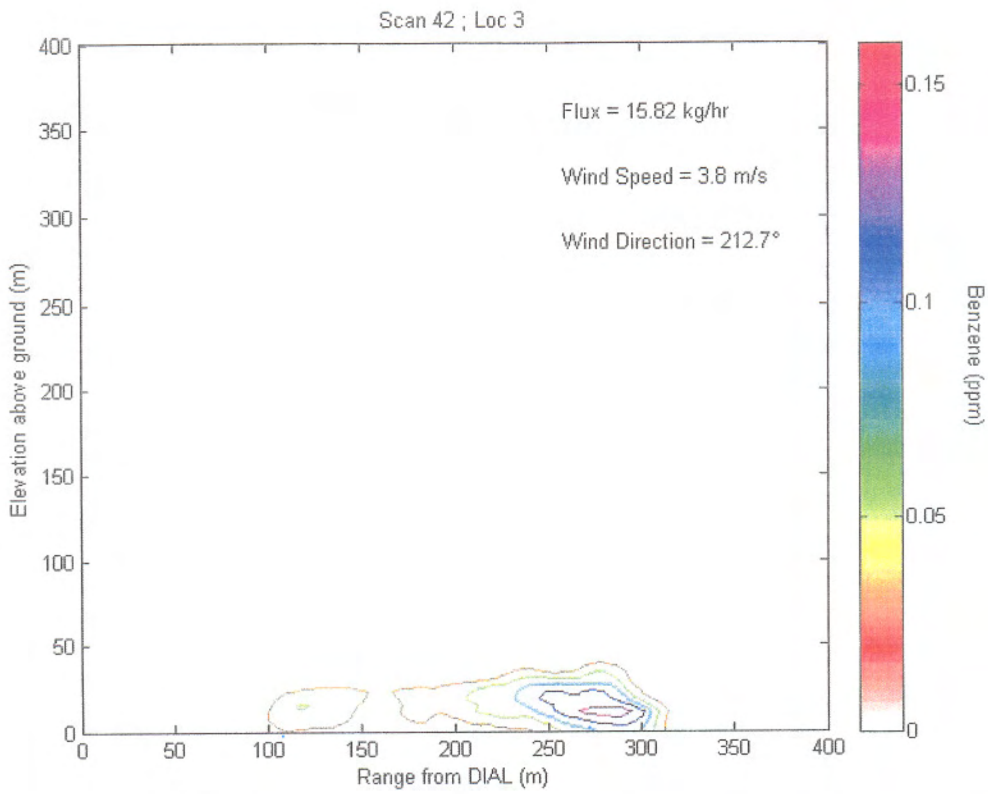

Figure 2.3b1 Contour plot of concentration profile for Scan 42 representing LOS1.

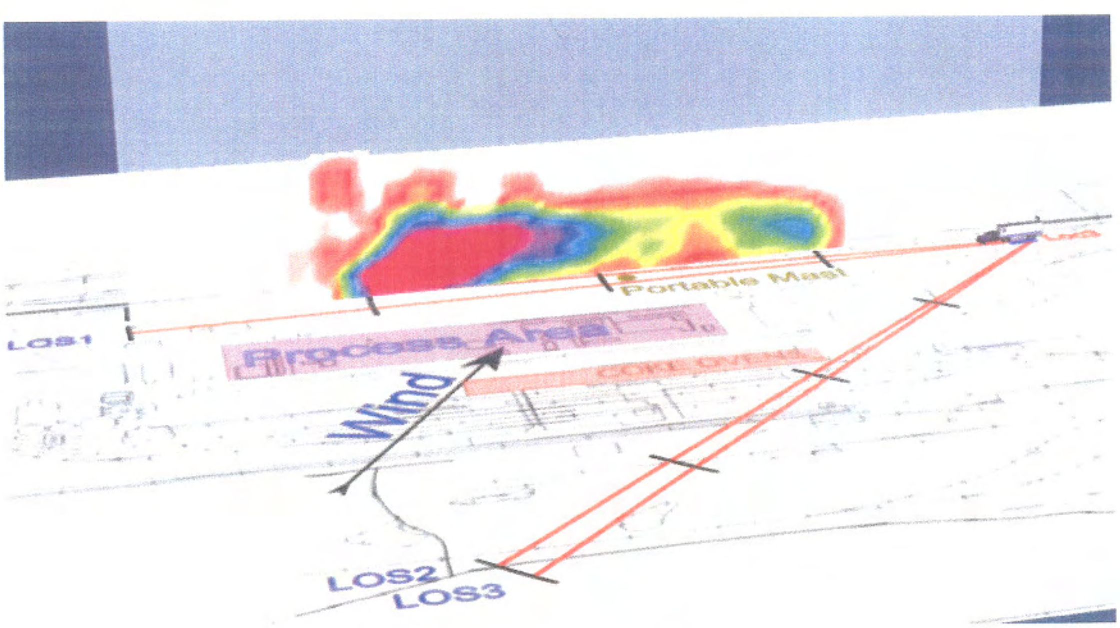

Figure 2.3b2 Visualisation of flux measurement for Scan 42 representing LOS1.

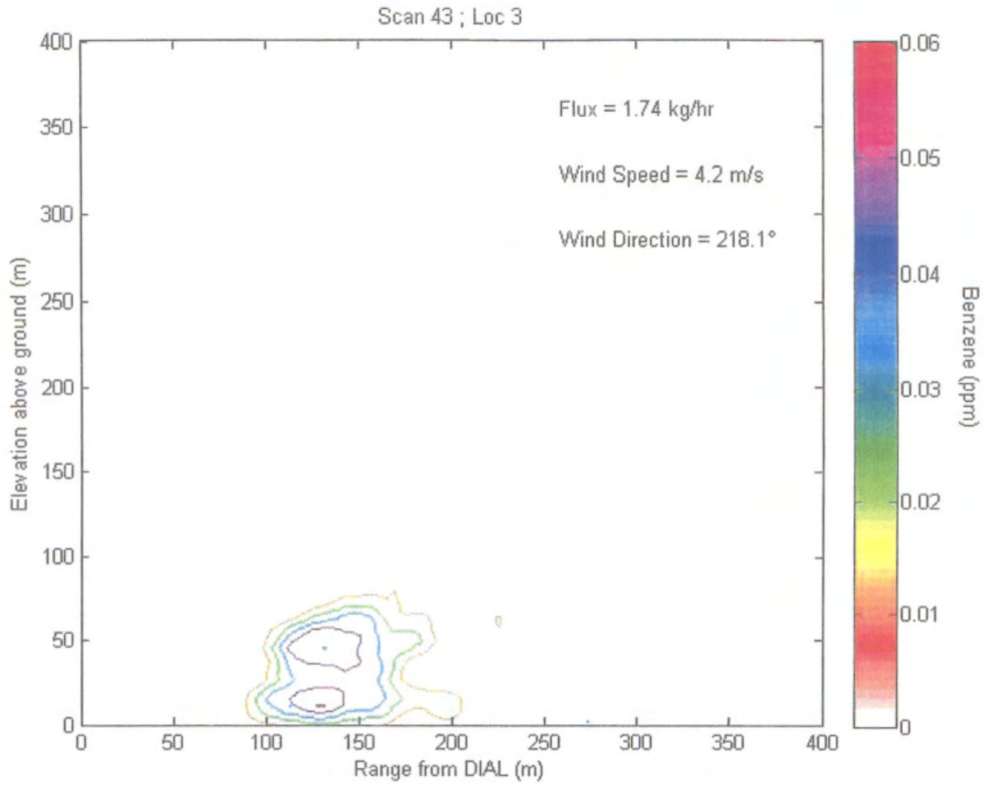

Figure 2.3c1 Contour plot of concentration profile for Scan 43 representing LOS3.

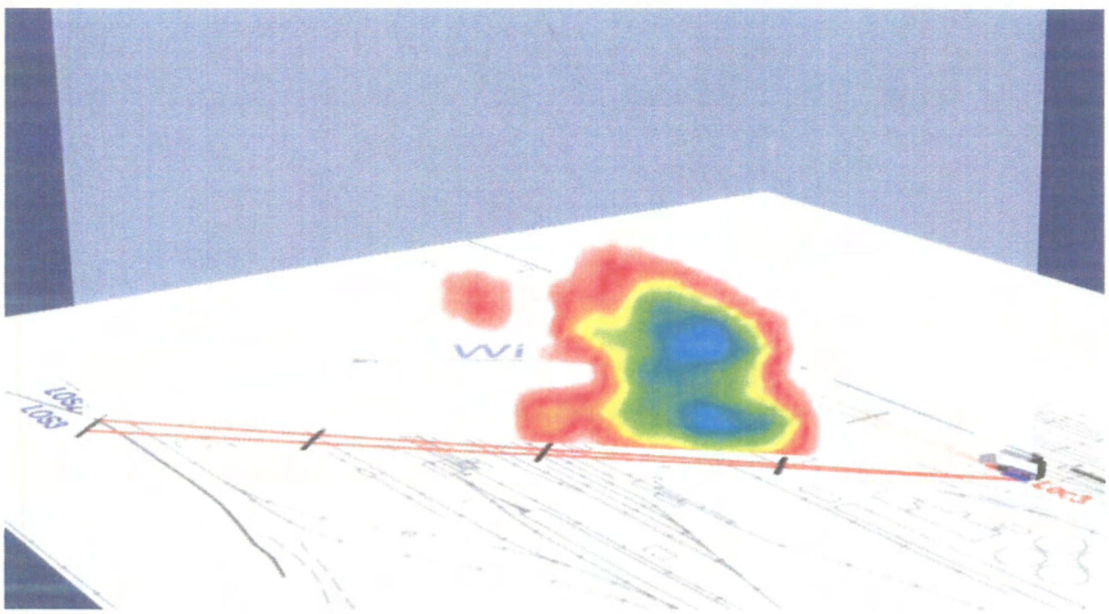

Figure 2.3c2 Visualisation of flux measurement for Scan 43 representing LOS3.

Table 2.4 Flux measurements from Loc4 on 26th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
48	Loc4/LOS1	16:47	17:04	4.2	217.4	8.05	Coke Ovens & Process
49	Loc4/LOS1	17:05	17:22	4.1	220.6	8.09	Coke Ovens & Process
50	Loc4/LOS2	17:25	17:34	4.4	216.0	-0.98	Background
51	Loc4/LOS2	17:34	17:43	4.4	216.0	0.27	Background
52	Loc4/LOS2	17:43	17:51	3.6	221.1	-0.09	Background
53	Loc4/LOS3	17:58	18:11	3.9	221.5	9.46	Coke Ovens & Process
55	Loc4/LOS3	18:13	18:31	3.3	214.6	10.38	Coke Ovens & Process
56	Loc4/LOS3	18:32	18:51	4.0	216.3	11.86	Coke Ovens & Process

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

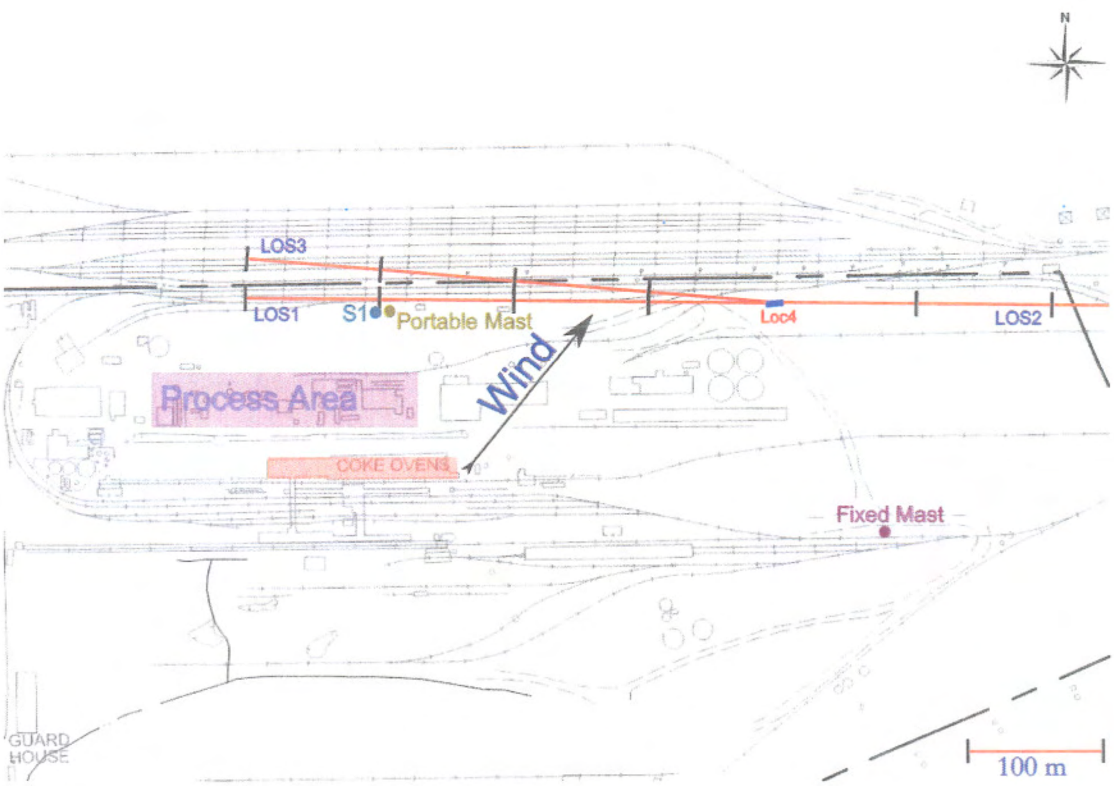

Figure 2.4 Measurement configuration for location Loc4 on 26th of May.

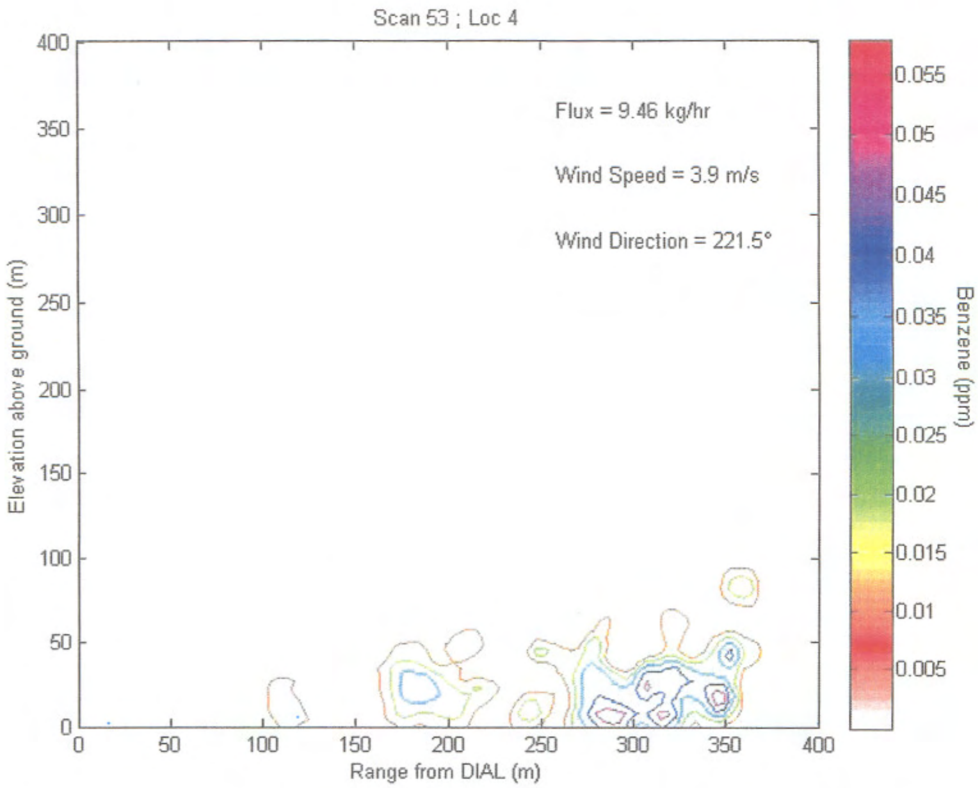

Figure 2.4a1 Contour plot of concentration profile for Scan 53 representing LOS3.

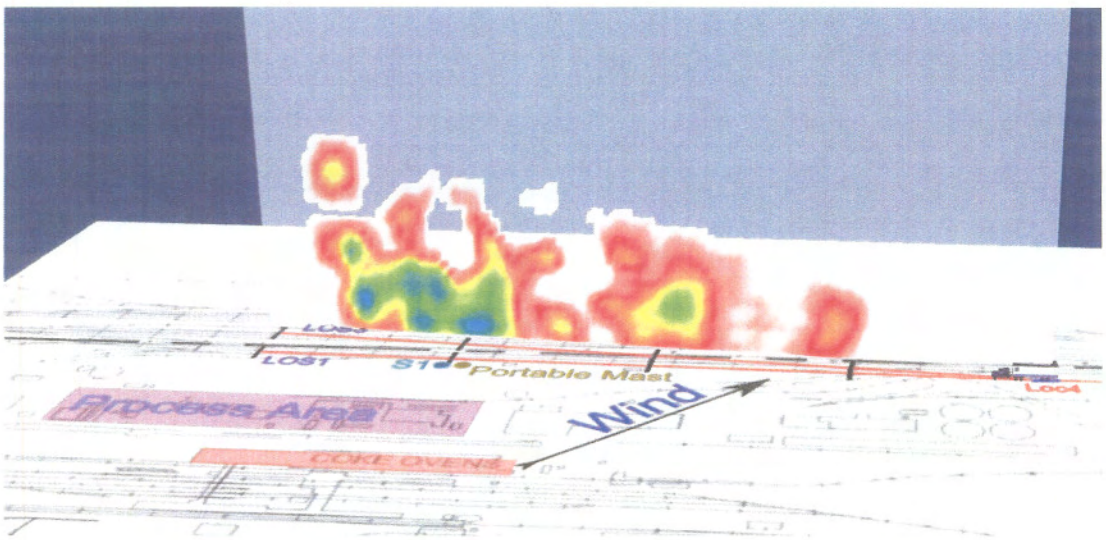

Figure 2.4a2 Visualisation of flux measurement for Scan 53 representing LOS3.

Table 2.5 Flux measurements from Loc5 on 27th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
58	Loc5/LOS1	10:41	10:56	2.9	180.1	1.05	Coke Ovens Low Elevation Angles
59	Loc5/LOS1	10:59	11:14	2.7	183.9	1.52	Coke Ovens Low Elevation Angles
60	Loc5/LOS1	11:14	11:29	2.2	198.2	1.05	Coke Ovens Low Elevation Angles
64	Loc5/LOS1	12:22	12:38	3.7	203.0	2.84	Coke Ovens Low Elevation Angles
65	Loc5/LOS1	12:39	12:54	2.4	218.2	2.56	Coke Ovens Low Elevation Angles
66	Loc5/LOS1	12:56	13:06	2.3	226.7	1.35	Coke Ovens High El. Angles
67	Loc5/LOS1	13:06	13:33	2.5	211.5	4.18	Coke Ovens All Elevation Angles
69	Loc5/LOS1	13:53	14:20	3.0	248.9	1.86	Coke Ovens All Elevation Angles
70	Loc5/LOS2	14:28	14:47	2.6	230.2	3.45	Coke Ovens & East of Process
71	Loc5/LOS2	14:47	15:05	3.4	221.5	4.54	Coke Ovens & East of Process
72	Loc5/LOS2	15:06	15:24	3.9	219.6	6.30	Coke Ovens & East of Process
73	Loc5/LOS3	15:36	15:51	4.2	218.8	3.21	Coke Ovens & Process
74	Loc5/LOS3	15:53	16:16	4.4	222.0	3.19	Coke Ovens & Process
75	Loc5/LOS3	16:23	16:49	3.8	235.6	4.88	Coke Ovens & Process
76	Loc5/LOS4	16:55	17:05	4.0	220.6	0.34	Downwind of Flare
78	Loc5/LOS4	17:31	17:41	4.3	226.7	0.87	Downwind of Flare
79	Loc5/LOS5	17:42	17:52	3.7	229.1	< 0.3	Upwind of Flare
80	Loc5/LOS6	17:54	18:04	3.7	219.6	< 0.3	Background
81	Loc5/LOS6	18:05	18:15	4.0	225.2	< 0.3	Background
82	Loc5/LOS3	18:21	18:38	2.9	225.0	5.03	Coke Ovens & Process

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

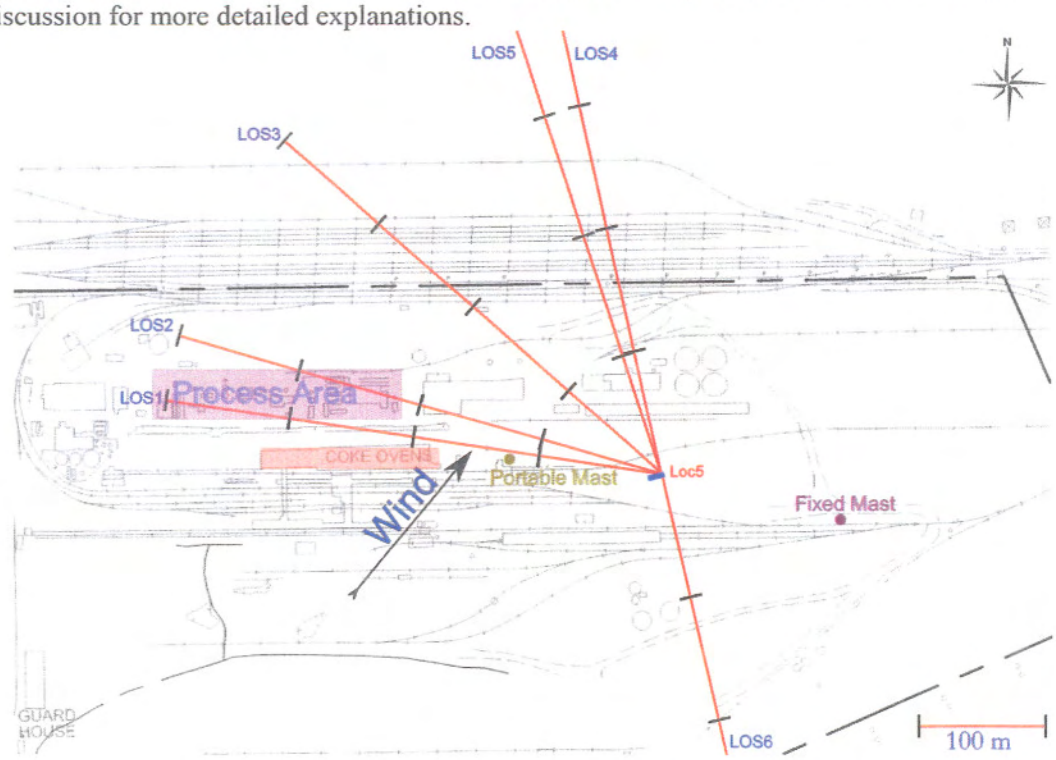

Figure 2.5 Measurement configuration for location Loc5 on 27th of May.

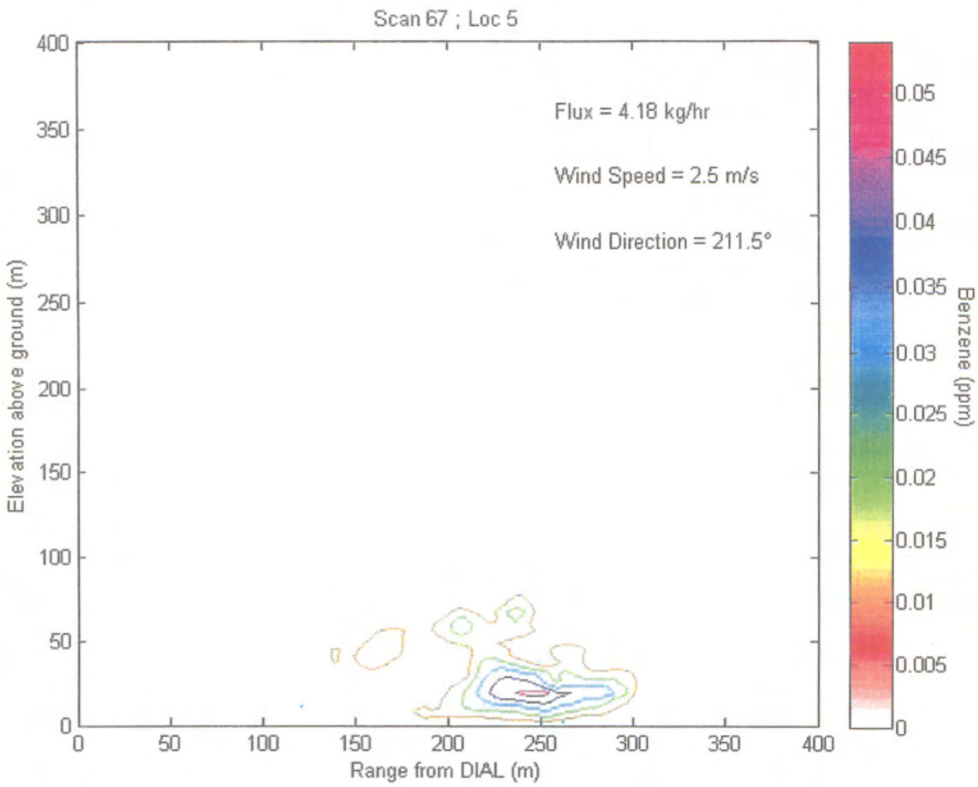

Figure 2.5a1 Contour plot of concentration profile for Scan 67 representing LOS1.

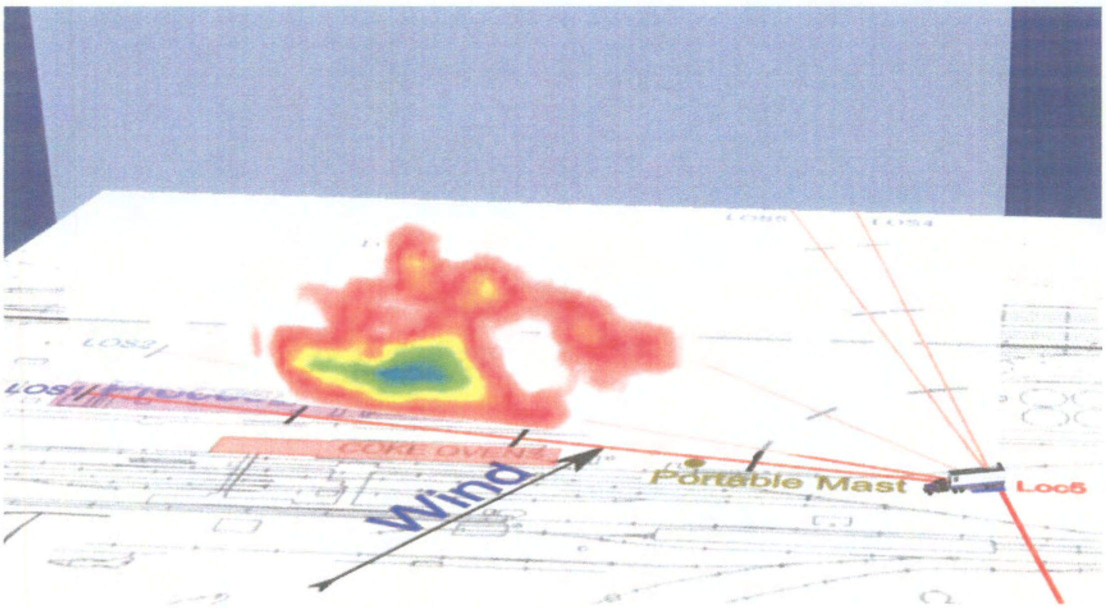

Figure 2.5a2 Visualisation of flux measurement for Scan 67 representing LOS1.

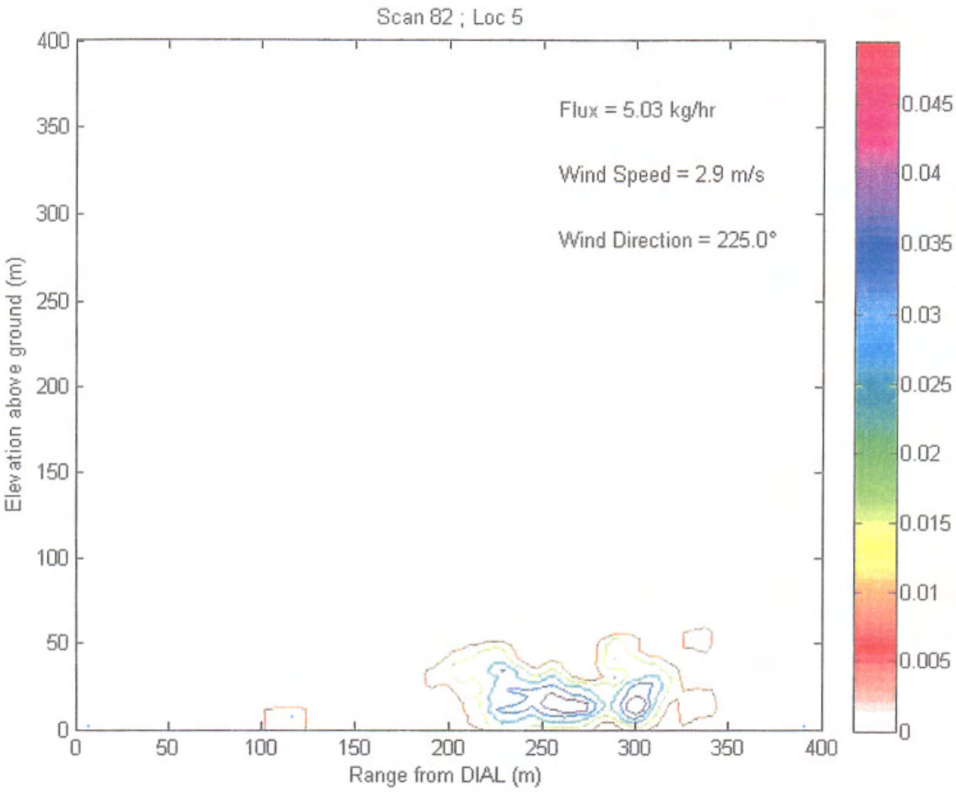

Figure 2.5b1 Contour plot of concentration profile for Scan 82 representing LOS3.

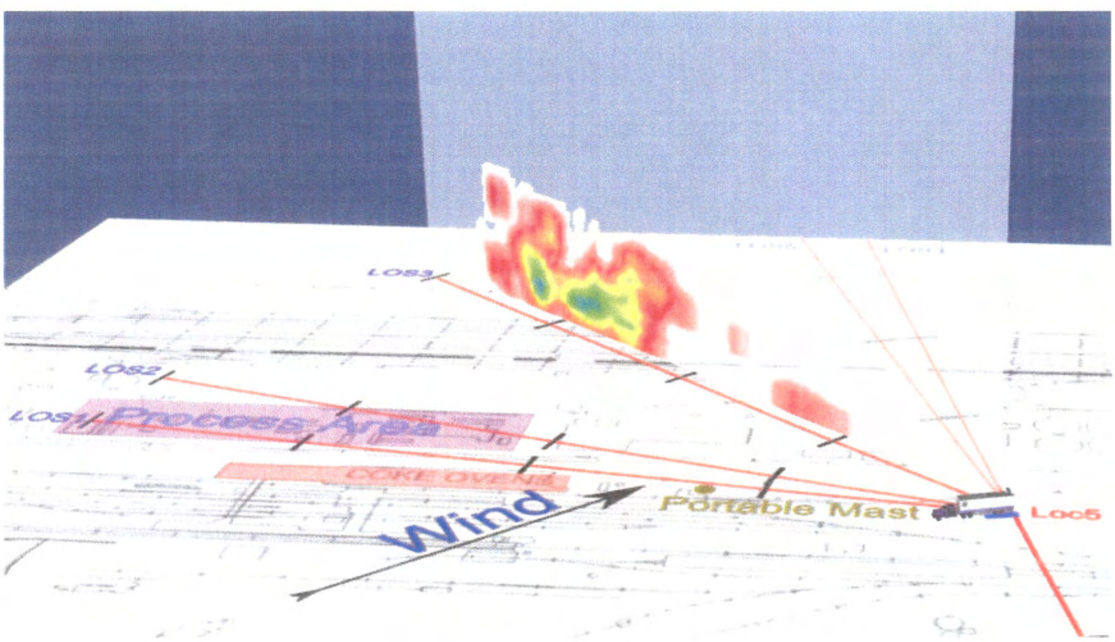

Figure 2.5b2 Visualisation of flux measurement for Scan 82 representing LOS3.

Table 2.6 Flux measurements from Loc5 on 28th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
87	Loc5/LOS1	10:22	10:34	2.5	42.0	2.70	North & East of Process
88	Loc5/LOS1	10:35	10:54	2.2	45.2	3.02	North & East of Process
89	Loc5/LOS1	10:54	11:13	1.7	28.8	3.75	North & East of Process
90	Loc5/LOS1	11:13	11:31	2.2	28.2	4.80	North & East of Process
91	Loc5/LOS1	11:34	11:40	2.3	11.2	1.62	N of Process Localised Emission
92	Loc5/LOS1	11:41	11:48	3.1	23.6	1.35	N of Process Localised Emission
93	Loc5/LOS1	11:50	11:58	2.7	34.3	1.42	N of Process Localised Emission
95	Loc5/LOS1	12:01	12:13	2.2	41.5	1.22	N of Process Localised Emission

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

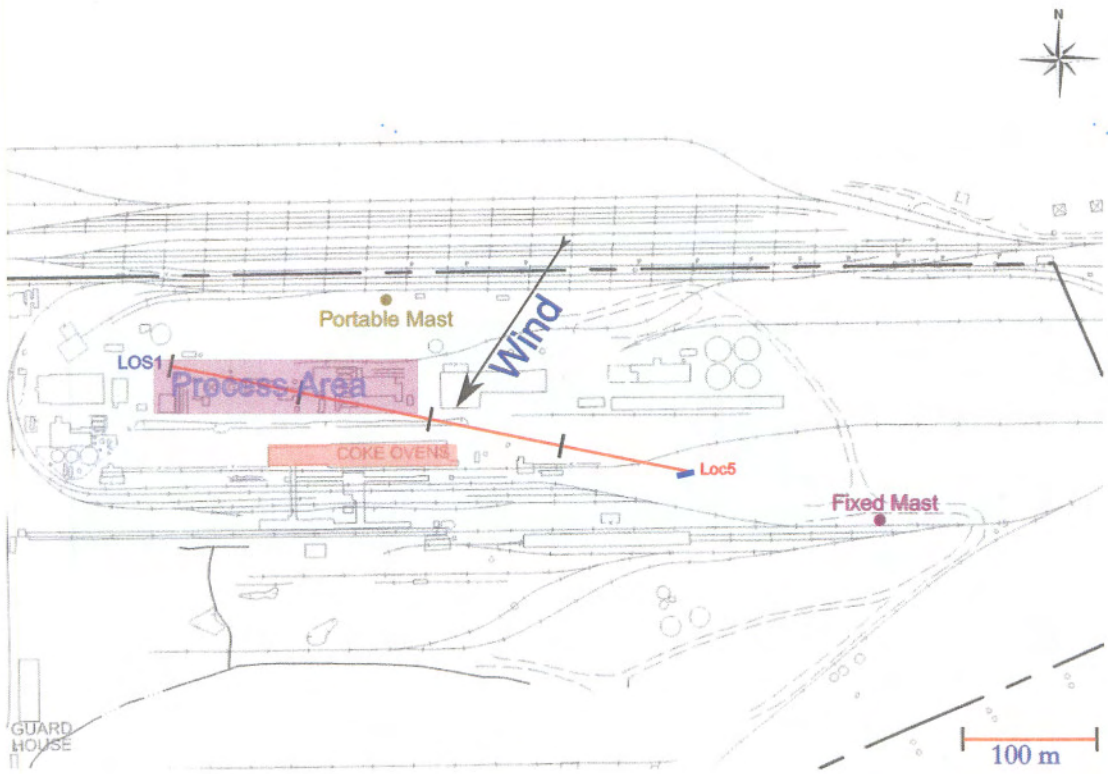

Figure 2.6 Measurement configuration for location Loc5 on 28th of May.

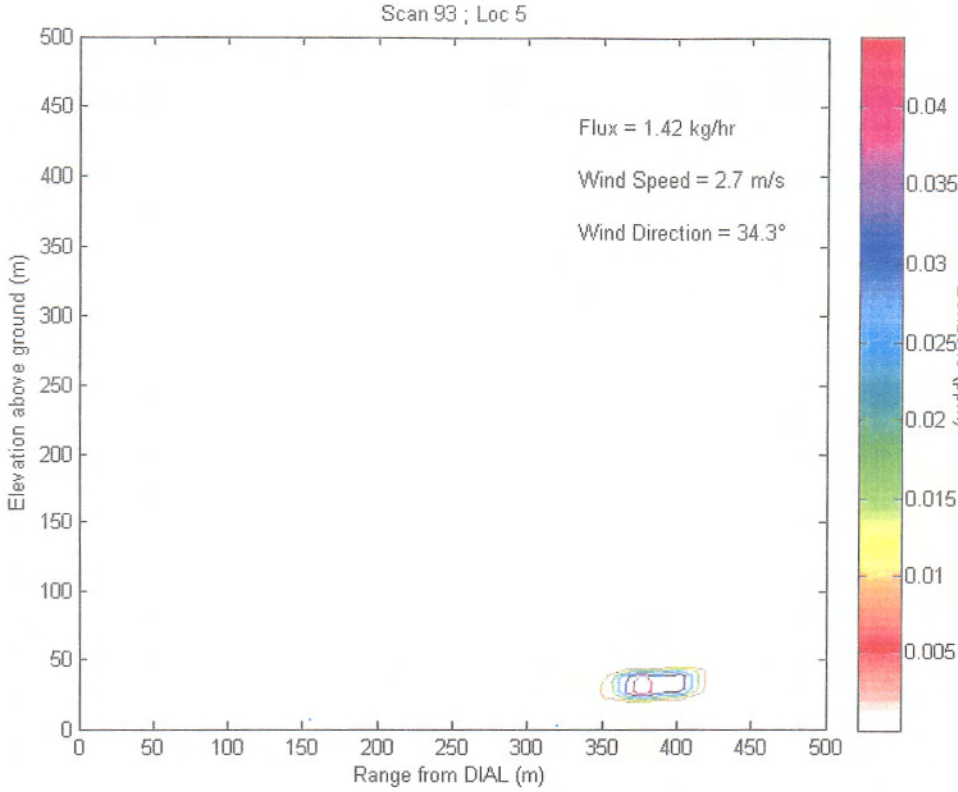

Figure 2.6a1 Contour plot of concentration profile for Scan 93 representing LOS1.

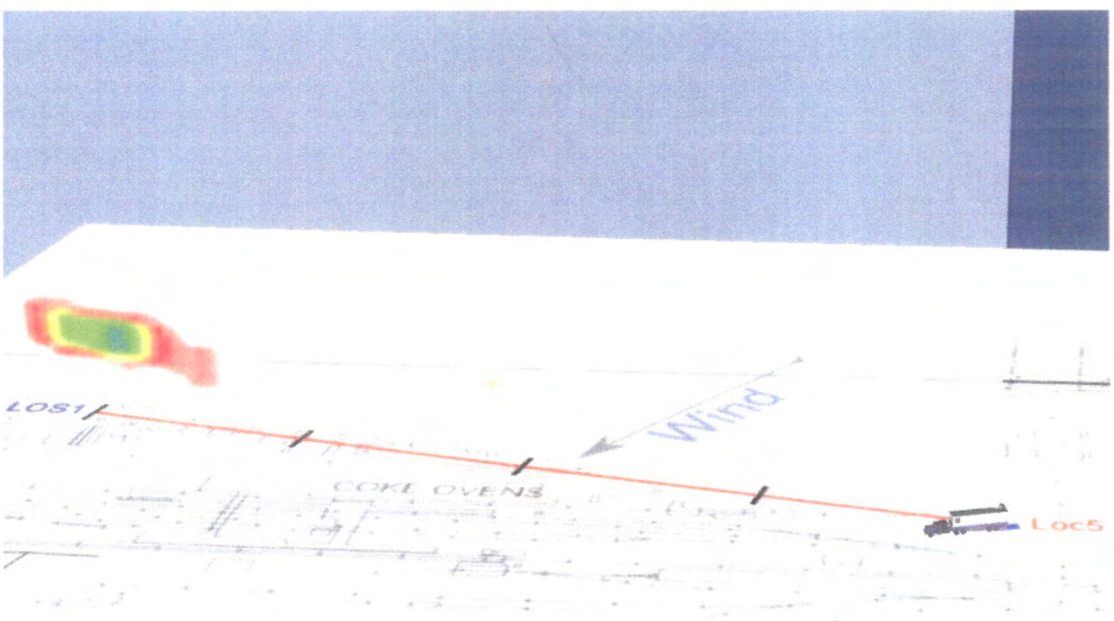

Figure 2.6a2 Visualisation of flux measurement for Scan 93 representing LOS1.

Table 2.7 Flux measurements from Loc6 on 28th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
98	Loc6/LOS1	13:09	13:27	3.6	2.3	5.53	Process Area
99	Loc6/LOS1	13:34	13:53	2.6	10.3	7.37	Process Area
100	Loc6/LOS1	13:53	14:11	1.4	40.9	6.82	Process Area

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

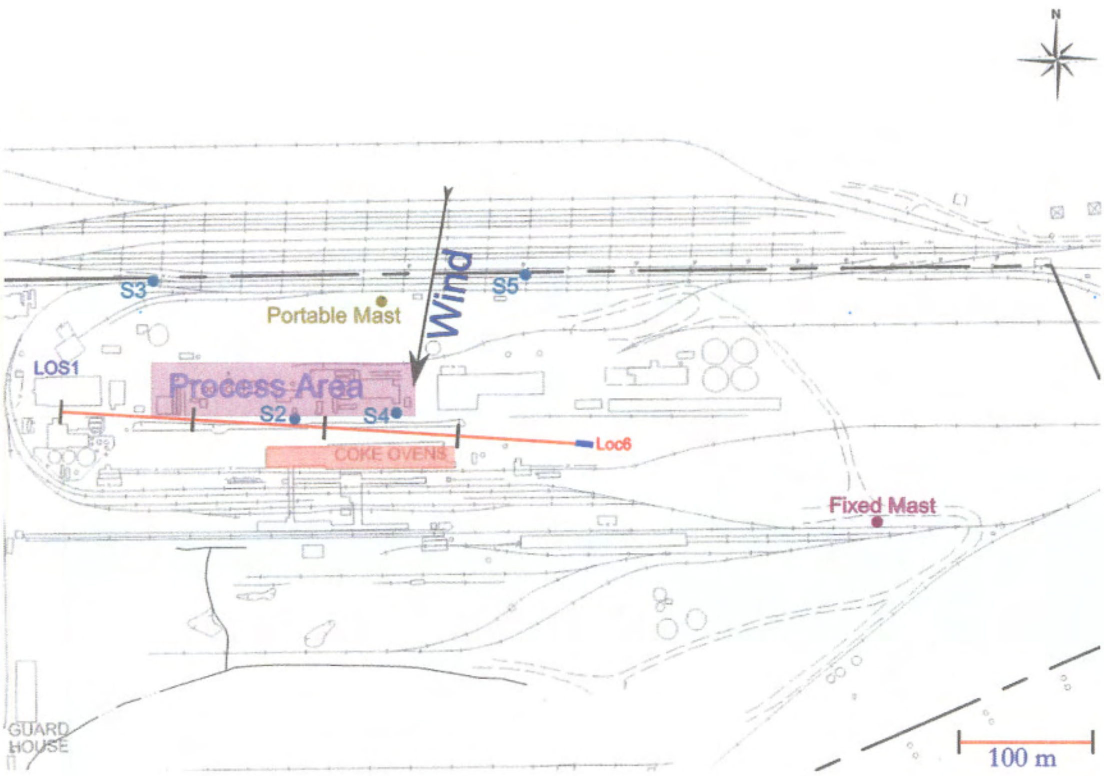

Figure 2.7 Measurement configuration for location Loc6 on 28th of May.

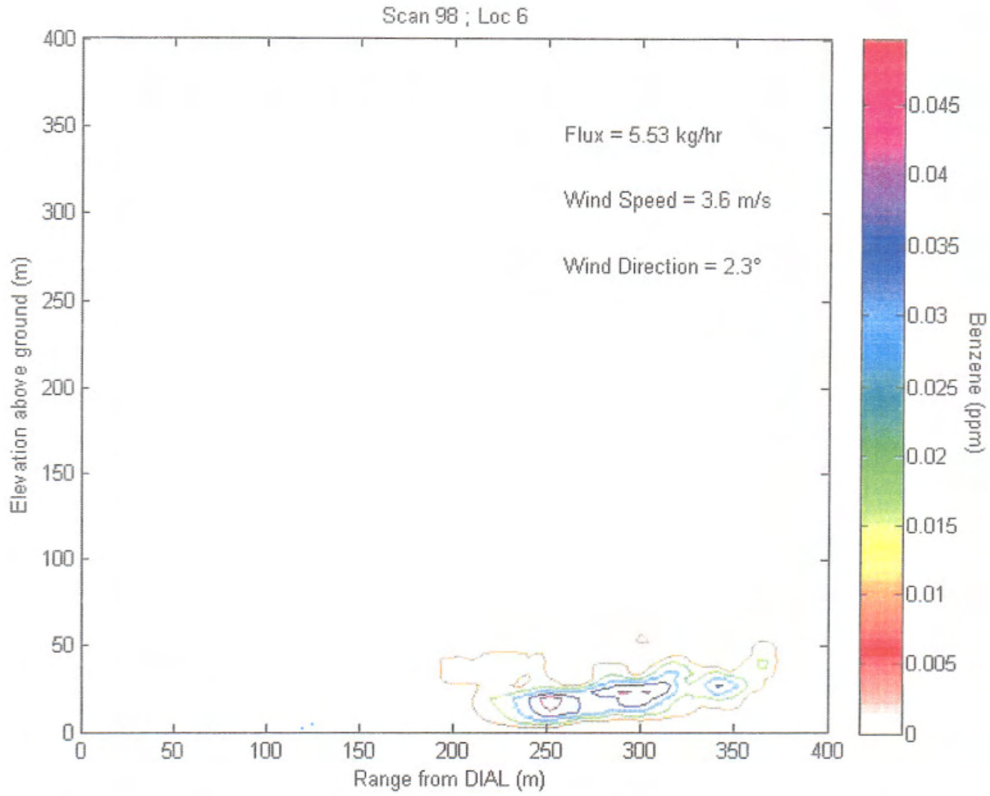

Figure 2.7a1 Contour plot of concentration profile for Scan 98 representing LOS1.

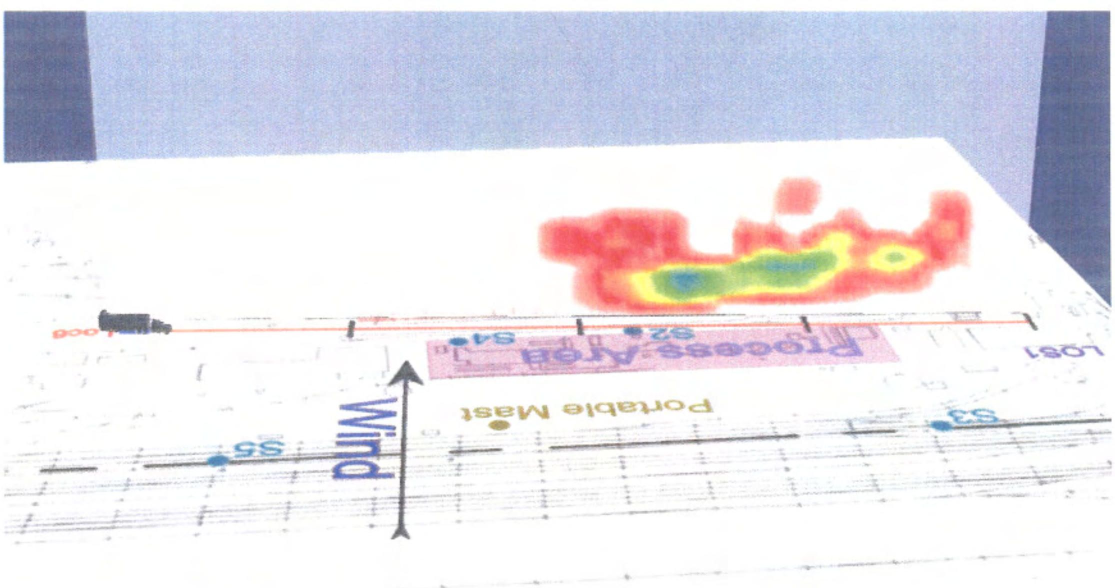

Figure 2.7a2 Visualisation of flux measurement for Scan 98 representing LOS1.

Table 2.8 Flux measurements from Loc7 on 28th of May.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes (*)
				m/s	Degrees	kg/hr	
102	Loc7/LOS1	15:01	15:12	3.0	9.3	7.45	Ovens & Process Low El. Angles
103	Loc7/LOS1	15:17	15:31	3.7	2.8	6.49	Ovens & Process Low El. Angles
105	Loc7/LOS1	15:35	15:49	3.6	359.5	7.88	Ovens & Process Low El. Angles
106	Loc7/LOS1	15:49	16:02	3.8	358.3	6.61	Ovens & Process Low El. Angles
107	Loc7/LOS1	16:03	16:18	3.5	359.5	6.32	Ovens & Process Low El. Angles
108	Loc7/LOS1	16:18	16:25	3.7	0.5	2.95	Ovens & Process High El. Angles
109	Loc7/LOS1	16:26	16:29	4.0	357.1	< 0.3	Further Higher Elevation Angles
110	Loc7/LOS1	16:31	16:41	4.1	354.4	9.47	Ovens & Process All El. Angles

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

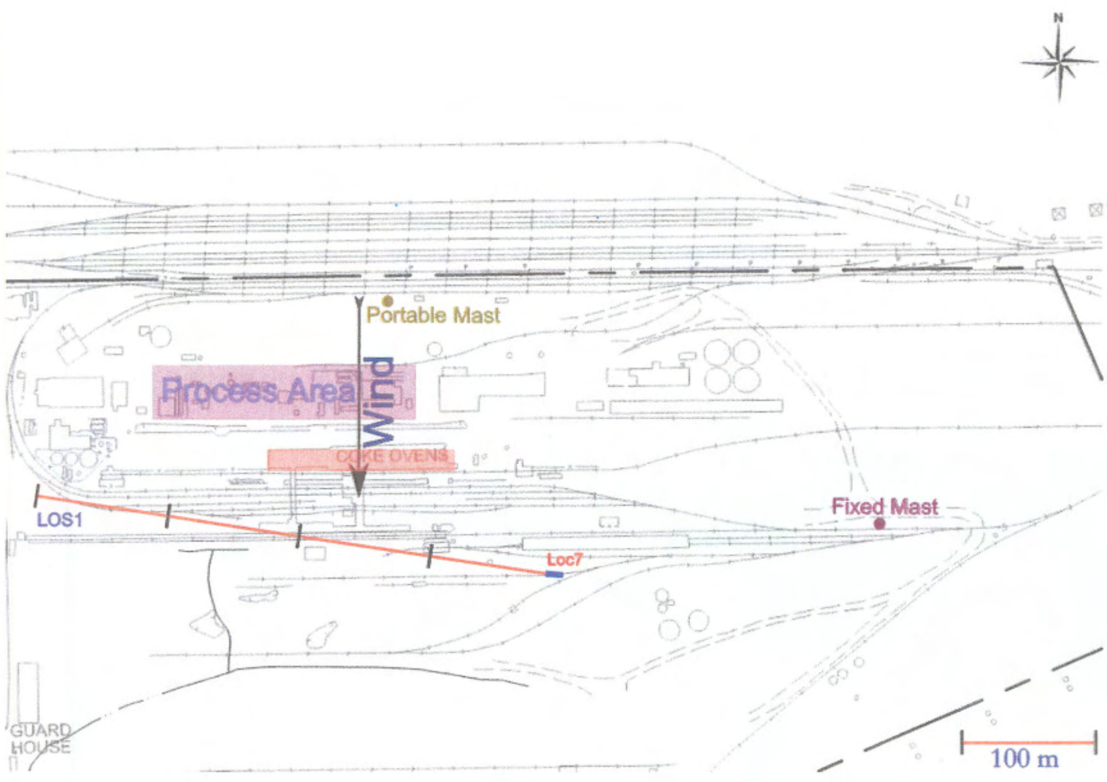

Figure 2.8 Measurement configuration for location Loc7 on 28th of May.

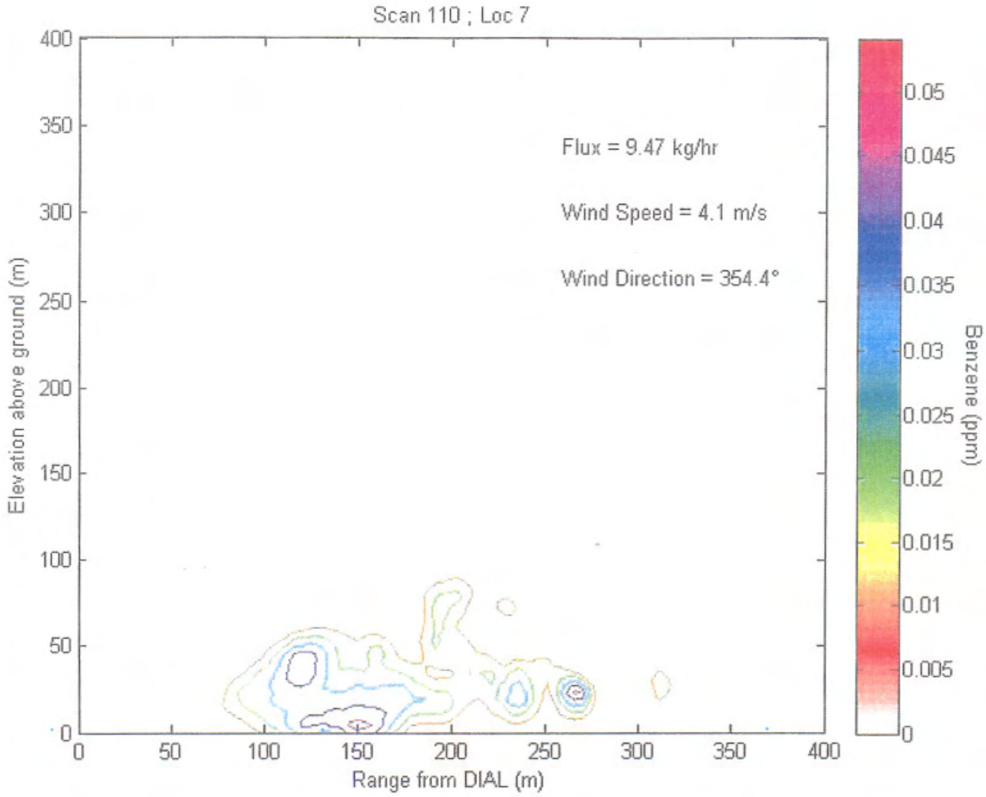

Figure 2.8a1 Contour plot of concentration profile for Scan 110 representing LOS1.

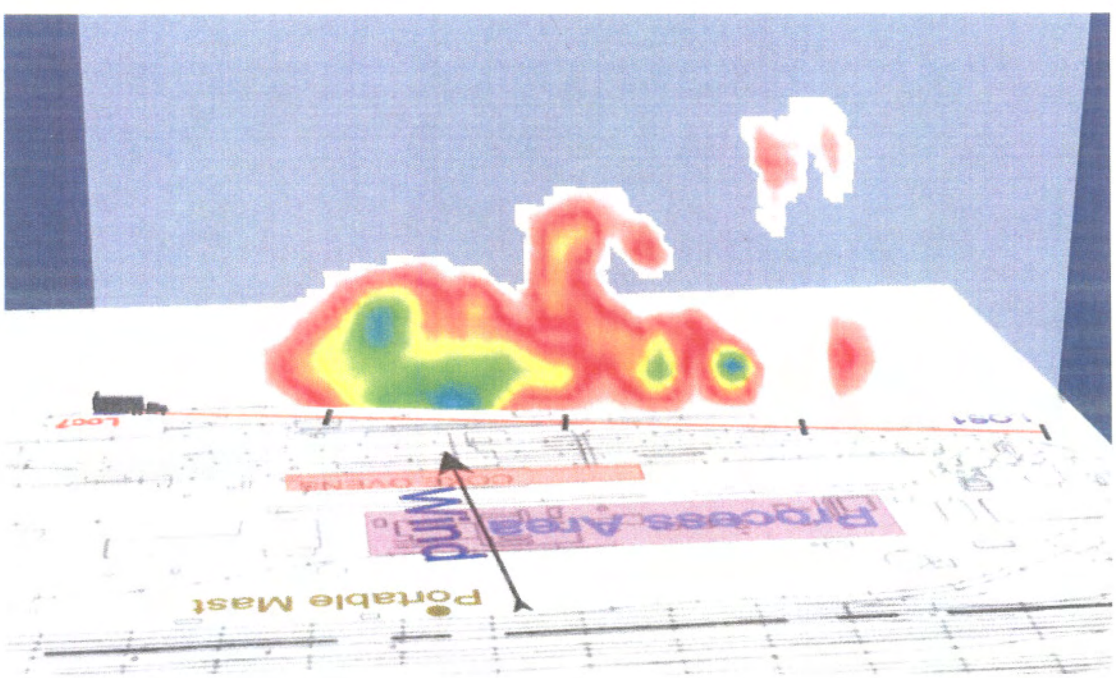

Figure 2.8a2 Visualisation of flux measurement for Scan 110 representing LOS1.

Table 2.9 Summary of benzene flux measurements. For each location and LOS the average flux and standard deviation (when more than one scan is available) are reported.

Date	Location/ LOS	Notes (*)	Average Flux kg/hr	Standard Deviation kg/hr
25-May	Loc1/LOS1	Coke Ovens & Mainly East of Process	3.2	1.0
25-May	Loc1/LOS2	Upwind	0.2	
25-May	Loc1/LOS2	Mainly Coke Ovens	3.7	
25-May	Loc2/LOS1	West Part of Coke Ovens	1.0	
25-May	Loc2/LOS1	East Part of Coke Ovens	2.8	1.1
25-May	Loc2/LOS2	Coke Ovens & Process (high uncertainty)	6.4	
25-May	Loc2/LOS3	Coke Ovens & East of Process	3.8	0.3
25-May	Loc2/LOS3	Coke Ovens Localised Emission	1.0	0.0
26-May	Loc3/LOS1	Coke Ovens & Process (1)	10.3	1.2
26-May	Loc3/LOS1	Ovens & Process High El. Angle	0.7	
26-May	Loc3/LOS2	Stack Plume	0.1	0.1
26-May	Loc3/LOS1	Coke Ovens & Process (2)	14.2	1.5
26-May	Loc3/LOS3	Upwind or Near Field Plume	1.8	0.1
26-May	Loc4/LOS1	Coke Ovens & Process	8.1	0.0
26-May	Loc4/LOS2	Background	-0.3	0.6
26-May	Loc4/LOS3	Coke Ovens & Process	10.6	1.2
27-May	Loc5/LOS1	Coke Ovens Low Elevation Angles	1.8	0.8
27-May	Loc5/LOS1	Coke Ovens High El. Angles	1.4	
27-May	Loc5/LOS1	Coke Ovens All Elevation Angles	3.0	1.6
27-May	Loc5/LOS2	Coke Ovens & East of Process	4.8	1.4
27-May	Loc5/LOS3	Coke Ovens & Process	4.1	1.0
27-May	Loc5/LOS4	Downwind of Flare	0.6	0.4
27-May	Loc5/LOS5	Upwind of Flare	0.0	
27-May	Loc5/LOS6	Background	0.0	0.2
28-May	Loc5/LOS1	North & East of Process	3.6	0.9
28-May	Loc5/LOS1	N of Process Localised Emission	1.4	0.2
28-May	Loc6/LOS1	Process Area	6.6	0.9
28-May	Loc7/LOS1	Ovens & Process Low El. Angles	6.9	0.7
28-May	Loc7/LOS1	Ovens & Process High El. Angles	3.0	
28-May	Loc7/LOS1	Ovens & Process All El. Angles (Scan 110)	9.5	

(*) The Notes are only indicative of the area measured in a specific LOS. Refer to the results discussion for more detailed explanations.

The calculations of the benzene emission flux from the different locations are described in the following sections.

1.3 MEASUREMENTS FROM LOC1 ON THE 25TH MAY

DIAL measurements were made the 25th from Loc1 with a variable wind direction (mainly from SW, see Figure 2.1) and are summarized in Table 2.1.

For scans from LOS1 with an analysis range of about 350 m from DIAL, the emission from the Coke Ovens and the Process area is spatially separated. Figures 2.1a1 and a2 show a visual representation of the emissions in Scan 3 where the plume in the 150 - 200 m region is from the Coke Ovens while the emission in the 250 - 350 m region is mainly from the east part of the Process area since the wind is from SW. For scans from LOS1 and westerly wind the emission flux should also include the emission from west of Process area. The average emission flux is 3.2 kg/hr, see Table 2.9, but it is important to note that the lowest elevation angle that was possible to use for LOS1 was 4.5 degree. As a consequence, if there is any low elevation emission this would not be detected, see Figure 2.1a1. Therefore, it is slightly debateable whether these scans represent all of the emission or not, as some low elevation emissions were observed from the process area in scans such as Scan 42.

Scan 9 from LOS2 with west wind is a background measurement showing no emission arising upwind of the plant.

Scan 10 from LOS2 with NW wind and an analysis range of 100 - 300 m from DIAL gave an emission flux of 3.7 kg/hr from the Coke Ovens. Figures 2.1b1 and b2 show a visual representation of the emission in Scan 10, where it is possible to notice that lower elevation emission has been detected compared with the Scans from LOS1 as in Figures 2.1a1 and a2. This could be the reason why the emission flux in Scan 10 from the Coke Ovens is higher than the average emission flux from LOS1 that includes both Coke Ovens and Process area.

1.4 MEASUREMENTS FROM LOC2 ON THE 25TH MAY

DIAL measurements were carried out the 25th from Loc2 with a variable wind direction (mainly from north, see Figure 2.2) and are summarized in Table 2.2.

Scan 12 from LOS1 with south wind gave an emission flux of 1.0 kg/hr from the west part of the Coke Ovens. Scans 15, 16 and 17 from LOS1 and northerly wind gave an average emission flux of 2.8 kg/hr, see Table 2.9, mainly from the east part of the Coke Ovens. Figures 2.2a1 and a2 show a visual representation of the emissions in Scans 17. A total emission of approximately 3.8 ± 1.1 kg/hr can be estimated for the Coke Ovens by adding the flux from Scan 12 to the average flux measured from the other scans from LOS1.

Scans 18, 19, 20 and 24 from LOS3 with northerly wind and an analysis range of 100 - 250 m from DIAL give an emission flux of 3.8 kg/hr from the Coke Ovens and east of Process area. The reported flux values therefore don't include any potential emission from the far west of the Process area This value compares well with emission flux from the Coke Ovens estimated from Loc2/LOS1 and with the Scan 10 measurement from Loc1/LOS2.

A localized emission plume was observed from the above scans from LOS3 at the higher elevation angles. Scans 21, 22 and 23 were carried out to specifically look at this plume by scanning only at the elevation angles where the plume was observed, Figures 2.2b1 and b2 show a visual representation of the emission in Scans 23. The average emission flux of this localized plume is 1.0 kg/hr, see Table 2.9.

Scan 13 from LOS2 with west wind is a measurement of the Coke Ovens and the Process area. The emission flux of 6.4 kg/hr is higher of the previous measurements of only the Coke Ovens indicating that some of the emission is coming from the Process area. During the eighteen minutes scan time the wind moved from south to north and the wind rose from Loc2, Figure A 3.2, shows that the wind wasn't actually coming from a westerly direction for long. Consequently, the uncertainty on this measurement is high and it is questionable if the scan represents the whole site emission or not, or rather if it does it should be given a low weighting.

1.5 MEASUREMENTS FROM LOC3 ON THE 26TH MAY

DIAL measurements were carried out the 26th from Loc3 with SW wind, see Figure 2.3, and are summarized in Table 2.3. Scans 27, 28 and 29 from LOS1 gave an average emission flux of 10.3 kg/hr, see Table 2.9, from the Coke Ovens and Process area. Figures 2.3a1 and a2 show a visual representation of the emissions in Scan 27 where the plume in the 100 - 200 m region from DIAL is from the Coke Ovens while the emission in the 200 - 350 m region is from the Process area. Scan 30 is at higher elevation angles with respect to the previous scans from LOS1 showing still some, albeit small, emission from the Coke Ovens in a region 100 - 200 m horizontal distance from the DIAL at higher elevations. If the Coke Ovens contribution to the flux was just less than 4 kg/hr as measured on the 25th, the emission from the Process area can then be determined as approximately 6 kg/hr.

Scans 40, 41 and 42 from LOS1 coincide with a quench process in the Coke ovens. The average emission flux is 14.5 kg/hr, see Table 2.9, which is higher than the previous measurements from LOS1. The increased emission during this period is 3.9 ± 2.0 kg/hr calculated by subtracting the average flux measured in the morning from the emission measured during the quench. High emission were not seen in the clearly visible steam plume from the quench, therefore the increased emission may be associated to other processes happening during this period and not necessarily related to the quench itself. Figures 2.3b1 and b2 show a visual representation of the emissions in Scan 42. It is clear by comparing Figures 2.3a2 and 2.3b2 that the emission at less than 200 m range apparently arising from the Coke Ovens is very similar. On the other hand, the benzene concentration from the Process area, in particular in the 250 - 300 m range from DIAL region is higher in Figure 2.3b2 with respect to Figure 2.3a2.

Scans from LOS3 with a wind almost parallel to the LOS could be an upwind measurement for LOS1 (i.e. a measurement of the emission coming from east of LOS3) or a measurement of the emission coming from west of LOS3, i.e. from the Coke Ovens. It mainly depends on the local wind behaviour. The average emission flux is 1.8 kg/hr (see Table 2.9) and Figures 2.3c1 and c2 show a visual representation of the emissions in Scan 43. The plume is wide and high in the 100 - 200 m region from DIAL and most likely it is associated to an emission from the east part of the Coke Ovens crossing LOS3.

Scans from LOS2 are measurements carried out to specifically observe the stack plume, by scanning only at high elevation angles where the plume was visible. The wind was not ideal since it was almost parallel to LOS2, nonetheless the stack plume showed observable benzene concentrations, and therefore no emission.

Between 12:00 and 12:50 a series of measurements were made along a fixed measurement path alongside the Differential Optical Absorption Spectroscopy (DOAS) system. For these measurements the DIAL was not scanned, and a flux was therefore not determined. The DIAL elevation was about 2 m higher than the DOAS. Figure 2.9 shows the results of the peak concentration measured from DIAL and DOAS, plotted as a time series of average concentrations over a 180 m measurement path. As can be seen, the agreement between the DIAL and the DOAS data is good and the two techniques see similar trends. The DIAL measurement path was approximately 2-4 metres higher than the DOAS path.

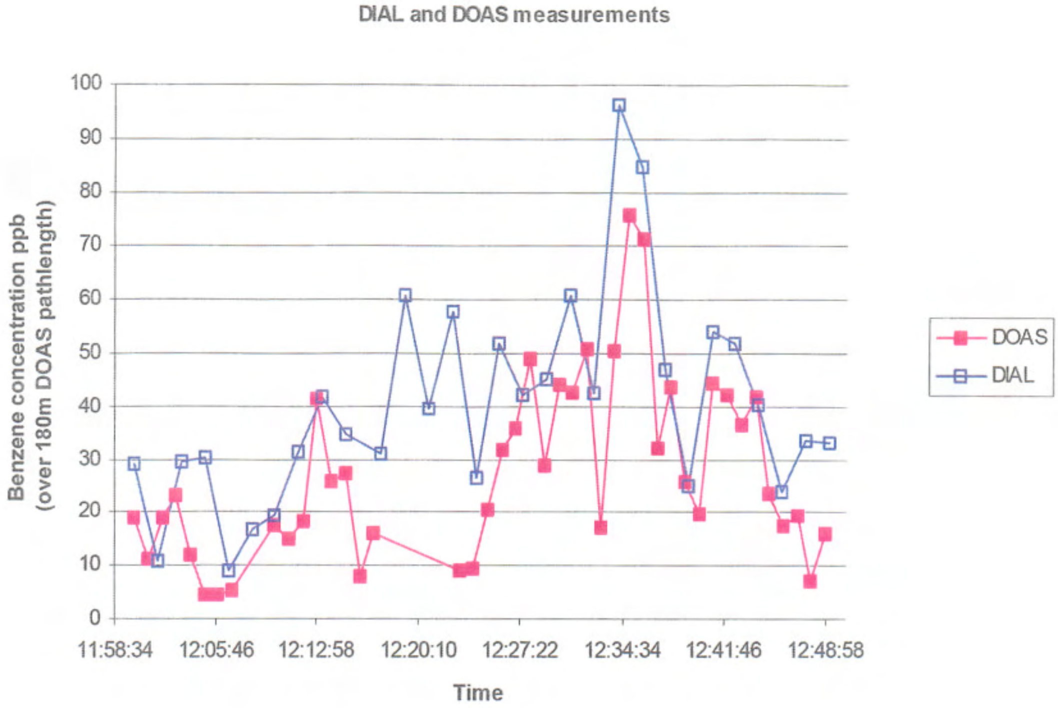

Figure 2.9 DIAL and DOAS measurements comparison.

1.6 MEASUREMENTS FROM LOC4 ON THE 26TH MAY

DIAL measurements were made on the 26th from Loc4 with a SW wind, see Figure 2.4, and are summarized in Table 2.4. Scans from LOS1 and LOS3 gave average emission fluxes of 8.1 kg/hr and 10.6 kg/hr respectively, from the Coke Ovens and Process area (see Table 2.9). Both values compares well with the emission from the Coke Ovens and Process area obtained from Loc3/LOS1 in the morning. Figures 2.4a1 and a2 show a visual representation of the emissions in Scan 53.

Scans from LOS2 are background measurements showing no emission fluxes from upwind sources.

1.7 MEASUREMENTS FROM LOC5 ON THE 27TH MAY

DIAL measurements were carried out the 27th from Loc5 with SW wind, see Figure 2.5, and are summarized in Table 2.5. Scans 58, 59, 60, 64 and 65 from LOS1 are at lower elevation angles and they gave an average emission flux of 1.8 kg/hr (see Table 2.9) from the Coke Ovens. Scan 66 at higher elevation angles only gave a flux of 1.35 kg/hr that can be added to the flux at lower elevation angles obtaining a total emission of about 3.2 ± 0.8 kg/hr for the Coke Ovens. Scans 67 and 69 at all the elevation angles gave an average emission flux of 3.0 ± 1.6 kg/hr from the Coke Ovens. These values compare well with emission flux from the Coke Ovens estimated from the measurements carried out on the 25th and 26th. Figures 2.5a1 and a2 show a visual representation of the emissions in Scan 67. The scans at lower and higher elevation angles show a high variability in the emission rate. This could be due to a real variation in the emission coming from the Coke Ovens.

LOS2 with an analysis range of up to approximately 300 m from DIAL gave an emission flux of 4.8 kg/hr, see Table 2.9, from the Coke Ovens and the Process area excluding the western part of it. The reported flux values therefore don't include potential emissions from the far west of Process area. This flux is just higher than the emission obtained from the Coke Ovens suggesting the east end of the Process area has low emission.

The measurements from LOS3 with an analysis range just less than 350 m from DIAL gave the emission flux from both the Coke Ovens and the Process area. The measured flux is 4.1 ± 1.0 kg/hr, see Table 2.9, which is lower than the emission measured from Loc3/LOS1 and Loc4/LOS1 and LOS3. Inspecting Figure 2.5 it is clear that the building located northeast of the Coke Ovens is on the path of the flux from the Coke Ovens toward LOS3. Figures 2.5b1 and b2 show a visual representation of the emissions in Scan 82 where no emission is detected in the 120 - 200 m region due to the presence of the building. Some of the emission from the Coke Ovens would pass west of the building and some would pass east of it. If some of the emission crossed LOS3 at ranges less than 100 m it would not be detected. However, only a low concentration benzene plume was seen at ranges shorter than the building, indicating that most of the plume passed to the far side of the building and therefore was captured by the DIAL. These scans may be representative of the full site.

The emission from the flare measured from LOS4 is 0.6 ± 0.4 kg/hr, see Table 2.9. It is a small value with a relatively high uncertainty but above the upwind flux from LOS5 and the background measurements from LOS6 that show no emission.

1.8 MEASUREMENTS FROM LOC5 ON THE 28TH MAY

DIAL measurements were made on the 28th from Loc5 with NE wind, see Figure 2.6, and are summarized in Table 2.6. Scans 87, 88, 89 and 90 from LOS1 gave an average emission flux of 3.6 ± 0.9 kg/hr (see Table 2.9) from the east and north part of the process area. The main emission is from the northwest corner of the process area and a localized emission was identified in the 350 - 400 m range DIAL. Scans 91, 92, 93 and 95 from LOS1 were carried out to specifically look at this plume, by scanning only at the elevation angles where the plume was observed and using a smaller stepsize. Figures 2.6a1 and a2 show a visual representation of the emission in Scan 93. The average emission flux for the localized emission is 1.4 kg/hr as reported in Table 2.9.

1.9 MEASUREMENTS FROM LOC6 ON THE 28TH MAY

DIAL measurements were carried out the 28th from Loc6 with northerly wind, see Figure 2.7, and are summarized in Table 2.7. Measurements from LOS1 are downwind of the Process area and the average emission flux is 6.6 kg/hr (see Table 2.9). This value compares well with the emission from the Process area obtained from Loc3/LOS1 in the morning and from Loc4/LOS1 and LOS3 once the emission of just less than 4 kg/hr from the Coke Ovens is subtracted. Figures 2.7a1 and a2 show a visual representation of the emission in Scan 98. The plume is detected only over the 200 m range from the DIAL confirming the west part of the

Process area as the main emission source. At the time Scan 98 was carried out, four air samples were taken and the results presented in Annex 2 agree with the DIAL measurements.

1.10 MEASUREMENTS FROM LOC7 ON THE 28TH MAY

DIAL measurements were carried out the 28th from Loc7 with northerly wind, see Figure 2.8, and are summarized in Table 2.8. Measurements from LOS1 are downwind of both the Coke Ovens and the Process area. Scans 102, 103, 105, 106 and 107 are at lower elevation angles and they gave an average emission flux of 6.9 kg/hr, see Table 2.9. Scan 108 was carried out at higher elevation angles and gave a flux of 2.95 kg/hr that can be added to the flux at lower elevation angles. This gives a total emission of about 9.9 ± 0.7 kg/hr. Scan 109 was taken at higher elevation angles with respect to Scan 108 and it shows no emission. Scan 110 was carried out covering all the elevation angles and gave an emission flux of 9.5 kg/hr consistent with the value calculated by adding Scan 108 to the average emission flux from the scans at lower elevation angles. Figures 2.8a1 and a2 show a visual representation of the emission in Scan 110.

The emission from the Coke Ovens can be estimated by subtracting the emission from Process area from Loc6/LOS1 to the emission from Loc7/LOS1. The result, 3.3 ± 1.2 kg/hr, compares well with previous measurements of the Coke Ovens emission.

1.11 CONCLUSION

The Coke Ovens and Process Area are two potential sources of emission. Due to wind conditions, most measurements carried out may have contained some component of emissions from both these sources. Measurements downwind of both Coke Ovens and the Process area or part of them are consistent with each other. The only exception is the measurements taken from Loc3/LOS1 the 26th afternoon showing higher emission flux. From the data it was possible to associate this higher emission to the Process area rather than the Coke Ovens. The data also show that the Process area (as marked in the Figures) is probably the main emission source.

As discussed in Annex 1 a single DIAL flux measurement typically has an uncertainty of between 10 - 15 % under simple wind conditions. Under complex wind conditions as likely at this site, the uncertainty for a single measurement may be higher than this, typically 20-30%. A measure of the uncertainty of the measurements may be obtained from the variability of the measurements made under the same conditions and the overall variation seen in all measurements of the same sources.

The scans that could be considered to represent the emission from the entire site are:
27, 28, 29, 40, 41, 42, 48, 49, 53, 55, 56, 73, 74, 75, 82, (102, 103, 105, 106, 107) + 108, 110.
The average flux emission from the selected scans is 9.4 ± 3.2 kg/hr. The standard deviation is about 34% of the measurement and this is an appropriate uncertainty for the conditions observed at the site. It would account for the effects of the source variability, for the DIAL measurement uncertainty and also for the influence of other variable factors such as the wind speed and direction.

ANNEX 1: DESCRIPTION OF THE DIAL TECHNIQUE

1.12 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.

1.13 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.

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

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, and are not interfered with by other atmospheric constituents.

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

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

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

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

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 of the on- and off-resonant signals respectively.

This path-integrated concentration represents the total concentration of the target species in the atmosphere along the measured line-of-sight out to the range r.
The range-resolved concentration can then be derived by differentiating the path-integrated concentration (Equation 3).

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

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

1.14 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 12 m meteorological mast with wind speed, direction, temperature and humidity measurements.

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

The following sections describe the DIAL system in more detail.

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

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

After amplification the signals from these detectors are digitised using 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 significant levels of backscattered light is present.

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

iii) Calculation of path-integrated concentration
The path-integrated concentration of the target species, out to the range r, is calculated 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 with a selectable range resolution, 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, taking into account the wind speed profile as a function of elevation.
(b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.

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

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

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

- The DIAL measurement is of concentration per unit length rather than just concentration. So the sensitivity applies for a specified pathlength – 50 metres in this case. Measurements over a shorter path would have a lower sensitivity, and would be more sensitive over a longer path length.
- Since the backscattered lidar signal varies with range, generally following a $(\text{range})^{-2}$ function, the sensitivity is also a function of range. The sensitivity values given in the 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 3.75 metres along the measurement beam, and a vertical and horizontal scan resolution which can be less than 1 metre at 100 metres. However, the actual range resolution determined by the signal averaging used, will depend on atmospheric conditions and the concentration of the measured pollutant, and may be of the order of 20-30 m.

The DIAL is able to make measurements of a wide range of compounds, including benzene and other aromatics, individual VOCs and total VOCs, see Tables 2a and 2b. NPL has the spectral expertise, access to spectral libraries and an in-house spectroscopic capability to assess the DIAL sensitivity for additional individual species.

Table A1.1 Ultraviolet capability of NPL DIAL Facility

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 A1.2 Infrared capability of NPL DIAL Facility

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

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

1.15 RELATIONSHIP BETWEEN FLUX AND CONCENTRATIONS

Where concentrations are provided as an indication of the levels observed in a measurement scan, the reported concentration is the maximum concentration seen in a cell in the measurement plane, the resolution of the planes used is equal to the DIAL system resolution and is 3.75 m, so each cell is 3.75 m square. Figure A1.2 shows how the flux is calculated: the concentration assigned to each cell is multiplied by the perpendicular wind field determined for that cell, and then the individual fluxes are summed to give the total flux through the plane. This figure shows two example plumes (the cell grids are for indication and are not to scale), one which has a small plume, and therefore a small integrated flux, and the other which has a larger plume, and therefore represents a larger emissions flux, although the peak concentration in both is similar, and indeed may even be higher in the small plume then the large plume.

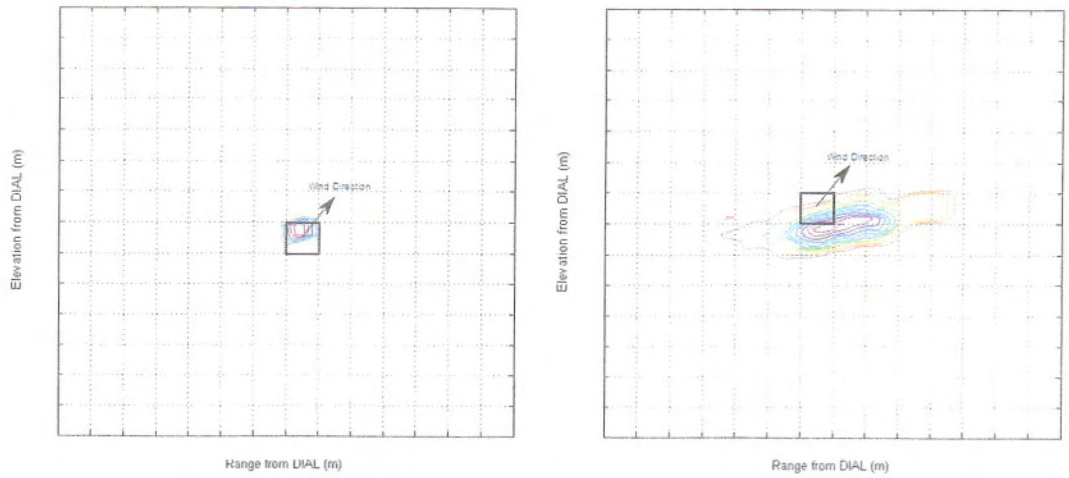

Figure A1.2 Illustration of the flux calculation approach

Figure A1.3 shows a schematic representation of two measurement plane configurations observing the same plume. One has a nearly perpendicular orientation to the plume, and the wind direction is therefore also perpendicular to the measurement plane. The other is at an angle through the plume, and therefore the wind is not normal to the plane of the measurements. If only the concentration profile were observed the left hand measurement configuration would show a larger plume (as it cuts obliquely through the plume). However, when the wind direction is taken into account, the normal component of the wind vector is used, and this therefore reduces the flux determined from this scan, resulting in the same flux being determined for both measurement orientations.

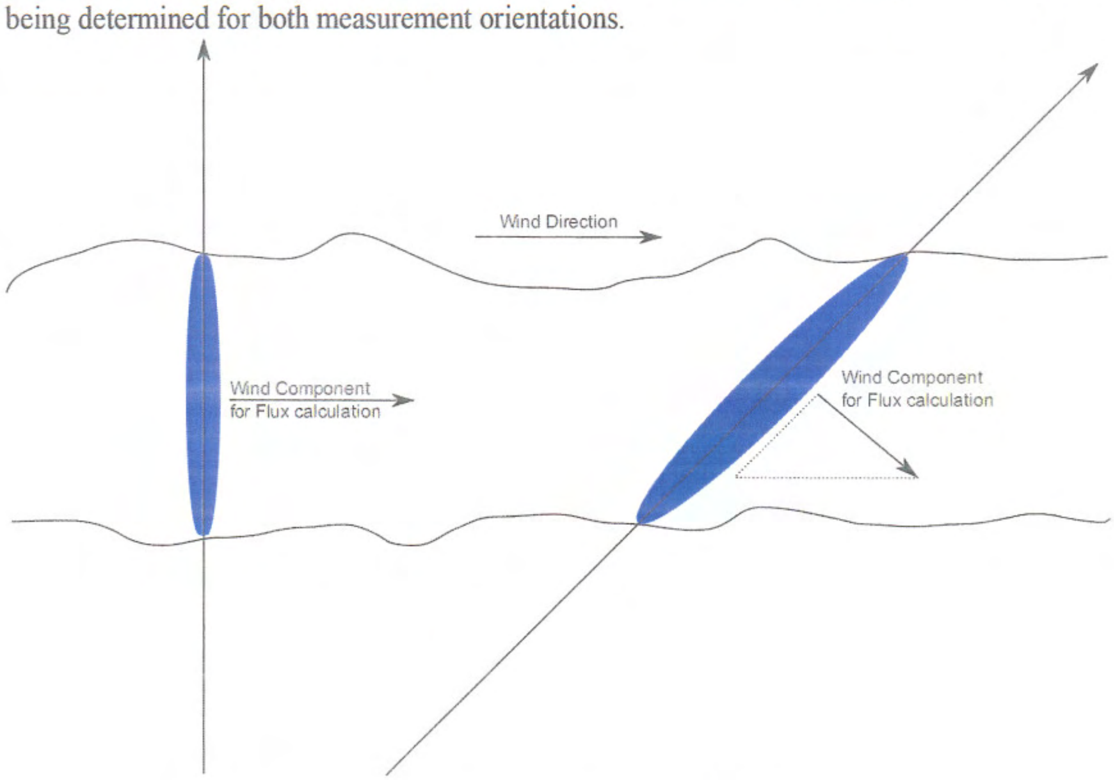

Figure A1.3 Schematic showing relationship between flux and wind direction

1.16 CALIBRATION AND VALIDATION

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

1.17 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: AIR SAMPLES

Air samples were taken while the DIAL was at Loc4 and Loc6 and the sample location is marked in Figures 2.4 and 2.7. The air samples were taken using pumped Perkin Elmer Automatic Thermal Desorption (ATD) tubes each sampling for about half an hour. The sampler tubes, carbon black (Carbopack X), contained approximately 200 milligrams to 300 milligrams of sorbent. The ATD tubes analyses were carried out by NPL's in house accredited analysis laboratory only for BTEX and the results are shown in Table A2.1.

Table A2.1 Results from pumped samples.

Tube	Location	Volume	Benzene	Toluene	Ethylbenzene	m/p-Xylene	o-Xylene	Total C4-C10 Hydrocarbons
		ml	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3	μg/m^3
CX1719-9	TRV BLK A	1217.1	1.4	<8	<8	<8	<8	<80
CX152-9	TRV BLK B	1217.1	2.4	<8	<8	<8	<8	<80
CX281-9	S1	1121.4	166.2	43.3	<8	9.7	<8	358
CX3729-9	S2	1206.4	109.9	30.7	<8	7.7	<8	237
CX1701-9	S3	1323.4	5.3	<8	<8	<8	<8	<80
CX1545	S4	1189.0	9.0	<8	<8	<8	<8	<80
CX1582	S5	1245.4	5.6	<8	<8	<8	<8	<80

The sample on location S1 was taken at 17:10 on 26th of May while the DIAL was on Loc4 as shown in Figure 2.4. The sample was downwind of the Process area and 166.2 μg/m^3 (52 ppb) of benzene was detected. This compares well with the benzene measured from Loc4/LOS1, during the comparison with the DOAS concentrations in the range 10 – 100 ppb were observed close to the tube sample location.

On 28th of May four samples were taken at about 13:10, the samples' locations are marked in Figure 2.7. Sample S3 and S5 are upwind of the site and they show very low level of benzene. Sample S4, downwind of the east part of the process area, has very low level of the benzene indicating very low emission from this part of the process area. Sample S2, located downwind of the Process area measured 109.9 μg/m^3 (34 ppb) of benzene, consistent with the DIAL measurements. DIAL scan 98, taken at a similar time to the tube sample, showed concentrations in the same region as S2, of 10 – 35 ppb.

ANNEX 3: QA CHECKS

Cell scans were performed at the beginning of the day and the QA limits for the Pyro ratios are defined from these scans. The users keep the Pyro ratio under observation during the day and note its value at the beginning and at the end of each scan. If during the day the Pyro ratio gets close to the upper or lower limit, the system is tuned and a new cell scan is carried out. Table A3.1 shows the QA limits for the Pyro ratio obtained during the four days campaign. Note that the acceptable range limits change depending on the laser energy available and this can drift during the course of a day as the laser ages. Hence the changing limits seen on the 27th and the 28th of May.

Table A3.1 Daily benzene cell scans to define the QA limits for Pyro ratio.

Date	Acceptable Pyro Ratio Range Limits	
	Lower	Upper
25-May	0.27	0.40
26-May	0.28	0.41
27-May	0.39	0.58
27-May	0.33	0.50
27-May	0.38	0.58
28-May	0.27	0.41
28-May	0.34	0.50

As further QA check, a cell measurement is carried out at least three times during the day. A cell with a known concentration of benzene is inserted in the beam path. The acceptable column due to the cell ranges from 0.08 to 0.12 ppm. If during the day the column from a cell measurement gets close to the upper or lower limit, like in Scan 61, the system is tuned and a new cell measurement is carried out. A cell scan is also performed in order to obtain the new Pyro ratio limits. Table A3.2 presents the cell column values measured during the campaign.

Table A3.2 Daily cell measurements results.

Scan ID	Date	Cell Column
		ppm
6	25-May	0.10
11	25-May	0.09
25	25-May	0.08
26	26-May	0.11
44	26-May	0.11
57	26-May	0.08
61	27-May	0.07
62	27-May	0.08
63	27-May	0.11
77	27-May	0.08
83	27-May	0.08
85	28-May	0.12
86	28-May	0.11
101	28-May	0.11
111	28-May	0.12

ANNEX 4: METEOROLOGICAL MEASUREMENTS

Wind data were collected from a fixed mast located just outside the E side of the site. The location is shown in Figure 1.2. Figure A3.1 shows a picture of the meteorological mast. Wind speed and direction measurements were collected at two elevations, 11 m and 3 m.

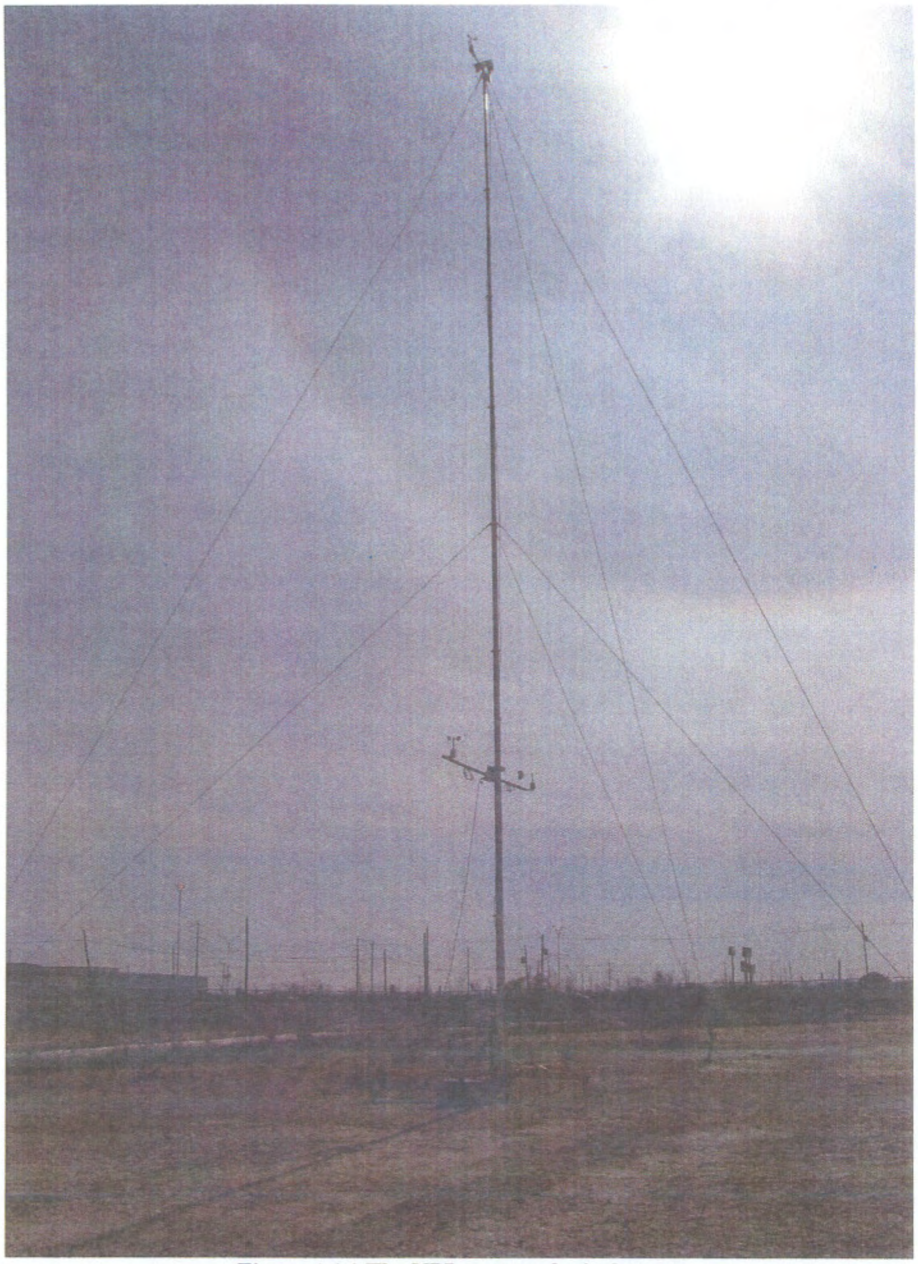

Figure A4.1 The NPL meteorological mast.

The following figures present the average wind roses for the measurement periods on each location from the 25th to the 28th May 2010.

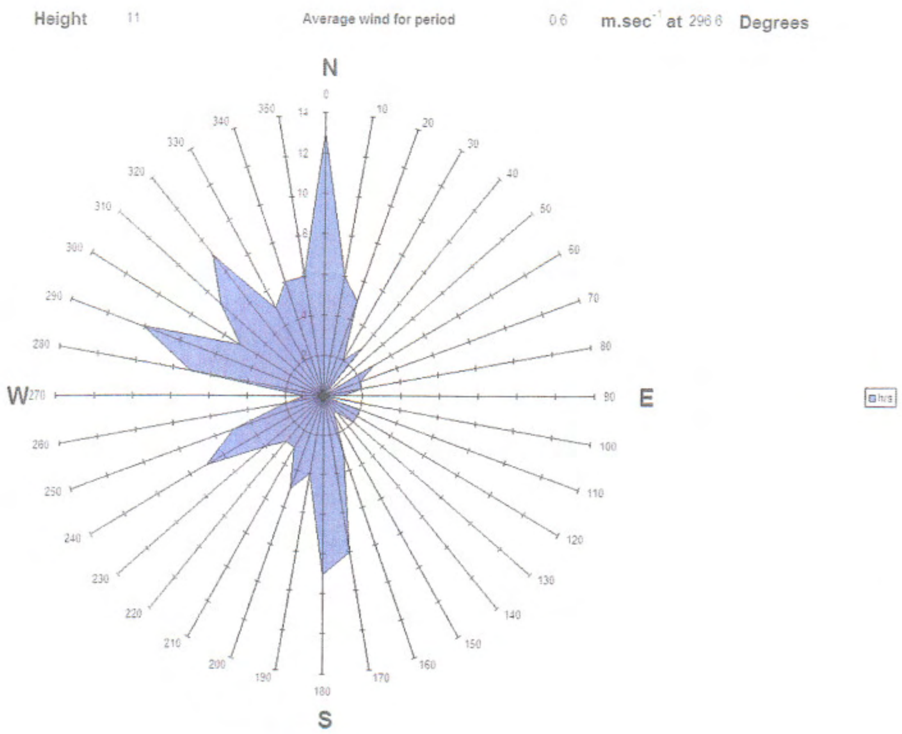

Figure A4.2 Wind rose for 25th May during measurements from Loc1, 10:53 - 13:44

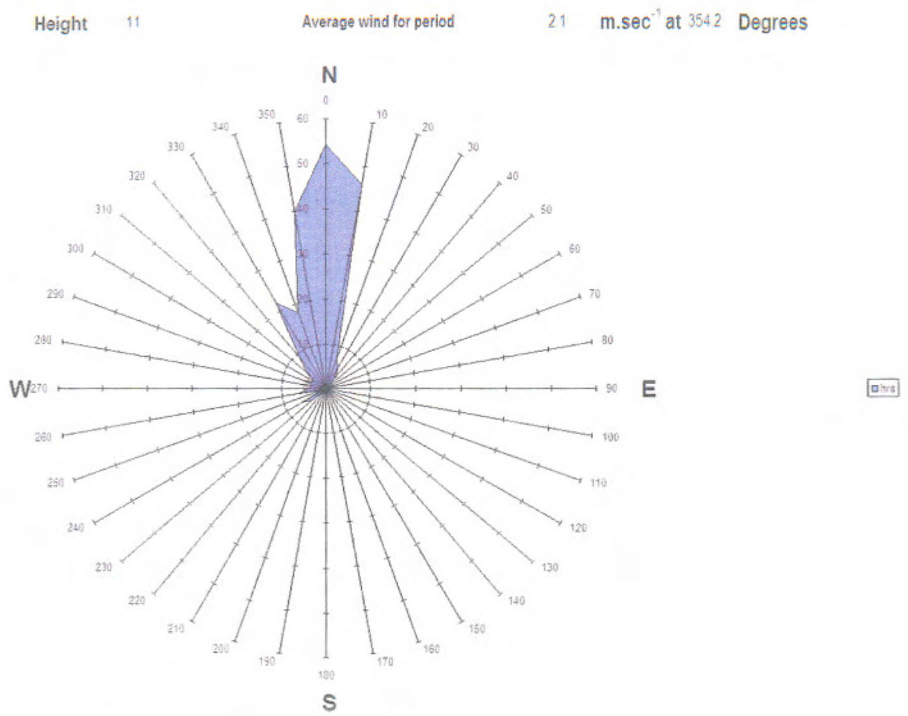

Figure A3.3 Wind rose for 25th May during measurements from Loc2, 14:20 - 19:11

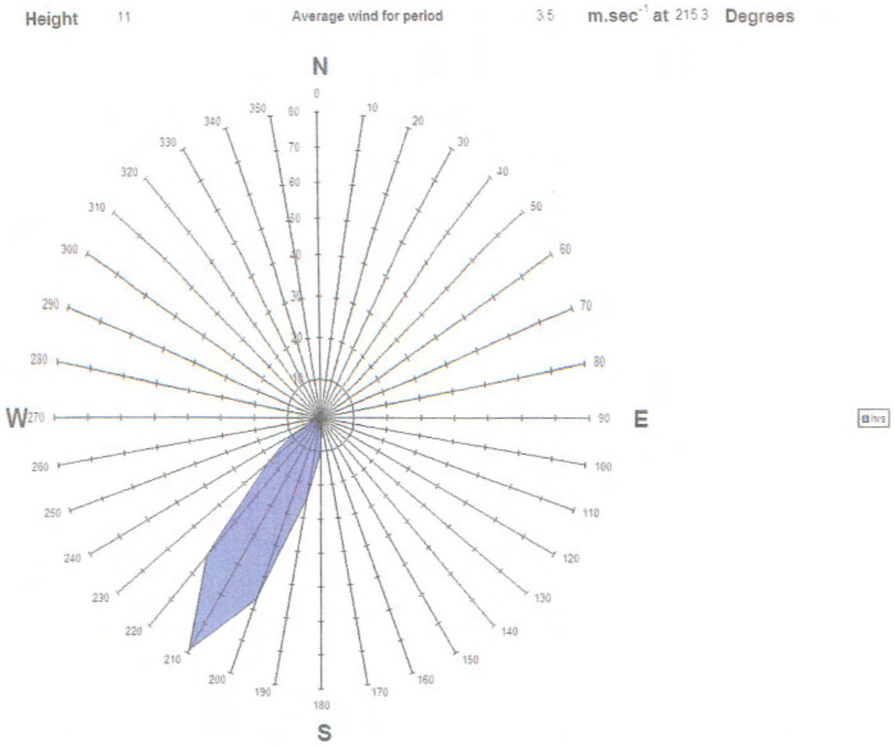

Figure A4.4 Wind rose for 26th May during measurements from Loc3, 11:12 - 15:55

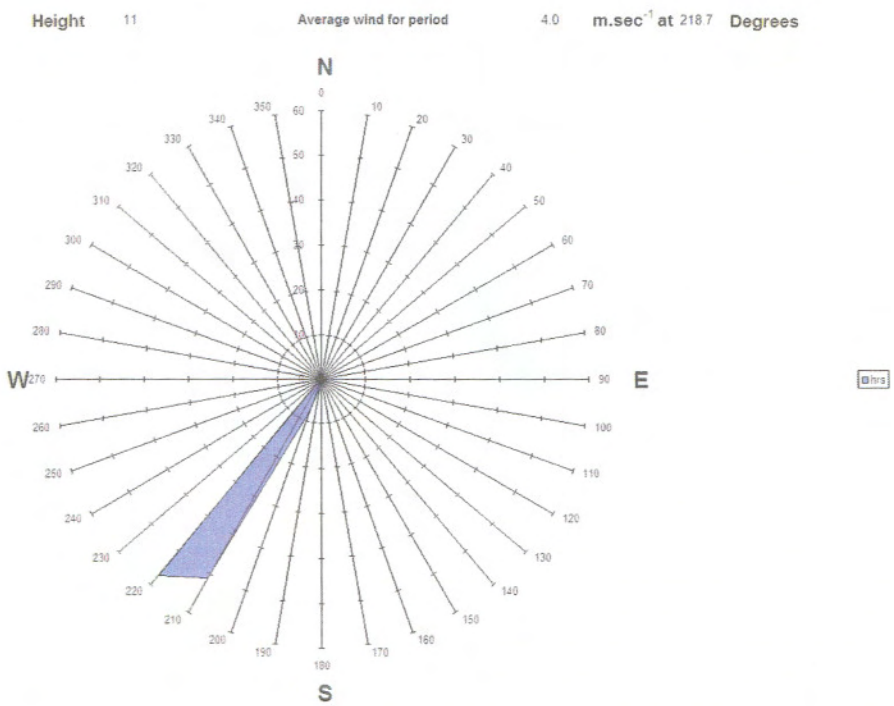

Figure A4.5 Wind rose for 26th May during measurements from Loc4, 16:47 - 18:51

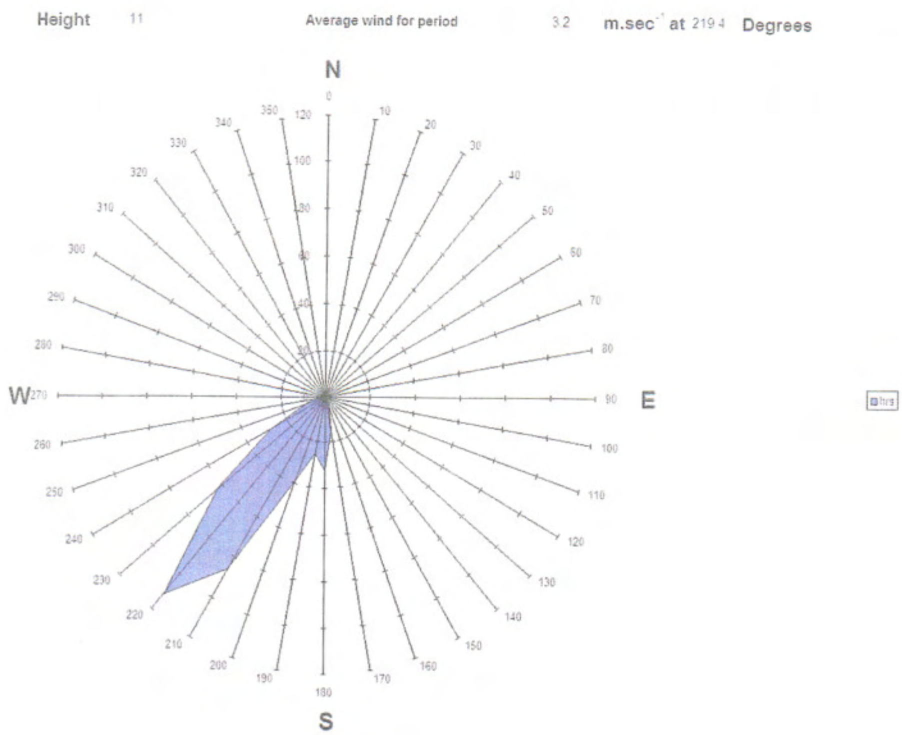

Figure A4.6 Wind rose for 27th May during measurements from Loc5, 10:41 - 18:44

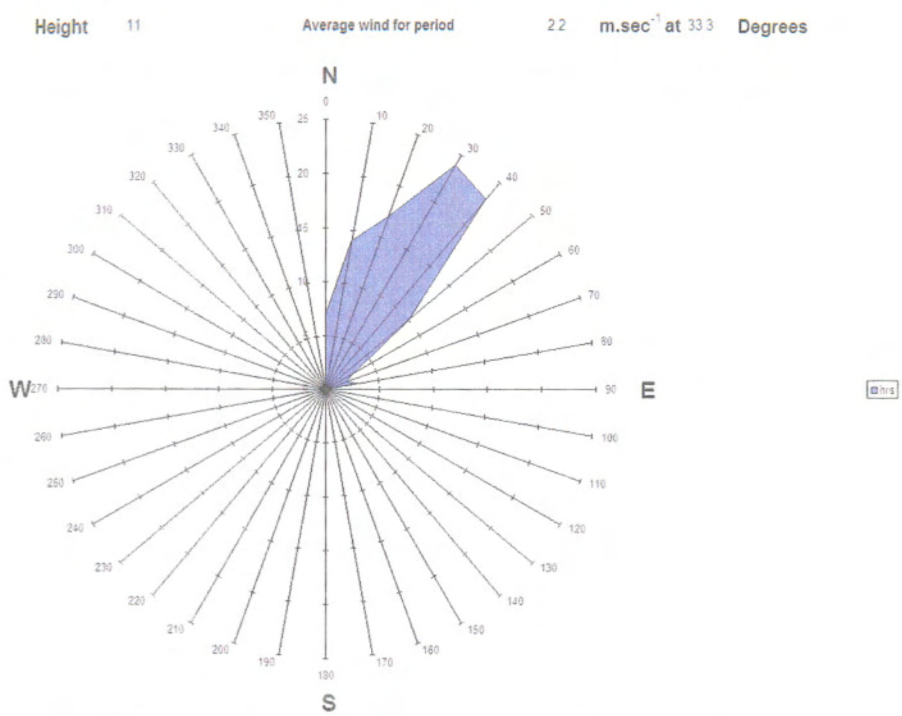

Figure A4.7 Wind rose for 28th May during measurements from Loc5, 9:46 - 12:13

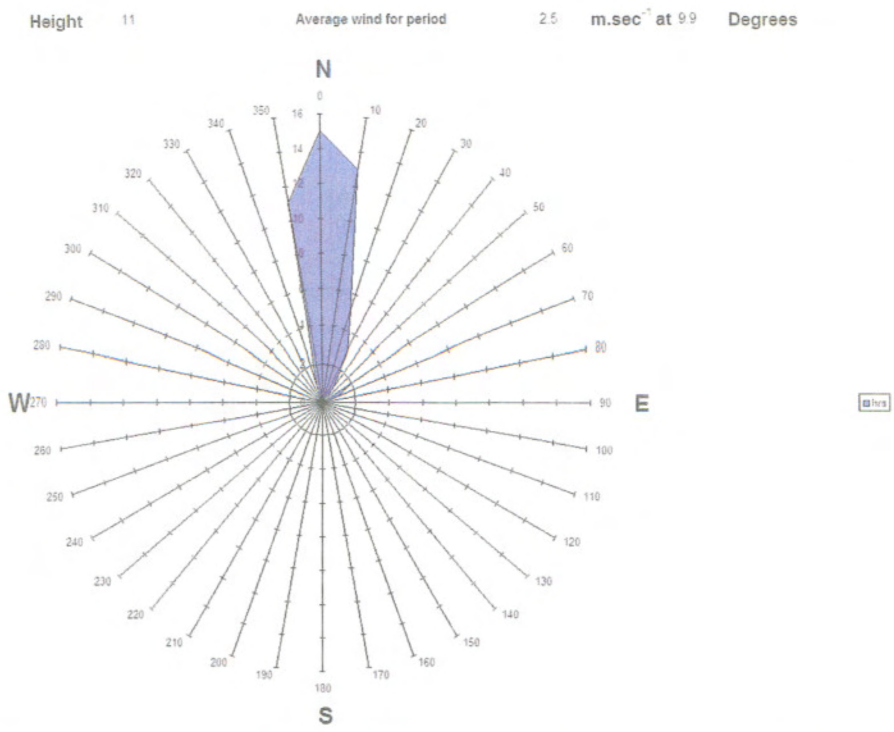

Figure A4.8 Wind rose for 28th May during measurements from Loc6, 13:09 - 14:21

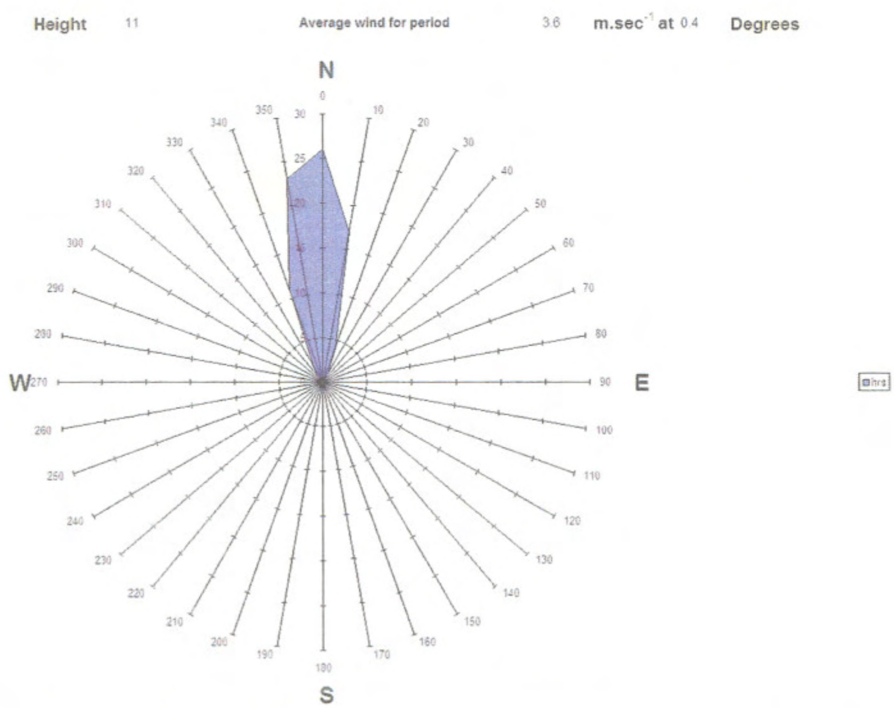

Figure A4.9 Wind rose for 28th May during measurements from Loc7, 15:01 - 16:53