

Differential Absorption Lidar Measurements of VOC Emissions from Wytch Farm Crude Oil Gathering Station

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and P T Woods**

ABSTRACT

This report describes work funded by Department for the Environment, Transport and Regions (DETR) and carried out by the National Physical Laboratory (NPL), with support from the National Environmental Technology Centre, to measure the gaseous emissions from an onshore crude stabilisation plant. The measurements were made using the NPL Differential Absorption Lidar (DIAL) facility at the BP Exploration Wytch Farm Gathering Station. This site receives crude oil from local wellsites, stabilises the crude, separates LPG and natural gas, and then exports the products by pipelines. The DIAL facility was used to measure controlled and fugitive emissions of VOCs from all areas of the site. Measurements took place over a 5 day campaign, from 23/3/97 to 27/3/98. The measurements were used to determine an estimate of the total site emission factor of $\sim 0.04\% \pm 0.005\%$ by mass.

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Approved on behalf of Managing Director, NPL
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1. INTRODUCTION

This Report describes work carried out by the National Physical Laboratory (NPL), with support from the National Environmental Technology Centre, under funding from the Department of the Environment, Transport and Regions (DETR), to measure non methane volatile organic compound(s) (NMVOC) emissions to atmosphere from the BP Exploration Wytch Farm Crude Oil Gathering Station. This site gathers crude oil from the local onshore well sites, stabilises the crude and separates liquid petroleum gas (LPG) and natural gas components. The aim of the work was to locate and quantify emissions to atmosphere of VOCs from different areas of the site and determine emission factors for NMVOCs. The Differential Absorption Lidar (DIAL) facility developed by NPL was used in a five day measurement campaign to undertake these measurements.

AEA Technology provides technical policy support to the Department of Environment, Transport and Regions (DETR), Air Quality Division, on a range of issues relating to atmospheric emissions and air quality in the UK. One of the major areas of this programme is to provide valid estimates of the emissions of volatile organic compounds (VOCs) to atmosphere [1]. These VOC emissions arise from a wide variety of industrial sectors. Work to date has shown that the oil and petrochemical industries contribute significantly to the total UK emissions of VOCs, but the emission estimates for these industries are of low data quality. Recently, measurements have been made with a mobile remote-sensing differential absorption Lidar facility developed by the National Physical Laboratory (NPL) which has provided more accurate data on some of the sources of emissions within oil refinery, petrochemical plant [2, 3] and Retail Petroleum Filling Stations [4, 5]. As a consequence, a constructive dialogue has been established with representatives of the refinery and petrochemical industries, with resulting improvements in their estimated emissions.

The emissions from the industry involved with the upstream supply of crude product, however, still has significant uncertainties and requires additional research. The current emission factors recommended by United Kingdom Offshore Operators Association (UKOOA) [6] for the UK's Onshore Oil Terminals are based on API figures for onshore terminals obtained for American installations in 1980. There have been no recent measurements of total VOC emissions from oil terminals[7].

The measurements described within this report have been undertaken in order to improve the emission inventory for such facilities.

2. OBJECTIVES OF THE MEASUREMENT CAMPAIGN

- 2.1 To measure, using NPL remote monitoring technology, the total fluxes of volatile organic compounds emitted to atmosphere by a Crude Oil Terminal which processes crude oil to stabilise it and to produces LPG and sales gas for export.
- 2.2 To compare the measured emission fluxes with the industry's estimation techniques [6,7].
- 2.3 To use the results of these VOC flux measurements to improve the UK inventory of VOC emissions from identified process units.
- 2.4 Produce a report with content suitable for inclusion in the Task Force Emission Inventories (TFEI) Atmospheric Emission Inventories Guidebook where appropriate [8].

3. THE WYTCH FARM GATHERING STATION SITE

Figure 1 is a map of the Wyitch Farm Gathering Station site, with key areas highlighted. It is important to note that all directions given in this report are with respect to site north.

This facility, operated by BP, uses plant which is typical of the onshore oil terminals in the UK (Wyitch Farm, Flotta, St. Fergus, Moss Moran, and Sullom Voe). The total emissions of VOCs from the plant at the site were monitored, together with emissions from on site storage. The site also utilises ground flares, and these were monitored as a part of the exercise. The results of the measurement work will be used to compare with the emission estimates, provided by industry, which are currently used in the National Atmospheric Emissions Inventory (NAEI) [9].

For the purposes of this study the site was divided into five principle areas :-

- **Process plant (including stabilisation, power generation and water treatment)**
This plant includes the de-ethaniser, de-butaniser and de-propaniser, gas compression plant, refrigerant plant, odourisation plant, the gas turbine power generation plant and the water treatment system. There are potentially fugitive emissions from all the hot/pressurised systems, from open settling pools in the water treatment area and the site discharge interceptors. There is one stack associated with each of the two gas turbines.

- **LPG Storage**
This area contains 12 covered pressurised LPG bullets and associated plant. Emissions from the storage tanks are expected to be low, however the high pressure plant associated with them may be a source of emissions.
- **Crude Oil Export and Metering**
This plant area, which is close to the LPG plant, is associated with the metering of crude oil exported from the site. There is the possibility of fugitive emissions from the high volume metering and valve systems in this plant.
- **Water Injection**
There is a small potential for emissions from re-circulated water which may contain low concentrations of hydrocarbons.
- **Flares**
The 3 flares at Wytch Farm, are ground flares. Each flare is associated with different process units and these are known as the low temp (LT), low pressure (LP) and high pressure (HP) flares respectively. They each consist of a set of burners contained within an open topped box. There is a potential for emissions of unburned hydrocarbons if the burners are not operating at high combustion efficiency. The burners are continuously purged with fuel gas to prevent the build-up of explosive mixtures.

The above sources can be categorised using the Selected Nomenclature for Air Pollution 1994 (SNAP94) [8]. Most of the sources are categorised under SNAP group 05, 'Extraction and Distribution of Fossil Fuels', more specifically 05.02.01 - 'Extraction, First Treatment and Loading of Liquid Fossil Fuels - Land Based Activities'. Combined oil and gas extraction facilities are explicitly grouped under this code. This excludes flaring which is included under SNAP code 09.02.08 and combustion processes which are included under SNAP code 01.05 more specifically the main on-site combustion sources are the gas turbines which are included under SNAP code 01.05.04.

The TFEI Atmospheric Emission Inventories Guidebook [8] lists some emission factors for sources under the above categories, however few are relevant to Wytch Farm. Under SNAP code 05.02.01 the guidebook lists measured emissions for combined facilities, however these only cover vented emissions. Wytch Farm Gathering Station does not vent any emissions, all controlled emissions are flared (although there are vented emissions at the associated well sites). The guidebook also quotes an equation for fugitive emissions which is very general and is based on offshore platform operations.

4. MEASUREMENT TECHNIQUE AND METHODOLOGY

4.1 DIAL TECHNIQUE

The National Physical Laboratory (NPL) has, for a number of years, been involved with the development of new techniques for remote measurements of industrial and urban pollution, and for monitoring air quality [10, 11, 12]. These techniques operate on spectroscopic principles using wavelength-tunable sources. They rely on the fact that each gaseous species in the atmosphere has a characteristic absorption spectrum, and that the wavelength of the source can be chosen so that it coincides with one feature of this spectrum. Then, tuning the source wavelength on and off the spectral absorption feature and measuring the absorption that occurs, allows the concentration of the selected species to be determined. The performance of these remote techniques have been extended continually at NPL, particularly in terms of the number of gaseous species that are detectable, their detection sensitivities, and the measurement range. Field trials have been carried out regularly to demonstrate the extending capabilities of these new measurement techniques. One of these remote monitoring facilities uses a principle similar to optical radar, known as differential-absorption lidar (DIAL).

A full description of the DIAL facility developed and operated by NPL is given in Appendix 1. The following section describes some of the sources of uncertainty present within this measurement campaign.

4.1.1 Validation and Uncertainty of the NPL DIAL Measurements

There are a large number of different sources of uncertainty which can effect the accuracy of flux measurements made using the DIAL technique. Some of the more significant of these are listed below :

- the meteorological conditions experienced at the time of measurement.
- the accuracy of the absorption coefficients used for a particular species.
- the concentration levels of the target species present in the atmosphere.
- the presence of any interfering species.
- the accuracy of the wind field measurements.

All of these factors, and more, need to be taken into account when determining the uncertainty in a particular measurement.

A number of flux validation experiments have been undertaken with the NPL DIAL facility, some of which are described in Appendix 1. These experiments have indicated an accuracy of between 10% and 20% for flux measurements made with the NPL DIAL facility.

4.2 METEOROLOGICAL MEASUREMENTS

Meteorological measurements of wind speed and direction were made throughout the period. Figure 6 shows the location of the fixed meteorological station which was operated continuously throughout the campaign. This mast mounted two monitoring arms at 15 m and 8m elevation and measured wind speed and direction at each height. A third wind station, installed on a 15 m mast attached to the DIAL facility, was also used whenever DIAL measurements were being made.

The results of these meteorological measurements were combined with the DIAL concentration measurements to generate the mass flux results described in section 6.

4.3 AMBIENT AIR SAMPLES

A small number of ambient air samples were taken at various locations around the site to determine the compositional distribution of volatile organic compounds (VOCs) at each location. The samples were drawn into previously-evacuated gas cylinders which have specially-passivated internal walls to ensure that their interiors are inert to the VOCs being sampled. The sampling procedure entailed opening the valve of the cylinder so that the flow rate into the 5 litre capacity cylinder was about 1 l/minute. The sampling time for a particular cylinder was therefore usually 5 minutes. The cylinder valve was then closed and the contents were analysed at NPL using gas chromatography (detection sensitivity achievable ~ 2 parts in 10^{11} by volume). Calibration was carried out using internationally-validated gravimetric multicomponent VOC standards held at NPL. This method thus provides short-term snapshots of the concentrations of a very wide range of hydrocarbon species present in the atmosphere. The results obtained during this exercise are discussed in Section 6.5.

4.4 VOLATILE ORGANIC SPECIES MEASURED DURING CAMPAIGN

The accuracy of the DIAL technique depends critically on the wavelengths selected for a given measurement application. These wavelengths are chosen to avoid interference due to gaseous atmospheric species which may potentially have overlapping spectra and to avoid spectral interference from other gaseous pollutants which may be present.

Before any field measurement exercise is carried out, a list of possible species emitted from the selected site is studied and spectral regions unique to the target molecules are chosen for the measurements. An in-house spectroscopic facility at NPL enables target wavelengths for a large number of gaseous species to be selected from their absorption

coefficients, which are available on a comprehensive database. The gas mixtures used to produce this database are generally prepared gravimetrically at NPL.

For the measurements at Wytch Farm the DIAL system was tuned to wavelengths which are sensitive to a range of hydrocarbons typical of emissions from industrial facilities. The exact wavelengths were carefully selected to give mass equivalent absorptions for each of the alkanes (C3-C7) which were nearly identical. In this way the measurement of total mass of detectable hydrocarbons is not sensitive to the relative concentrations of these hydrocarbons. The absorption coefficient used was derived from measurements of the absorption spectra, at these wavelengths, of a known mass of petroleum vapour. This absorption coefficient is then adjusted to take into account the mass of the species present in the vapour to which the DIAL system, at these wavelengths, has a lower sensitivity.

For provisional data analysis it was assumed that the hydrocarbon mixture being measured had a similar ratio as petroleum vapour, of detected to non-detected hydrocarbons. In most situations this assumption is valid. The results were then corrected using data from the analyses of ambient air samples taken at Wytch Farm (see Section 4.3). This correction particularly took into account the relatively high levels of ethane which were present, to which the DIAL system had a lower response at the chosen wavelengths, and therefore resulted in a higher proportion by mass of undetected hydrocarbons for a given measured absorption. The results quoted in this report are the corrected values. A different correction has been applied for each source measured, based on the different air samples taken. For the boundary fence measurements, where a number of sources contributed, an average correction has been applied. The correction does not take into account the levels of methane present, which was not measured by the DIAL system as it was configured at Wytch Farm nor by the ambient air analyses. (Note, the NPL DIAL facility is capable of measuring methane emissions specifically - but this was not part of the requirements for this project). The figures quoted in this report are in units of mass of total NMVOC (irrespective of the relative concentrations of individual VOCs). The speciation may be obtained from the ambient air analysis.

The process unit contains plant associated with coolant processing. The spectra of the refrigerants used in this process were checked and no potential interference was found. There were no other potentially significant sources of interference at, or near, the site.

Table 1 gives the DIAL measurement wavelengths and the approximate detection limits under the conditions experienced during the measurement campaign.

5. WORK PROGRAMME

5.1 A programme of work was defined, in collaboration with AEA Technology and in consultation with DETR, to employ NPL remote monitoring technology to determine, for Wytch Farm Gathering Station, the emission factors of volatile organic compounds.

5.2 A preliminary site visit took place on 3/3/98. During this visit the scope of the measurements was agreed with Mr R Finney of BP. A site survey also took place to identify suitable monitoring locations.

5.3 A measurement exercise was carried out at the site using the NPL DIAL facility. This determined :

the fluxes of volatile organic compounds emitted to atmosphere from identified plant on the BP site, including valve and switching areas;

the fluxes of volatile organic compounds emitted to atmosphere from storage areas on site;

the fluxes of volatile organic compounds emitted to atmosphere from flaring areas of the site;

the total fluxes of volatile organic compounds emitted to atmosphere from the whole site;

The five day measurement campaign took place between 23/3/98 and 27/3/98.

The required meteorological parameters, including wind speed and direction, were logged continuously throughout the measurement period.

Preliminary results of the DIAL measurements were reviewed in near-real time by NPL. This information was used to plan the ongoing measurement strategy.

As noted in Section 4.3 ambient air samples were taken at various locations around the site (see Figure 7), and subsequently analysed at NPL using gas chromatography.

6. RESULTS FROM THE MEASUREMENT CAMPAIGN

A total of 79 measurement scans were carried out during the measurement period. Each scan measured the concentration distribution of VOCs in a vertical plane defined by the measurement line-of-sight. Table 3 lists all these scans, and also contains the following information :

the date of the measurement;

the location of the DIAL facility. Each location is shown in Figure 6;

the data file containing the scan results;

the scan ID within the data file;

the time of the scan;

the measurement line-of-sight (LoS) along which the concentration distribution was being measured - these lines-of-sight are also shown in Figure 6.

the vector-averaged wind speed and wind direction during the scan. This data is taken from the 15 m and 8 m elevation wind measurements located at fixed sites (location M on Figure 6). The 15 m elevation wind direction was generally used as being most representative of wind directions across the plant.

The results of the measurements are presented in sections 6.1 to 6.4 below. Each table shows the date and time of the individual measurements made of the emissions from a particular area, and gives VOC mass emission fluxes. The individual flux results have then been averaged to give a mean flux for that measurement set.

An entry in the flux column of 'sat.' indicates that a mass flux could not be determined for a particular measurement due to intermittent saturation of the backscattered DIAL signal. This had a variety of causes but was mainly due to rain or mist. It is important to note that this does not indicate a high concentration of the measured species, just that enhanced backscatter had saturated the detector so that the differential absorption could not be accurately calculated.

The average values obtained for the emissions from each plant area have been annualised. These values have been obtained by assuming a pro-rata emission over the year. To achieve this, it has been assumed that the emissions measured during this campaign are representative of the average operating state of the plant. It is also assumed that the site throughput is representative of normal operations. This assumption should be recognised when interpreting the annualised DIAL figures.

The published annual throughput for Wytch Farm in 1996 was 4728,000 tonnes per year, which is equivalent to 539726 kg/hour. Assuming the same annual throughput for 1998, and comparing this figure with those in Table 14, we can see that during the period of the measurements the site was operating at 9% above the 1996 pro-rata throughput. The annualised figures calculated within this Report have not been corrected for this.

The following table summarises the meteorological conditions which occurred during the measurement campaign.

6.1 MEASUREMENTS OF VOC EMISSIONS FROM THE PROCESS AREAS

Several sets of measurements were made of emissions from the main process areas of the site. This area included the stabilisation plant, the power generation plant and to the south east, the waste-water treatment area.

Tables 4, 5, 6 and 7 present the results of these measurements. Each set was made on a different day under different meteorological and process conditions. The averages of each set of measurements are 18.4 ± 3.2 kg/hr , 37.5 ± 5.4 kg/hr, 16.9 ± 2.0 kg/hr and

25.2 ± 1.3 kg/hr respectively. It is possible the last value contains a contribution from the LPG and crude export areas. These figures correspond to emissions of 0.003 - 0.006 percent (by mass) of the total plant crude throughput. The average of these measurement sets is 24.5 ± 4.7 kg/hr. In producing this average it has been assumed that these measurements are samples of a population representing the mean operating state for the plant. The uncertainty in this figure is thus derived from the spread of the mean values of the separate measurement sets. The spread of these values is larger than the individual uncertainties of each mean value which implies that there are process and other factors which vary over timescales greater than the periods of each measurement set (typically from half an hour to 2 hours). The average emissions from the process area are equivalent to an annual emission value of 215 ± 42 tonnes of NMVOC.

Further sets of measurements along the eastern boundary indicate low localised (<3kg/hr) emissions from the waste-water treatment area, though it is was not possible separate and quantify them.

6.2 MEASUREMENTS OF EMISSIONS FROM THE LPG STORAGE AND CRUDE OIL EXPORT AREAS

Tables 8 and 9 list the results of measurements of the emissions from the LPG storage and crude export areas. Table 9 lists measurements which include a minimal contribution from the crude export plant. These give an emission value for the LPG storage of 34.5 ± 2.7 kg/hr. Subtracting this figure from the measurement of the combined emission from LPG and crude export given in Table 9 produces an estimate of 75.2 ± 14.8 kg/hr for the crude export plant alone. These figures are equivalent to an emission of 303 ± 24 tonnes per year from the LPG storage and 658 ± 130 tonnes NMVOC per year from the crude oil export plant.

6.3 MEASUREMENTS OF EMISSIONS FROM FLARES, THE HOT OIL HEATER AND WATER INJECTION SYSTEM

Table 10 lists measurements of emissions from the LT flare which proved to be a localised and significant source of VOC emissions and was actively flaring at the time of the measurements. The average of these measurements was 100.9 ± 5.7 kg/hr. Two single measurements confirmed the low level of emissions from the LP and HP flares which were not actively flaring during the measurement period but were being purged with a constant flow of fuel gas. These two flares have emissions which are each approximately 5 kg/hr. No significant emissions were attributable to the hot oil heater.

6.4 MEASUREMENTS OF THE VOC EMISSIONS AT SITE BOUNDARIES

Two sets of measurements were made along the site boundaries. One set along the northern edge, is summarised in Table 11, and one along the eastern edge, is given in

Table 12. A further set made along the Eastern fence line have been excluded because the line of site offered poor coverage of the full extent of the emissions.

Measurements along the northern boundary gave an average total emission of 243.9 ± 5.7 kg/hr. Measurements of emissions along the eastern boundary gave an average emission of 282.4 ± 29.0 kg/hr. These two measurement sets give annualised emission estimates of 2137 ± 50 tonnes per year and 2474 ± 254 tonnes per year respectively. The northern boundary measurements may have excluded some emissions from the southern end of the site, similarly the eastern boundary measurements excluded some emissions from the flares.

A further estimate of the total emission flux from the site may be made by combining the individual emission fluxes measured for each identified area within the plant. This gives a further estimate of the total emissions of 245 ± 16 kg/hr - which is equivalent to 2150 ± 143 tonnes NMVOC per year.

6.5 AMBIENT AIR ANALYSIS

A series of ambient air samples were taken at various locations around the site, as shown on Figure 7. These locations were chosen to be representative of the air quality downwind of each of the main emission sources described above. Table 13 gives the results of the air sample analyses. Figure 8 shows the relative percentage by mass of compounds within the air samples, grouped by carbon number. Analysis of these samples showed significant variations in the distribution of the concentrations of hydrocarbon species at selected locations downwind of different plant areas. Not surprisingly, higher levels of low carbon number VOCs were measured in the VOC emissions from the LPG storage area and the flares, than from other areas. The emissions from the crude export pumps and metering station had the highest levels of higher C-number compounds.

6.6 DETERMINATION OF THE EMISSION FACTOR FOR THE SITE

Table 14 summarises the daily throughput of crude oil at the site. It has been assumed, (with the agreement of BP), that the plant throughput was approximately constant during the measurement days and hence the hourly rate was approximately $1/24^{\text{th}}$ of this value. A value for the density of crude oil of 840 kg/m^3 has also been assumed (from UKOOA guidelines [6]). The average hourly total mass flow throughput of crude oil has been calculated from this and it has then been used to calculate the emission factor for each of the measured areas.

7. COMPARISON OF THE MEASURED EMISSIONS WITH THE ESTIMATED EMISSIONS

BP Exploration, of Wytch Farm estimates its fugitive emissions using the industry standard American Petroleum Institute (API) emission factors. Within this API procedure, emissions of NMVOCs from specified Integrated Pollution Control (IPC)

regulated sources (eg Gas Turbines, Ground Flares and the Hot Oil Heater stacks) are derived from fuel gas usage by application of the appropriate IPC-assigned emission factor. These emission estimates are determined in tonnes per year and these are annually verified by external auditors as required by the site's EMAS registration. The results are then reported to the Environment Agency and BP Group for publication in BP Facts and hence are available in the public domain.

The measured values have been annualised. In order to compare the measured emissions with current estimation techniques. To convert to annual figures, the hourly emission values have been multiplied pro-rata as discussed in Section 6, and this should be noted when interpreting the annualised figures. The following Sections present a comparison of the results obtained from annualised measured emissions and from the API calculated estimated values and the advantages and limitations of the two approaches are also summarised.

7.1 MEASUREMENTS OF EMISSIONS FROM PROCESS AREAS

BP Wytch Farm's internally reported fugitive emissions from the process areas of 157.1 tonnes per year of NMVOCs in 1995, with a calculated reduction of ~18% to 128.0 tonnes per year of NMVOCs in 1997. There are no controlled vented emissions from the plant area, since all process vents are piped to the flares. These figures are calculated from field screening values obtained in accordance with US EPA Method 21, using the API correlation equations, in keeping with the recommendations of United Kingdom Offshore Operators Association (UKOOA) and the BP Group. They are therefore dependent on the total crude oil throughput of the plant.

There are two stacks within the process area which vent flue gas from the gas turbines. The reported emissions in 1997 were 9.15 tonnes per year of NMVOCs, calculated using the IPC Licence emission factor of 0.00042 tonnes per tonne of fuel gas. The figure of 9.15 tonnes per year is equivalent to 1 kg/hr which is below the DIAL detection limit achievable during this campaign. There were no measurable emissions observed from this stack during the monitoring campaign, which is consistent with this.

The NPL DIAL measurements produced an average annualised value of 215 ± 42 tonnes per year for the process area. This includes emissions from the gas turbines, the stabilisation plant, gas compression plant, gas odourisation and refrigerant plant. This figure is similar to the reported calculated annual emission estimate for 1995 of 157 tonnes per year. The ratio of DIAL measured values are equivalent to a loss of 0.004% (by mass) of crude oil throughput, with the assumption that all other crude oil passes through the process units.

7.2 MEASUREMENTS OF EMISSIONS FROM THE LPG AND CRUDE OIL EXPORT AREAS

The reported emissions from the LPG storage at Wytch Farm Gathering Station in 1995 were 16 tonnes per year, calculated using the API factors. It should be noted that the

emissions from the crude oil export plant are included in the reported plant fugitive emissions estimate but are not reported specifically.

The DIAL estimates are equivalent to an annual NMVOC emission of 303 ± 24 tonnes per year for the LPG store and 658 ± 130 tonnes per year from the stabilised crude oil export plant. The figure for loss from the LPG storage is significantly higher than the API calculated values. During the period of measurements the contents of the LPG storage was approximately 1111 tonnes of LPG (both butane and propane). The DIAL measurements of LPG storage are equivalent to an emission of 0.83 tonnes of NMVOC per day, which is equivalent to a loss of 0.07% (by mass) of the total LPG storage. The emissions from crude export plant are equivalent to a loss of 0.013% (by mass) of total plant throughput (this calculation does not take into account the losses and removals from the crude volume before it reaches the export plant. However the correction from total throughput to exported volume is considered negligible (ie <0.5%)). Fugitive losses associated with export of stabilised crude would be expected to be small, given that the more volatile components have been removed prior to this phase. This has been verified by previous fugitive emissions surveys at Wytch Farm and other similar sites.

7.3 MEASUREMENTS OF THE VOC EMISSIONS FROM THE GROUND FLARES AND THE WATER RE-INJECTION PLANT

The annualised total emissions of NMVOC from the flares at Wytch Farm Gathering Station which were derived from the NPL DIAL measurements are 974 ± 51 tonnes per year (2.67 ± 0.1 te/day) . This assumes however, that active flaring is occurring at a level similar to that from the LT flare (which had measured emissions of NMVOCs of 100.9 kg/hr or 02.42 te/day during the measurement period) continuously throughout the year ; this however is not necessarily the case. Operational flaring occurs at Wytch Farm only during trips, shutdowns and the start-up after shutdown. For the remainder of the time, the flares are purged with low volumes of fuel gas, which will have emissions similar to those recorded for the LP and HP units during the DIAL experiment i.e. 5kg/hr. NMVOC per flare (0.12 te/day).

The reported estimated emissions of NMVOCs in 1997, calculated from actual gas flared using the emission factor assigned by the site IPC Licence was 487 tonnes per year. This is comfortably within the IPC consent level of 1020 tonnes per year NMVOCs.

The metered flare fuel gas rate during the period of the DIAL flare measurements was 29.9 tonnes per day. Using the site NMVOC emission factor for ground flare efficiency of 0.0203 te/te produces an emission estimate equivalent to 222 tonnes NMVOC per year. The DIAL measurements correspond to an emission factor of 8.9% NMVOC by mass for all the flares.

The breakdown of metered gas to each flare was 6.9 te/day to the LP flare, 14.9 te/day to the LT flare and 7.7 te/day to the HP flare. The DIAL measurements of each flare produce emission factors of 16.2% NMVOC by mass for the LT flare and 1.6%

NMVOC by mass from the LP and HP flares. These figures highlight the relative inefficiency of the LT flare during flare operations.

Previous studies at Wytch Farm in Summer 1997 showed there to be damage to several flare burner units causing combustion inefficiencies. Defective burner units were replaced during a scheduled site shutdown in May 1998. Thus additional performance improvement is likely in the short term. Wytch Farm in accordance with the policy of the BP Group, is actively pursuing measures to minimise flaring and to reduce emissions associated with flaring and is converting the ground flares to a purge with inert nitrogen during 1998.

7.4 MEASUREMENTS OF VOC EMISSIONS AT THE SITE BOUNDARIES

The prevailing wind direction in the locality is from the south-west and this was true for the DIAL measurement period. Hence, to obtain estimates of the total emissions burden from the Gathering Station, measurements were taken downwind of the site, beyond the northern and eastern boundaries. The two sets of boundary fence measurements gave annualised total site NMVOC emissions of 2137 ± 50 tonnes per year at the northern boundary and 2474 ± 254 tonnes per year at the eastern boundary. The measurements at the north boundary will not have included all emissions from the southern end of the site, similarly the measurements of the eastern boundary will not have included emissions from the flares. The estimated emissions of NMVOC in 1997 from the Wytch Farm Gathering Station were 504 tonnes per year, calculated using industry-standard emission factors. This is a factor of 4-5 lower than the DIAL values. The average total site emissions burden derived from the two DIAL estimates is 2137 ± 143 tonnes NMVOC per year. This is equivalent to a total mass loss of 0.04% NMVOC by mass of the total crude throughput.

The total reported emissions for the site in 1996 were 1098 tonnes NMVOC, including 941 tonnes NMVOC reported under IPC (flares, hot oil heater and gas turbines) and 157 tonnes NMVOC reported as estimated fugitives derived from API factors. The total site production was 4728 ktonnes. The estimated total site emission factor, combining all separately estimated emissions was 0.0235.

8. SUMMARY

The emissions monitored at Wytch Farm are summarised in the following Table 15, which gives the total annualised emission figures and the emission factors (in tonne/tonne) for each area, together with its SNAP code.

Table 15: Summary of results from DIAL measurements at Wytch Farm Gathering Station

Area	Snap Code	Annualised Emission (tonnes)	Emission factor by mass ¹ (tonne/tonne)	Current emission factor ² (tonne/tonne) [IPC]or(kg/hr.) [API]
Process (inc gas turbines)	05.02.01 (01.05.04)	215 ± 42	0.00004	Gas turbines 0.00042 [IPC]; Valves 9.76x10-05.(SV)0.96 [API] ³)
Crude Export	05.02.01	658 ± 130	0.00013	Valves 9.76x10-05(SV)0.96 [API]
Flares	09.02.08	974 ± 51 (total)	0.089 (of metered gas to flare) 0.00019 (of total site throughput)	Ground Flares 0.0203 [IPC] (of flared gas)
LPG storage	05.02.01	303 ± 24	0.0006 (of total LPG storage)	Valves 9.76x10-05(SV)0.96 [API]
Hot Oil Heater	01.05.	<5		0.00042 [IPC]
Water injection		<5		N/A

¹ The emission factor is by mass of total site throughput unless otherwise stated, derived from the DIAL measured NMVOC emission values.

² This is the current emission factor used at BP Wytch Farm.

³ The total process fugitives calculated for 1996 using the API factor were 157 tonnes/year NB API specifies separate correlation factors for different plant components i.e. valves, connections, compressors etc.

SV refers to screening value derived from survey according to US EPA Method 21.

The following bullet points summarise the results of this measurement campaign.

- In general the DIAL measurements produced higher NMVOC emissions than the estimated values, although the figures were generally of the same order.
- Comparison with existing estimates within the TFEI Guidebook is difficult as no figures for this type of on shore facility have been produced. Data exist for venting activities, as estimates per facility. However at Wytch Farm all controlled releases are flared, so no venting was measured.

- The emission estimates are calculated by BP using two techniques; IPC factors for flares, hot oil heaters and gas turbines and API factors, based on component counts, for process fugitives.
- The DIAL measured the total emissions of NMVOC by plant area, some of these areas contained both fugitive and IPC regulated emission sources.
- The major sources identified were process fugitives, including crude oil export fugitives, LPG storage and processing fugitives and losses due to flare efficiency, particularly from the LT flare.
- The NMVOC emissions measured by DIAL were equivalent to 0.04% NMVOC by mass of the total throughput of crude. This is comparable to the sum of the 1996 estimated emissions which were 0.023% NMVOC by mass of the total throughput of crude.

9. ACKNOWLEDGEMENTS

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The NPL staff who have been involved in this project are

Rod Robinson
Tony Andrews
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Des Alphonso

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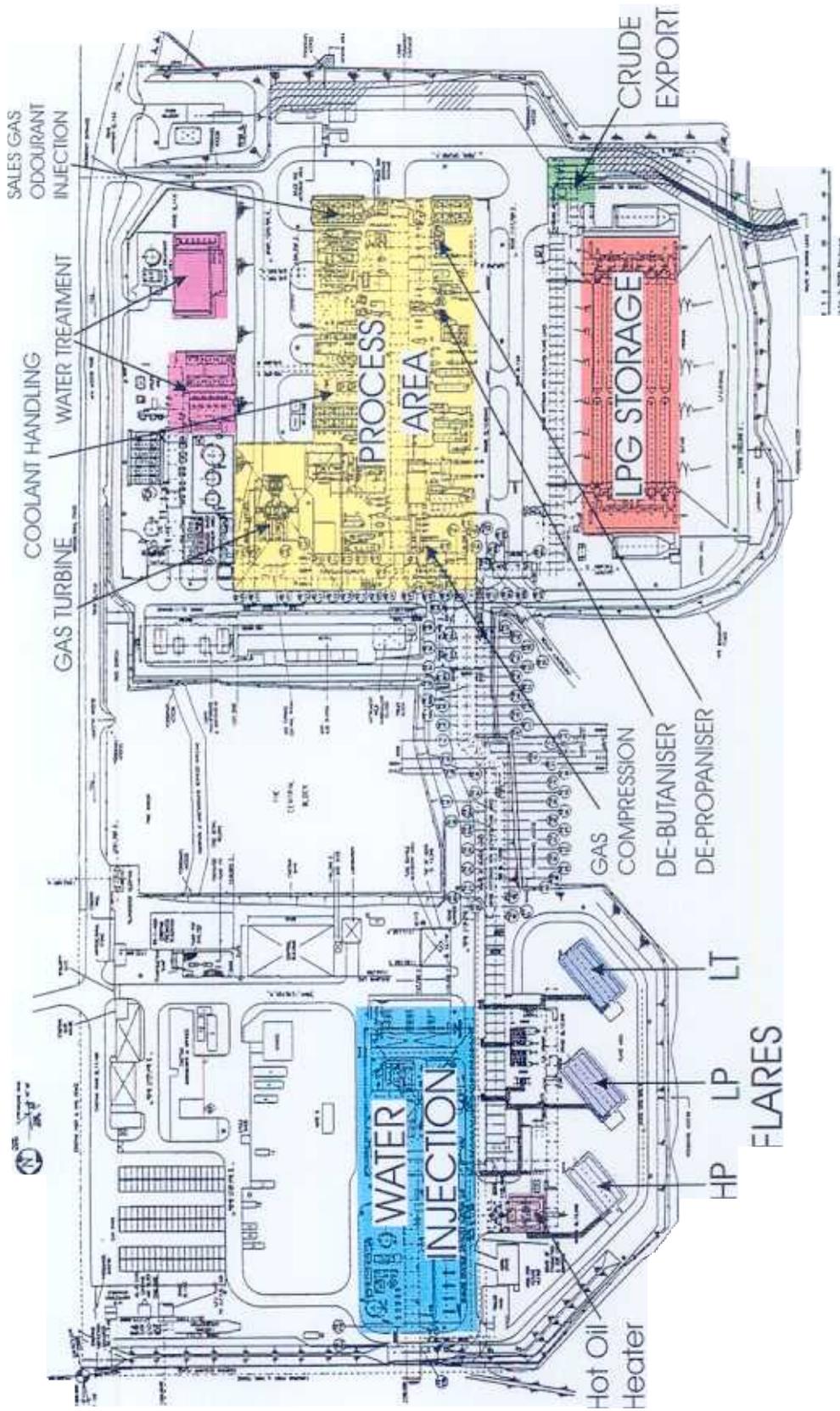
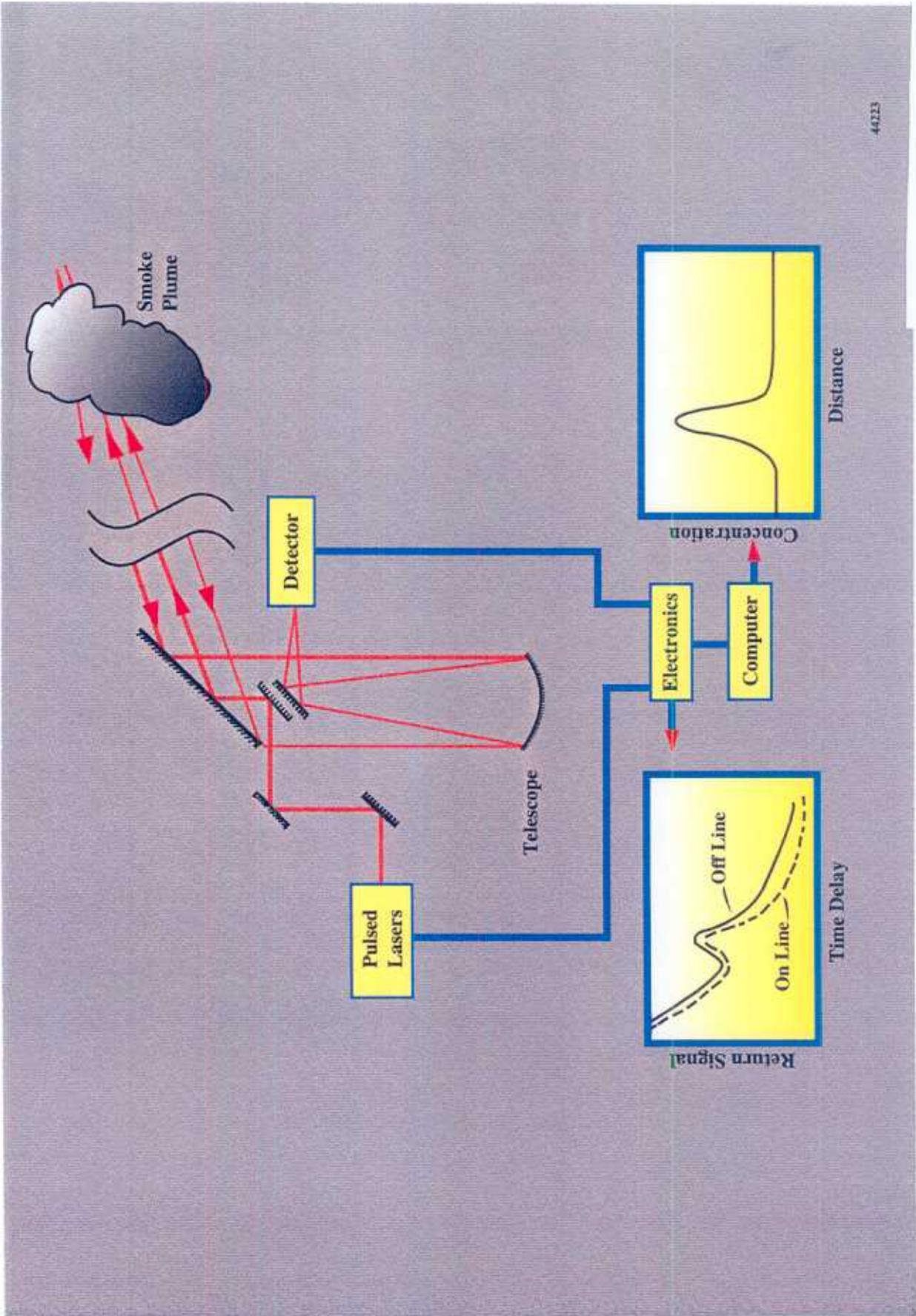


Figure 1. Site Map showing Potential Emission Sources



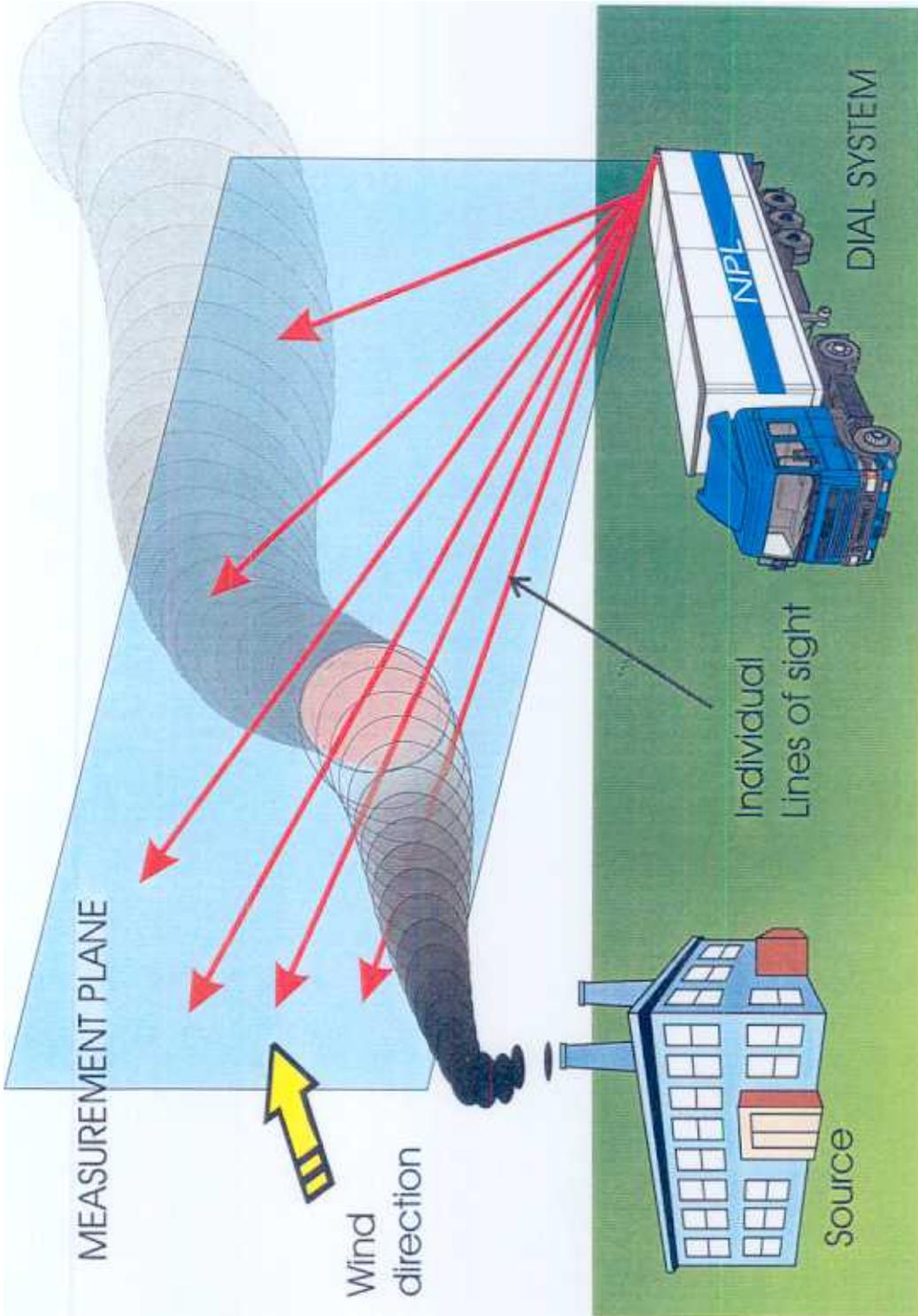
2. The DIAL Principle.



3. The NPL DIAL Facility.



4. View of DIAL Facility showing telescope.



5. Flux Measurement Technique.

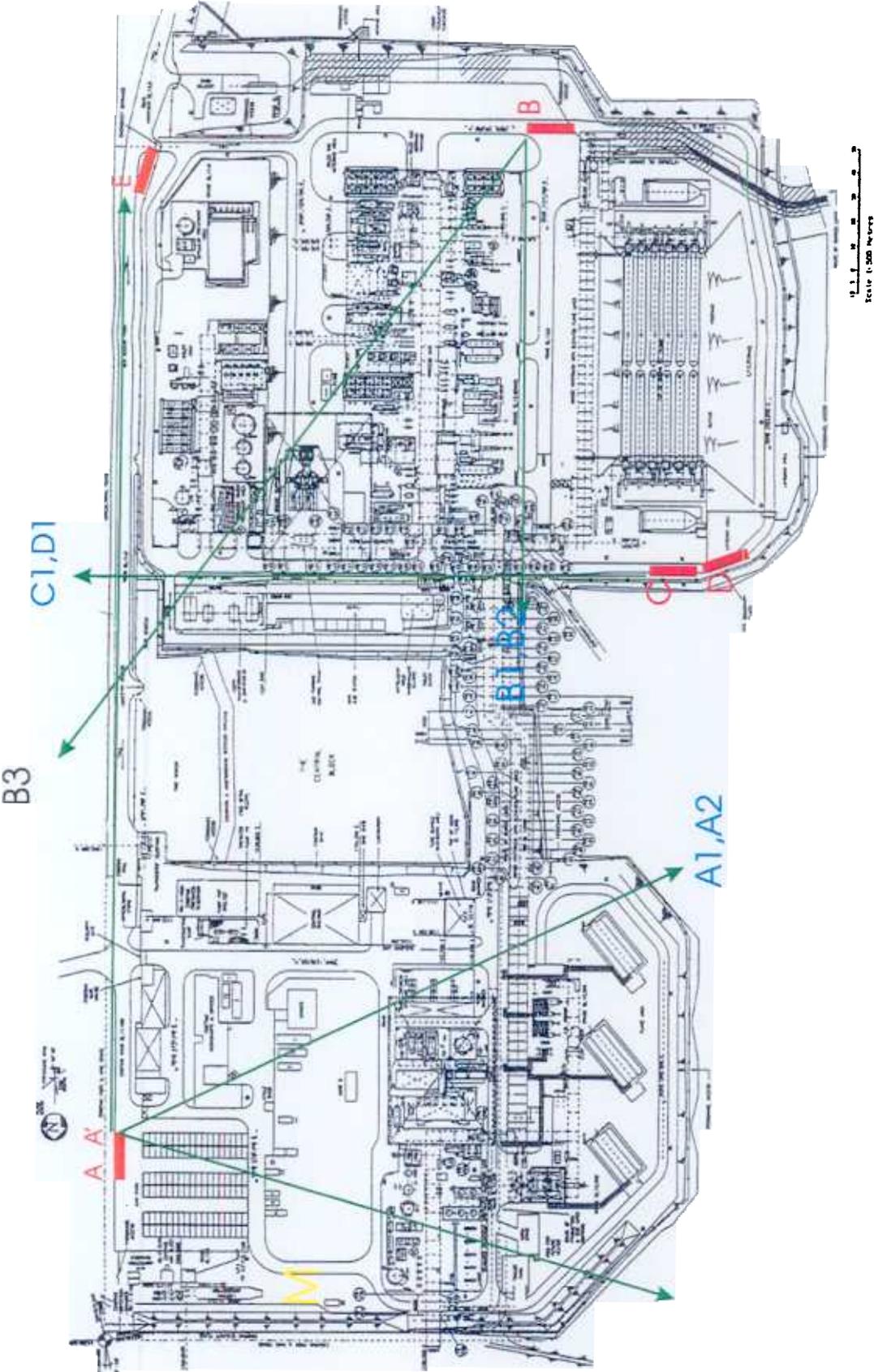


Figure 6. Site Map showing DIAL Measurement Locations, Lines of Sight and the Location of the fixed Meteorological Monitoring Equipment.

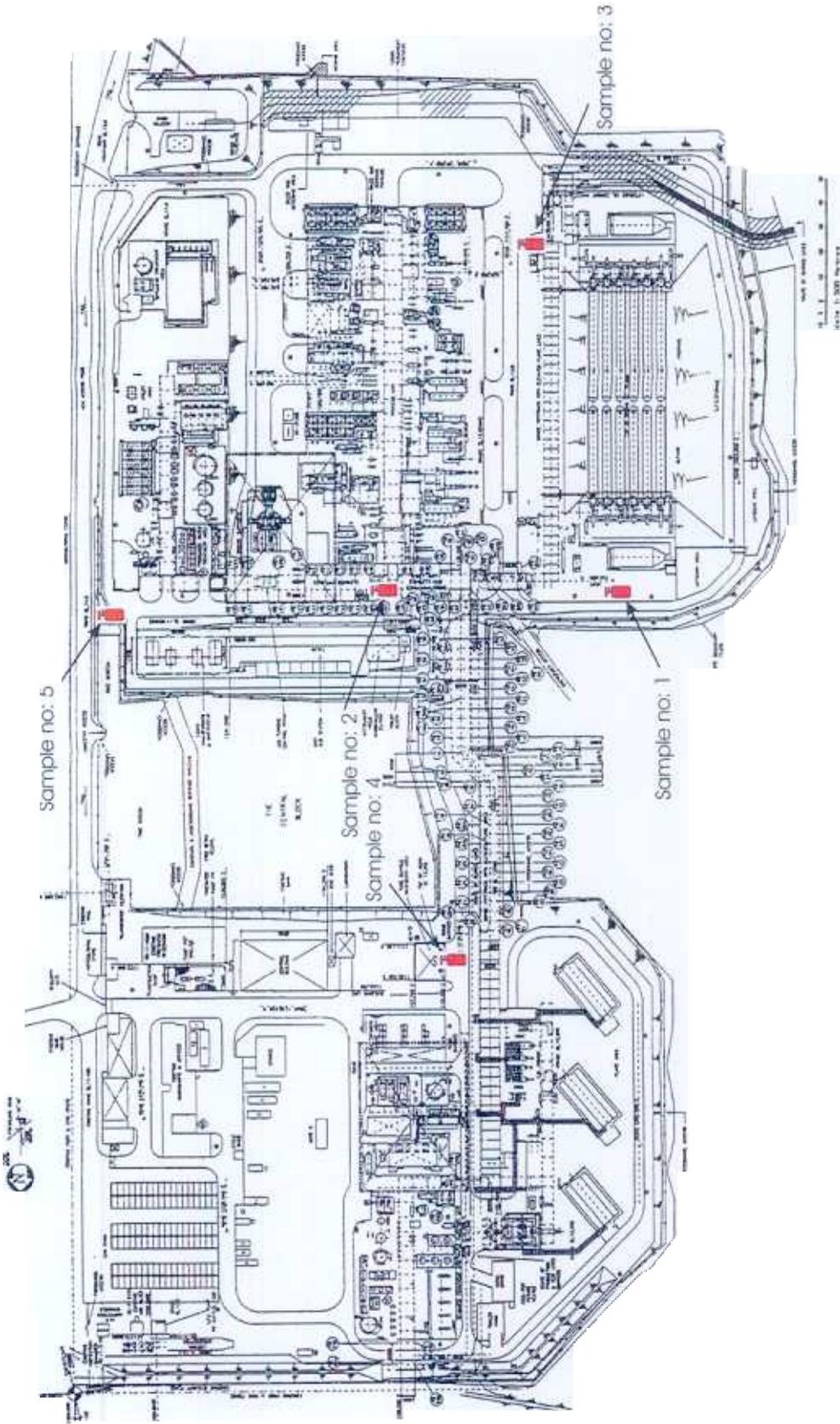
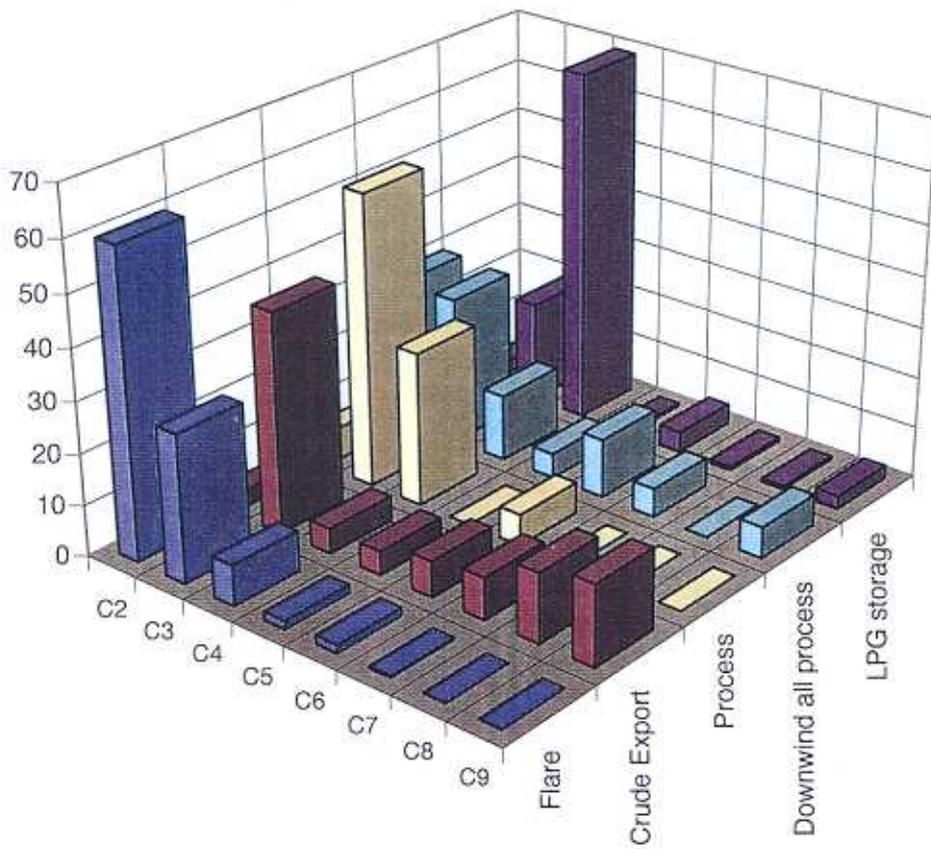


Figure 7. Site Map showing locations of air samples.

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Table 1: Measurement Wavelengths and Estimated Detection Sensitivities of Species Measured

Species	On-resonant Frequency (cm ⁻¹)	Off-resonant Frequency (cm ⁻¹)	Detection Limit (ppm.100 m)
Non Methane Hydrocarbons NMVOCs	2971	3002	0.05

Table 2: Summary of Meteorological Conditions

Date	Maximum daytime temperature	Minimum daytime temperature.	Wind Direction
23/3/98	10.4 °C	8.7 °C	NW
24/3/98	7.4 °C	5.6 °C	SE
25/3/98	7.9 °C	6.7 °C	S
26/3/98	10.2 °C	8.7 °C	SW
27/3/98	10.4 °C	9.6 °C	SW

Table 3: Summary of DIAL Measurement Scans

Date	Location	Raw File	Scan	Time	LoS	Wind speed 15m (m/s)	Wind speed 8m (m/s)	Wind direction(°)		
23/3/98	Pos A	mar231.wfx	A	13:56-14:17	A1					
			B	14:37-14:55	A1					
			C	15:00-15:09	A2					
			mar232.wfx	A	15:11-15:22	A2				
				B	15:23-15:47	A2				
			mar233.wfx	A	15:49-16:15	A2	2.70	1.79	287	
				B	16:16-16:40	A2	2.32	1.57	292	
			mar234.wfx	A	16:43-16:56	A3	2.67	1.79	283	
				B	16:57-17:07	A2	2.17	0.97	305	
				C	17:09-17:23	A4	1.71	0.85	322	
			mar235.wfx	A	17:25-17:35	A5	1.42	0.73	335	
				B	17:35-17:41	A4	1.42	0.73	335	
				C	17:42-17:54	A4	1.33	0.61	330	
				D	17:56-18:13	A4	1.45	0.69	335	
24/3/98	Pos A	mar241.wfx	A	10:16-10:34	A6	2.11	1.71	125		
			B	10:36-10:46	A6	2.96	2.33	148		
			C	10:47-10:52	A7	2.77	2.23	144		
				mar242.wfx	A	10:54-11:02	A7	2.10	1.66	155
					B	11:03-11:19	A8	2.71	2.20	145
					C	11:23-11:33	A6	2.98	2.43	153
		Pos B	mar243.wfx	A	13:01-	B1	2.53	2.06	156	
					B	-13:41	B1	2.53	2.06	156
				mar244.wfx	A	13:43-14:27	B1	2.72	2.13	157
				mar245.wfx	A	14:03-15:02	B2	2.62	2.08	153
					B	15:02-15:23	B2	2.60	2.01	155
				mar246.wfx	A	15:24-15:53	B2	2.23	1.75	153
					B	15:55-16:01	B2	2.60	2.17	156
				mar247.wfx	A	16:04-17:05	B1	2.16	1.71	149
					B	17:09-17:23	B1	2.17	1.64	149
					C	17:52-17:59	B3	1.63	1.21	145
				mar248.wfx	A	17:28-17:40	B3	1.56	1.21	120
					B	17:41-17:50	B3	1.63	1.21	145
		C	17:52-17:59		B3	1.63	1.21	145		
25/03/98	Pos A	mar251.wfx	A	10:07-10:27	A9	3.63	3.02	169		
			B	10:28-10:44	A9	4.29	3.51	170		
				mar252.wfx	A	10:48-11:08	A9	4.28	3.52	174
					B	11:09-11:25	A9	4.33	3.57	175
		Pos B	mar253.wfx	A	12:04-12:18	B1	3.98	3.31	178	

Date	Location	Raw File	Scan	Time	LoS	Wind speed 15m (m/s)	Wind speed 8m (m/s)	Wind direction(°)
			B	12:21-12:33	B1	3.48	2.90	178
			C	12:34-12:46	B1	4.46	3.75	173
		mar254.wfx	A	12:49-13:06	B1	3.80	3.03	179
	Pos C	mar255.wfx	A	13:27-13:47	C1	3.63	3.09	195
			B	13:47-14:05	C1	4.01	3.38	199
			C	14:05-14:30	C1	3.47	3.13	199
		mar256.wfx	A	14:31-14:55	C1	3.46	2.89	197
		mar257.wfx	A	14:58-15:23	C1	3.67	3.08	189
			B	15:26-15:39	C1	3.82	3.24	192
		mar258.wfx	A	15:43-16:02	C1	3.95	3.09	181
			B	16:03-16:24	C1	4.02	3.28	175
	Pos D	mar259.wfx	A	16:38-17:05	D1	3.21	2.86	194
			B	17:06-17:18	D1	3.98	3.23	197
		mar25A.wfx	A	17:20-17:41	D1	4.03	3.48	2.01
26/03/98	Pos E	mar261.wfx	A	11:29-11:41	E1	8.02	6.46	210
			B	11:45-12:05	E1	7.30	5.99	215
		mar262.wfx	A	12:11-12:27	E1	6.66	5.29	220
			B	12:34-12:51	E1	7.10	5.62	221
		mar263.wfx	A	12:54-13:04	E1	5.88	4.81	218
			B	13:06-13:16	E1	6.37	5.14	218
			C	13:17-13:28	E1	6.30	5.28	218
	Pos A'	mar264.wfx	A	14:04-14:59	A`1	6.94	5.63	218
			B	15:00-15:16	A`1	6.80	5.43	221
		mar265.wfx	A	15:18-15:32	A`1	6.76	5.31	224
			B	15:34-15:45	A`1	5.56	4.60	233
			C	15:46-15:55	A`1	6.18	5.16	233
		mar266.wfx	A	15:57-16:09	A`1	5.86	4.81	224
	Pos D		B	16:36-16:56	D1	5.07	3.98	226
		mar267.wfx	A	16:59-17:19	D1	4.85	4.00	230
			B	17:23-17:40	D1	5.53	3.49	225
		mar268.wfx	A	17:42-17:57	D1	4.52	3.58	226
			B	17:57-18:09	D1	4.53	3.58	227
27/03/98	Pos B	mar271.wfx	A	09:57-10:19	B1	3.95	3.36	212
			B	10:24-10:50	B1	4.48	3.74	208
		mar272.wfx	A	10:52-11:07	B1	4.10	3.50	215
			B	11:01-11:19	B1	4.23	3.62	215
		mar273.wfx	A	11:22-11:46	B1	4.67	3.96	212
			B	11:50-12:05	B1	3.77	3.18	223

Date	Location	Raw File	Scan	Time	LoS	Wind speed 15m (m/s)	Wind speed 8m (m/s)	Wind direction(°)
		mar274.wfx	A	12:08-12:23	B1	4.19	3.42	221
			B	12:25-12:41	B1	4.60	3.97	213
		mar275.wfx	A	12:43-12:58	B1	4.39	3.76	220
			B	12:59-13:18	B1	4.33	3.77	215

Table 4: Measurements of Process emissions on 24/03/98

Position : Pos A

Wind direction : 125-148

Sources : Process area including water treatment.

Scan Id	Flux (kg/hr)
mar241a	20.5
mar241b	12.2
mar242c	22.5
Average	18.4
Stdev of mean	3.3
Percentage emission (of total throughput)	0.0031%

Table 5: Measurements of Process emissions on 24/03/98

Position : Pos B

Wind direction : 156-149

Sources : Process area including water treatment.

Scan Id	Flux (kg/hr)
mar243a	36.8
mar243b	40.0
mar244a	76.2
mar245a	43.9
mar245b	20.0
mar246a	26.7
mar246b	24.8
mar247a	34.8
mar247b	35.3
Average	37.5
Stdev of mean	5.5
Percentage emission (of total throughput)	0.0064%

Table 6: Measurements of Process emissions on 25/03/98

Position : Pos B

Wind direction : 175-199

Sources : Process area including water treatment.

Scan Id	Flux (kg/hr)
mar256a	16.2
mar257a	19.4
mar257b	12.0
mar258a	12.5
mar258b	9.2
mar259a	26.8
mar259b	17.2
mar25Aa	21.7
Average	16.9
Stdev of mean	2.0
Percentage emission (of total throughput)	0.0029%

Table 7: Measurements of Process emissions on 26/03/98

Position : Pos D

Wind direction : 226-233

Sources : Process area including water treatment, possible contribution from LPG and crude export far upwind, however these will be dispersed into broad plumes and have been removed as background.

Scan Id	Flux (kg/hr)
mar266b	23.2
mar267a	27.4
mar267b	28.9
mar268a	22.7
mar268b	23.7
Average	25.2
Stdev of mean	1.3
Percentage emission (of total throughput)	0.0043%

Table 8: Measurements of LPG and Crude Export emissions on 27/03/98

Position : Pos B

Wind direction : 213-221

Sources : LPG storage area and crude export / metering area.

Scan Id	Flux (kg/hr)
mar271a	86.8
mar271b	136.7
mar272a	105.4
Average	109.7
Stdev of mean	14.6
Percentage emission (of total throughput)	0.019%

Table 9: Measurements of LPG emissions on 27/03/98

Position : Pos B

Wind direction : 213-221

Sources : LPG area, excluding crude export.

Scan Id	Flux (kg/hr)
mar273b	41.5
mar274a	35.3
mar274b	25.8
mar275a	38.4
mar275b	31.6
Average	34.5
Stdev of mean	2.7
Percentage emission (of total throughput)	0.0059%

Table 10: Measurements of Flare emissions on 23/03/98

Position : Pos A

Wind direction : 175-199

Sources : Flare LP,HP,LT

Scan Id	Flux (kg/hr)
Flare LT only :	
mar234b	116.4
mar234c	102.2
mar235b	87.3
mar235c	92.7
mar235d	106.1
Average	
	100.9
St.Dev of mean	
	5.7
Flare LP and HP :	
mar234a	10.3
Flare HP only	
mar235a	4.7
Total all flares	
	111.2
Percentage emission for all flares (of total throughput)	
	0.019%

Table 11: Measurements of site north boundary emissions

Position : Pos A

Wind direction : 155 - 175

Sources : All of North site + most of southern site, however some of southern site emissions may have been missed due to dispersion.

Scan Id	Flux (kg/hr)
mar242b	95.5*
mar251a	252.1
mar251b	238.7
mar252a	230.2
mar252b	254.6
Average	243.9
Stdev of mean	5.7
Percentage emission (of total throughput)	0.042%

* This measurement excludes some of the emissions from LPG/export and is not included in the average.

Table 12: Measurements of eastern site boundary -Southern Site emissions on 26/03/98

Position : Pos A'

Wind direction : 175-199

Sources : Process area including water treatment, LPG storage and crude export plant.

Scan Id	Flux (kg/hr)
mar264a	358.1
mar264b	340.0
mar265a	332.5
mar265b	181.5
mar265c	233.9
mar266a	248.5
Average	282.4
Stdev of mean	29.0
Percentage emission (of total throughput)	0.048%

Table 13: Analysis of Air Samples Taken at Wytch Farm Gathering Station

Grab Samples from Wytch Farm					
Analysis by Gas Chromatography for C2-C9 hydrocarbons					
Cylinder No:	clm 7963	clm 7975	clm 7609	clm 7977	clm 7964
Sample Location		export pump	process	down-wind process	gas storage
(ppb by Mole fraction)	ppb	ppb	ppb	ppb	ppb
ethane	879.7	9.4	13.4	65.3	11.4
ethene	8.1	2.2	0.8	1.0	1.2
propane	290.7	234.8	87.5	44.9	69.8
propene	*	0.7	*	*	*
i-butane	20.7	4.4	11.5	4.8	83.9
	39.9	8.2	23.2	10.4	99.1
	2.8	17.7	*	1.2	*
	*	1.4	*	*	0.9
cis-2-butene	*	3.8	*	*	*
i-pentane	4.5	2.1	*	1.9	0.4
n-pentane	5.7	4.3	*	2.7	0.7
propyne	*	0.7	*	*	*
1,3-butadiene	*	3.2	*	*	*
	*	1.5	*	*	*
2&3-methylpentane	1.5	2.8	*	2.3	*
n-hexane	1.8	3.6	*	1.8	0.4
isoprene	*	8.1	*	*	*
C6	*	5.9	*	*	*
n-heptane	0.7	9.0	*	1.4	0.4
benzene ¹	-	-	-	-	-
C7	*	5.8	*	1.9	*
toluene	0.7	5.3	*	0.6	0.8
	*	7.0	*	*	*
nonane	*	2.6	*	*	0.2
ethylbenzene	*	5.9	*	*	0.2
mp-xylene	*	10.2	*	*	0.7
o-xylene	*	6.9	*	*	*
C9	*	26.9	*	3.3	2.8

¹ An internal source of benzene was identified with some samples taken and so this species has not been reported.

* Below detectable limits

Table 15: Total throughput figures for Wytch Farm Gathering Station

Date	Throughput crude (barrels)	Throughput kg/hr ^(*)
23/3/98	106,772	593880
24/3/98	105,916	588840
25/3/98	104,809	582960
26/3/98	105,337	586320
27/3/98	104,988	584375
Average		587275

(*) Assuming density of crude of 840

APPENDIX 1. DESCRIPTION OF DIFFERENTIAL ABSORPTION LIDAR FACILITY OPERATED BY NPL

A1.1 OVERVIEW OF THE DIAL TECHNIQUE

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

A1.2 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.

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

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.

$$CL(r) = \frac{I}{2\Delta\alpha} \frac{1}{N} \sum_{i=1}^N \log \frac{S_{ONi}(r)}{S_{OFFi}(r)} \quad (2)$$

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).

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

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

A1.3 DESCRIPTION OF FACILITY OPERATED BY NPL

The DIAL system operated by NPL is housed in a mobile laboratory, shown in Figure 3. It can operate in the infrared, visible and ultraviolet spectral regions allowing coverage of a large number of atmospheric species. A scanner system, shown in Figure 4, 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 14 m mast with wind speed, direction, temperature and humidity measurements, and point monitors for measuring a variety of atmospheric gases.

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.

A1.3.1 Source

The source and transmission system employs two independent Nd-YAG pumped dye lasers, each with a repetition rate of 10 Hz. These two systems can be used concurrently to allow simultaneous monitoring of two species. The output laser pulse length is ~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. It is also possible to transmit a separate one micron Nd-YAG beam which allows a single

wavelength lidar channel to be operated simultaneously with the DIAL channels. Various non-linear optical techniques are used in the infrared system to achieve the required output wavelength and energy.

A1.3.2 Detection

The returned atmospheric backscatter signal is collected by the scanning telescope. This directs the collected light into three paths for the infrared, visible/ultraviolet and 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. The one micron lidar signal is detected using a high-speed avalanche photo-diode.

After amplification the signals from these detectors are digitised using 20 MHz 10 bit digitisers. The digitisers are clocked using an external 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.

A1.3.3 Data Analysis

The data acquired are analyzed, using the standard 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) 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.

ii) Background subtraction

Following normalisation for transmitted energy 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.

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, as described in section A1.2.

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

iv) Derivation of range-resolved concentrations.

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, as described in section A1.2.

v) Calculation of emission fluxes

Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile. 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.

A1.3.4 Calibration

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 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 all 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 the DIAL system. Examples of these 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 $\pm 15\%$. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within $\pm 20\%$.
- 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 $\pm 12\%$.
- iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission fluxes to within $\pm 15\%$.

NPL have also developed and operate a full-scale facility for the calibration of long 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 facility has already been employed to demonstrate the accuracy of the infrared DIAL measurement technique [13].

APPENDIX 2

QUALITY ASSURANCE AND DATA AUDIT TRAIL

The National Physical Laboratory has a comprehensive quality system covering its laboratory and field activities, whose scope and operation has been certified by Lloyd's Register Quality Assurance as complying with the international standard ISO 9001.

Details of the calibration procedures used for the DIAL measurements are given in Appendix 1, with the use of reference gases traceable to National Standards. The uncertainty of DIAL results is also discussed. These depend upon a number of factors, including the meteorological conditions during the measurement, so a fixed uncertainty cannot be given. However a number of validation exercises have been carried out, and these indicate that the typical uncertainty in a DIAL measurement is in the range 10-20%.

All raw data collected during the course of this measurement campaign will be held in a data store for at least six years.

A4.1 DIAL DATA AUDIT TRAIL

Raw Data stored on PDP format 8.5 inch floppies located in DIAL.

Files referenced in Data Summary Sheets held in folders in DIAL (one folder per day of measurement).

File Name : mmmddn.WFX

where mmm = month eg JAN, dd = day number eg 08,
n = sequential file number (1-9 then A-Z)

Each file can hold up to 60 records (numbered 0-59)

PROCESSED DATA STAGE 1 :

DIAL summary spreadsheets

WFXDSUM1.xls [held on PC 'RACK' in DIAL]
WFXSUM.xls

These spreadsheets (cross referenced by scan identifier) :

- lists all raw data files and the dates acquired.
- identifies the measurement scans within each file.
- lists the record numbers constituting each scan.
- gives the times of each scan
- gives the wind data used to process each scan.

The wind data is derived from files held on PC 'TOSH' in Rm 256, in directory C:\. Filename example : 15m2303.xls, referring to data from the 15m mast on 23/03/98. A printout of the wind measurements is held with the DIAL data summary sheets (in DIAL).

Individual DIAL records have been processed to give column data on DIAL processing system (LSI in DIAL) using D4V51P.SAV. See previous analysis notebook Q9ES31-ANALYSIS-01 for procedure used.

Processed data transferred to PC format (again see previous analysis notebook for procedure). See notebook Q9ES5801 - 02 for notes on the individual files transferred.

The PC data files have the same root name as the raw data files with a txt extension (mmmddn.txt) and are held in directory C:\wfx\mmmdd on PC 'TORSTEN' and PC 'RACK' both in DIAL, where mmm is the month and dd is the date of the scan.

PROCESSED DATA STAGE 2

Individual scans were loaded into Matlab and processed using script WFXPROC.m (this calls scripts which are part of DIAL data processing package PROCGA2.M).

Notes on individual scan results are in notebook Q9ES58 -02.

Input file : one file holding all data for that scan.

Input data :

- Wind direction (degrees) - from WFXSUM.XLS
- Wind speed (m/s) - from WFXSUM.XLS
- Line of Sight angles (LoS) - read from raw data files on LSI.
- Angle of elevation for each record - read from raw data files.
- Range and column results - from .col files (see above)
- Conversion factor for the species being measured - see notebook Q9ES58 01.

Output file

- matlab data file holding all data used to process a scan
- saved as mmmddns.mat where mmmddn is as above and the character 's' denoted which individual flux measurement the scan data refers to. Files stored in data directory c:\wfx\on PC 'Rack' in DIAL

Output data

- Output is the flux in kg/hr and peak concentration in ppm, stored in spreadsheet WFXDSUM1.xls. - sheet 'scan summary' on PC 'Rack' in DIAL

PROCESSED DATA STAGE 03

Scan results (flux in kg/hr) were grouped by source measured. The averages (mean) and standard deviations of the mean were calculated using excel functions.

Input data

Flux results from WFXDSUM1.xls sheet 'scan summary' on PC 'RACK' in DIAL

Site throughput of crude oil from BP supplied summary data in 'opus.xls' on PC 'Rack' in DIAL

Output data

Average fluxes and standard deviations for groups of measurements of the same sources. - WFXDSUM1.xls sheet 'Emission Calc' on PC 'Rack' in DIAL

These output data used this draft report, on PC 'Rack' in DIAL and PC 'Thunderchild' in rm 257 B95