

**DIFFERENTIAL ABSORPTION LIDAR (DIAL) QUANTIFICATION OF
PROPANE EMISSIONS FROM CONTROLLED RELEASES IN
ANAHEIM, USA, OCTOBER 2015**

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JANUARY 2017

Differential Absorption Lidar (DIAL) Quantification of Propane Emissions from Controlled Releases in Anaheim, USA, October 2015

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ABSTRACT

This report presents the results of propane emission measurements from controlled release experiments in Anaheim, USA, carried out using the NPL Differential Absorption Lidar (DIAL). The measurements were conducted between the 12th and 13th October 2015

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ISSN 2059-6030

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Approved on behalf of NPLML by
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1 INTRODUCTION

This report presents the results carried out using the National Physical Laboratory's (NPL) differential absorption lidar (DIAL) system (shown in Figure 1.1) to measure emission rates of propane from several controlled releases in Anaheim, USA, in October 2015. This was part of South Coast Air Quality Management District (SCAQMD) R&D project, "Application and Development of Advanced Optical Remote Sensing Technologies to Characterize and Quantify Fugitive and Stack Emissions from Refineries and Other Sources" for which NPL was selected to conduct validation and intercomparison work using the DIAL method. In order to obtain critically important quality assurance information on flux measurements and compare the performance of all participating optical remote sensing methods a controlled released experiment using the NPL Area Source Facility (ASF) was carried by out SCAQMD on the 12th and 13th October in the parking lot of the Anaheim Angels Stadium.

A brief overview of the DIAL measurement approach and experimental setup is given below. Section 2 presents summary tables and figures for each day of measurement. Section 3 presents a discussion of the controlled release results. Technical details for the measurement methodology are presented in Annex 1, which provides an overview of the DIAL technique, and discusses the calibration and validation procedures. Annex 2 provides a description of the ASF.



Figure 1.1 NPL DIAL facility on a site.

1.1 OVERVIEW OF MEASUREMENT APPROACH

The controlled release was setup by NPL in the parking lot of the Anaheim Angels Stadium and then operated by the SCAQMD staff during the experiment when variable amounts of a tracer gas,

unknown to the participants, were released using the ASF. The configuration and location of the controlled release was agreed by all project partners and was mainly driven by the requirements of the other techniques. Roughly a 400 m X 200 m portion of the stadium parking lot, east of the stadium, was allocated for the controlled-release experiment. A non-odorized propane gas was released from altitudes of 3 m, 6.4 m or 7.9 m using two release nodes of the ASF facility. Release points were placed on a scissor lift and lifted to the heights listed above. Blind propane rates were released ranging from 1.6 to 25.4 kg/hr for a total of ten different releases, three on the first day and seven on the second day. Each release lasted for approximately 45 minutes to one hour.

The NPL DIAL was used at two different locations on the south-east boundary of the allocated space and conducted propane emission monitoring downwind of the propane release tower, along a SE-to-NW line of sight. A portable weather station and a portable wind sensor were located near the propane release point.

Emission rates were determined as described in Annex 1, by scanning the DIAL measurement beam in a vertical plane downwind of the controlled release source, and measuring the total concentration of VOC in that plane. DIAL VOC measurement is targeted on C2+ hydrocarbons with a standard absorption coefficient based on gasoline vapour. A scaling factor to go from the standard DIAL VOC mass to the measured propane mass is then applied. The logarithmic wind field profile used for the emission rate calculations (see Annex 1) was determined from the speeds of a 9 m sonic anemometer operated by Fluxsense and the 3 m portable weather station. The wind direction measured from the portable weather station was used to define the wind direction for the emission rate measurements. During the first day the wind direction was slightly variable and predominantly from the W/SW with a wind speed at the release point height most of the time above 1 m/s representing conditions that are quite often found when measuring on refinery sites. On the second day the wind was stronger and more stable from the southwest.

1.2 SUMMARIES TABLES AND FIGURES

The lines-of-sight (LOS) used at each measurement location are shown in Figures 2.1 and 2.2. These figures also show the average wind direction measured over the full time frame during which the measurements from a given location took place.

Tables 2.1 and 2.2 report the emission rates determined for each scan made from each measurement location. The scan numbers are not necessarily sequential because some scans were recorded for data quality checks and also some scans may have been aborted by the operator. No valid scan has been eliminated from the report. The tables also list the location and the LOS used for each measurement. The wind directions and the wind speeds reported in the tables are from the portable weather station and the 9 m sonic anemometer used for the emission rate calculations.

Table 3.1 report the mean and standard deviation of the propane emission rates determined from each controlled release. The standard deviation given in the tables is the standard deviation of the individual emissions from which each mean emission rate value has been determined. The standard deviation will include effects of the source variability, DIAL measurement uncertainty and the influence of other factors such as the wind speed and direction variability during the course of individual measurements.

Because the DIAL flux measurement depends on several different experimental conditions, the detection limit can be experimentally estimated when the measured standard deviation is similar to the measured value. The standard deviation would then defines the detection limit for that set of measurements.

2 PROPANE CONTROLLED RELEASE MEASUREMENTS

Table 2.1 Emission rate determined from CR01 on 12th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
190	CR01/LOS1	13:01	13:07	1.5	262.6	6.80	Release 1 13:02-13:56 - 3m
191	CR01/LOS1	13:07	13:14	1.9	238.4	3.71	Release 1 13:02-13:56 - 3m
192	CR01/LOS1	13:14	13:22	1.0	213.7	5.14	Release 1 13:02-13:56 - 3m
193	CR01/LOS2	13:25	13:33	1.1	289.0	3.05	Release 1 13:02-13:56 - 3m
194	CR01/LOS2	13:33	13:41	1.4	308.6	5.51	Release 1 13:02-13:56 - 3m
195	CR01/LOS2	13:42	13:55	1.0	236.9	4.58	Release 1 13:02-13:56 - 3m
196	CR01/LOS2	14:00	14:13	1.8	233.8	11.67	Release 2 14:00-14:55 - 3m
197	CR01/LOS2	14:14	14:27	2.1	204.8	11.86	Release 2 14:00-14:55 - 3m
198	CR01/LOS2	14:28	14:35	1.7	239.3	9.68	Release 2 14:00-14:55 - 3m
199	CR01/LOS2	14:36	14:51	1.9	243.0	10.95	Release 2 14:00-14:55 - 3m
201	CR01/LOS2	15:06	15:21	1.6	226.5	18.38	Release 3 15:00-15:58 - 3m
202	CR01/LOS2	15:22	15:37	1.8	240.7	14.91	Release 3 15:00-15:58 - 3m
203	CR01/LOS2	15:37	15:52	1.0	237.4	12.33	Release 3 15:00-15:58 - 3m

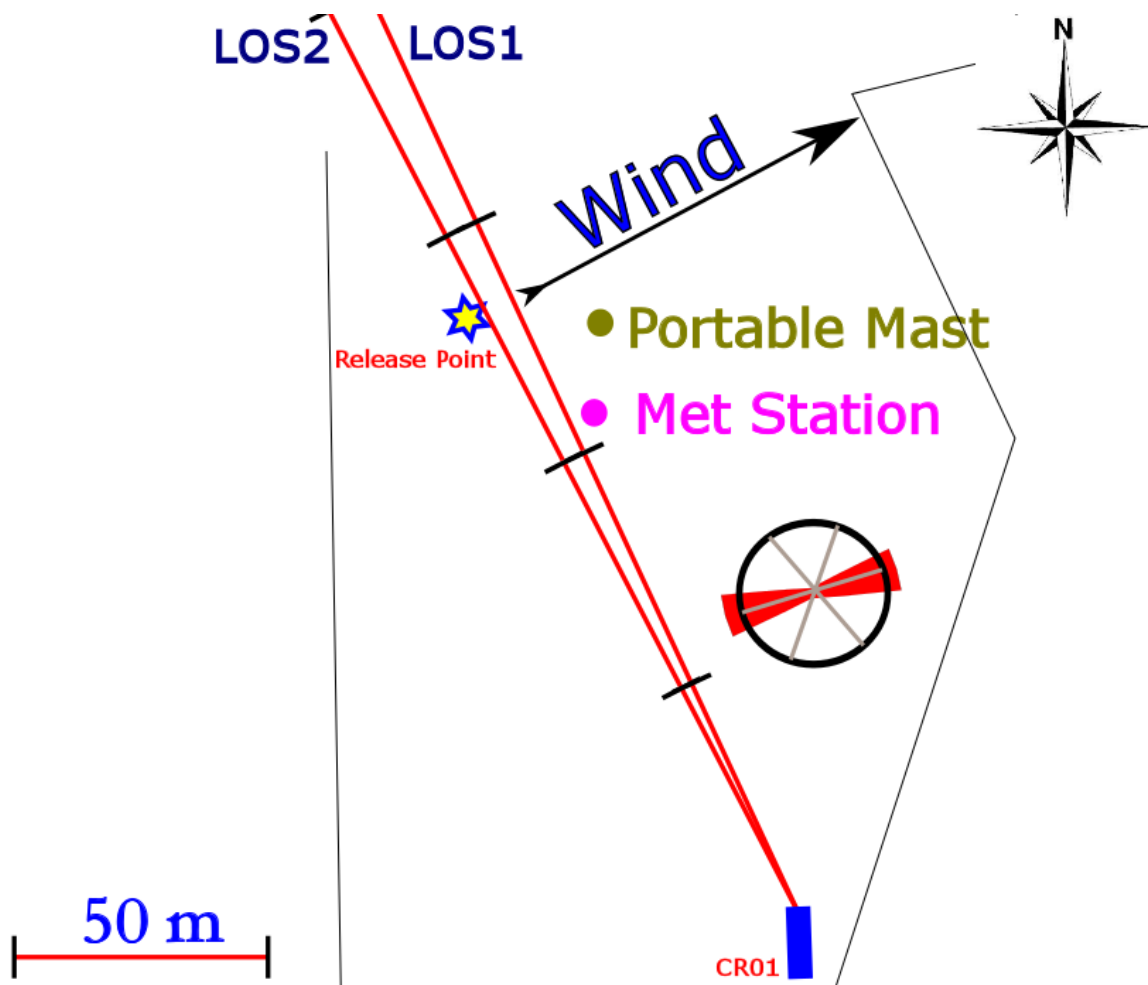


Figure 2.1 Measurement configuration for location CR01 on 12th of October.

Table 2.2 Emission rate determined from CR02 on 13th of October.

Scan ID	Location / LOS	Start Time	End Time	Wind Speed	Wind Direction	Emission Rate	Notes
				m/s	Degrees	kg/hr	
210	CR02/LOS1	10:47	11:01	2.0	203.6	11.07	Release 5 10:44-11:43 - 3m
211	CR02/LOS1	11:01	11:14	3.0	210.3	11.21	Release 5 10:44-11:43 - 3m
212	CR02/LOS1	11:16	11:29	2.2	193.8	14.46	Release 5 10:44-11:43 - 3m
213	CR02/LOS1	11:30	11:42	3.4	208.5	14.84	Release 5 10:44-11:43 - 3m
215	CR02/LOS1	11:59	12:04	4.1	223.4	3.70	Release 6 11:47-12:40 - 6.4m
216	CR02/LOS2	12:06	12:19	3.0	222.7	6.41	Release 6 11:47-12:40 - 6.4m
217	CR02/LOS2	12:19	12:33	3.5	221.4	5.96	Release 6 11:47-12:40 - 6.4m
218	CR02/LOS2	12:33	12:46	3.1	228.6	4.17	Release 6 11:47-12:40 - 6.4m
219	CR02/LOS3	12:47	13:01	2.3	218.7	12.49	Release 7 12:48-13:41 - 7.9m
220	CR02/LOS3	13:01	13:14	2.6	217.2	17.86	Release 7 12:48-13:41 - 7.9m
221	CR02/LOS2	13:15	13:28	3.5	218.7	17.79	Release 7 12:48-13:41 - 7.9m
222	CR02/LOS2	13:29	13:44	3.5	227.5	21.88	Release 7 12:48-13:41 - 7.9m
223	CR02/LOS2	13:47	14:02	4.3	221.1	1.61	Release 8 13:43-14:38 - 7.9m
224	CR02/LOS2	14:04	14:19	4.3	226.0	1.47	Release 8 13:43-14:38 - 7.9m
225	CR02/LOS3	14:20	14:35	3.8	226.7	0.23	Release 8 13:43-14:38 - 7.9m
227	CR02/LOS3	14:50	15:05	4.4	230.3	8.63	Release 9 14:44-15:39 - 7.9m
228	CR02/LOS3	15:06	15:19	4.2	223.3	9.25	Release 9 14:44-15:39 - 7.9m
229	CR02/LOS3	15:19	15:32	3.8	220.2	10.55	Release 9 14:44-15:39 - 7.9m
231	CR02/LOS2	15:46	16:00	4.5	219.1	26.56	Release 10 15:44-16:29 - 7.9m
232	CR02/LOS2	16:00	16:13	3.9	214.7	24.27	Release 10 15:44-16:29 - 7.9m
233	CR02/LOS2	16:13	16:27	4.1	221.2	24.26	Release 10 15:44-16:29 - 7.9m
235	CR02/LOS2	16:35	16:47	4.4	229.6	24.17	Release 11 16:34-17:16 - 3m
236	CR02/LOS2	16:47	16:59	4.4	229.3	24.81	Release 11 16:34-17:16 - 3m
237	CR02/LOS2	16:59	17:10	3.8	227.0	21.72	Release 11 16:34-17:16 - 3m

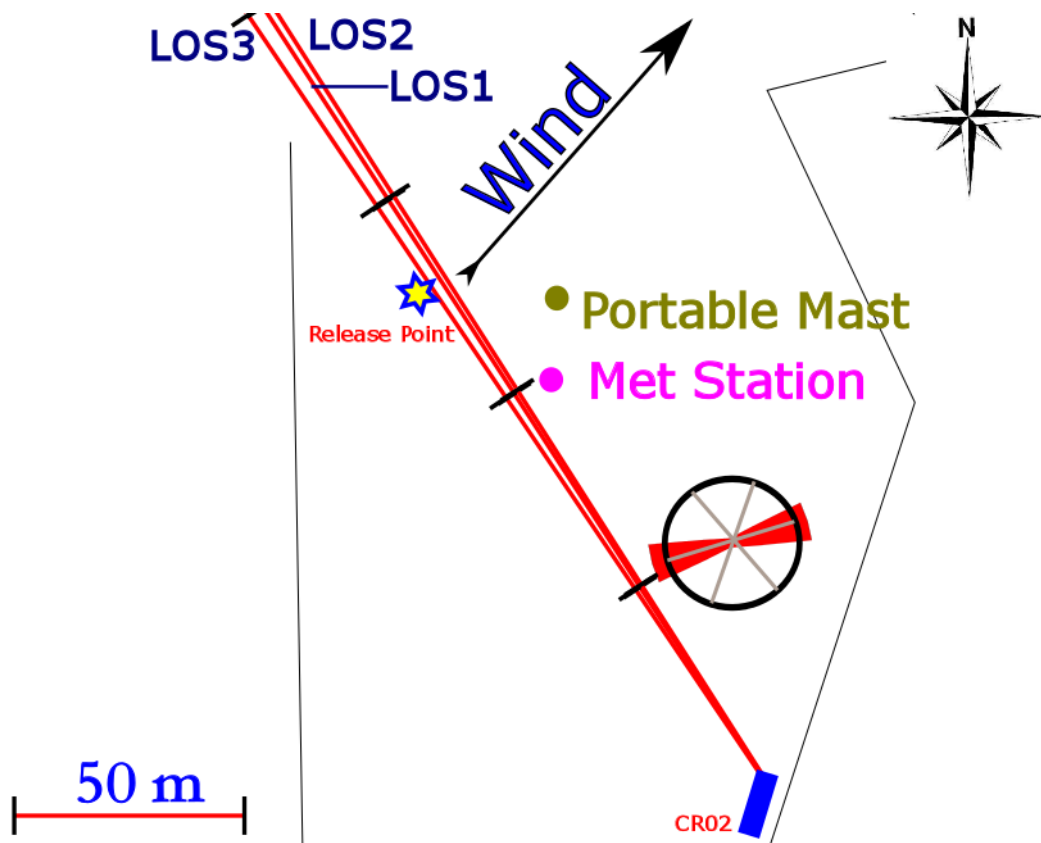


Figure 2.2 Measurement configuration for location CR02 on 13th of October.

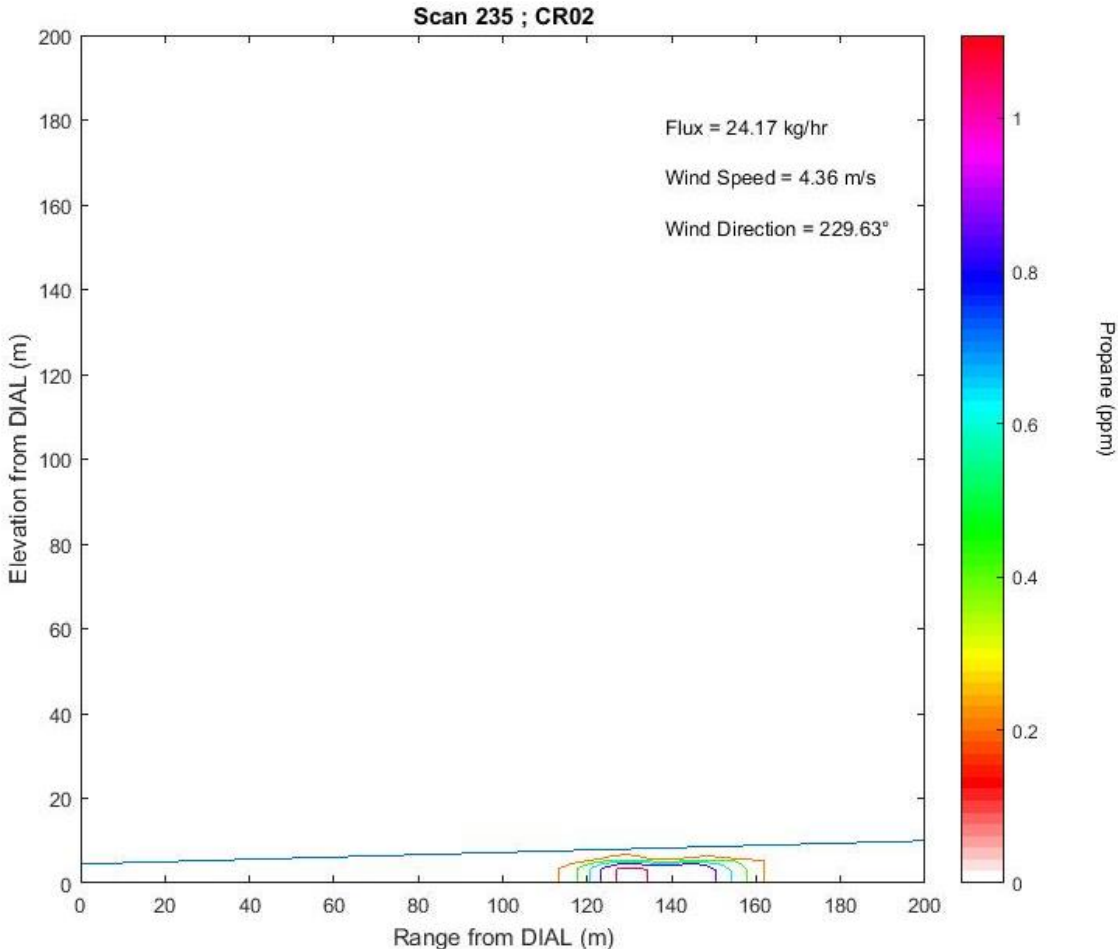


Figure 2.2a1 Observed propane concentration for Scan 235 representing CR02/LOS2.

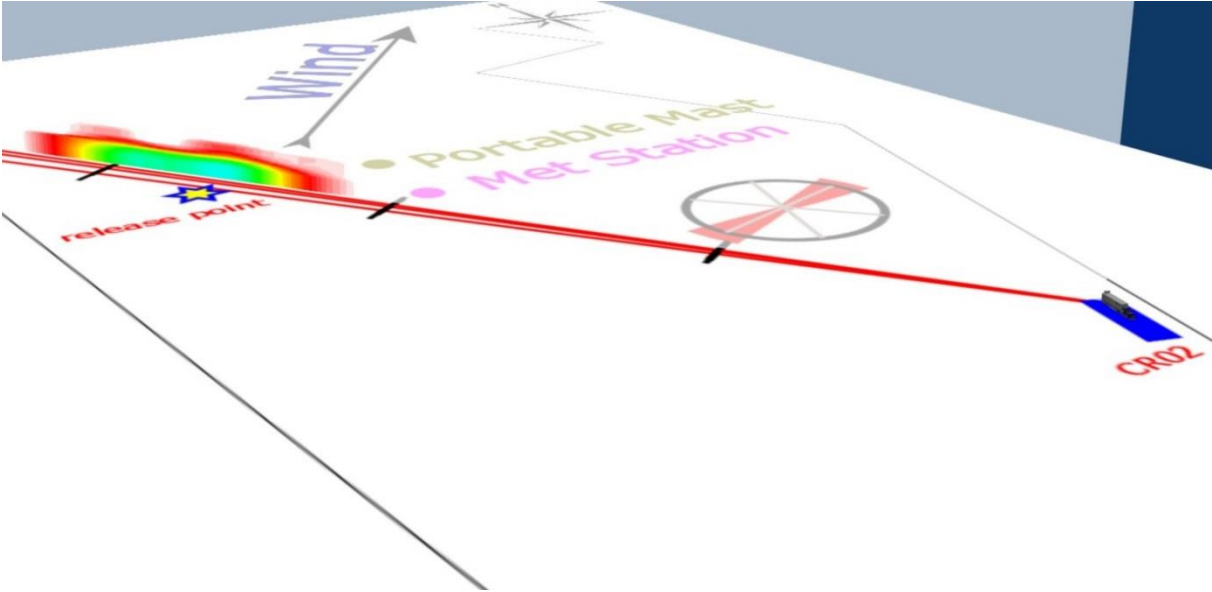


Figure 2.2a2 Visualisation of emission rate for Scan 235 representing CR02/LOS2.

3 RESULTS DISCUSSION FOR CONTROLLED RELEASE EXPERIMENT

Table 3.2 Summary of determined propane emission rates, for each controlled release the average flux and standard deviation are reported. Positive and negative % difference between measured and released rates corresponds to overestimation and underestimation of emissions respectively.

Date	Location/ LOS	Notes	Average Flux	Standard Deviation	Scans	Controlled Release	Difference	
			kg/hr	kg/hr			kg/hr	%
12-Oct	CR01/LOS1/2	Release 1 13:02-13:56 - 3m	4.8	1.3	6	5.8	-1.0	-17.3
12-Oct	CR01/LOS2	Release 2 14:00-14:55 - 3m	11.0	1.0	4	11.6	-0.6	-4.8
12-Oct	CR01/LOS2	Release 3 15:00-15:58 - 3m	15.2	3.0	3	17.4	-2.2	-12.6
13-Oct	CR02/LOS1	Release 5 10:44-11:43 - 3m	12.9	2.0	4	13.9	-1.0	-7.2
13-Oct	CR02/LOS1/2	Release 6 11:47-12:40 - 6.4m	5.1	1.3	4	4.6	0.5	10.0
13-Oct	CR02/LOS2/3	Release 7 12:48-13:41 - 7.9m	17.5	3.9	4	18.0	-0.5	-2.8
13-Oct	CR02/LOS2/3	Release 8 13:43-14:38 - 7.9m	1.1	0.8	3	1.6	-0.5	-31.1
13-Oct	CR02/LOS3	Release 9 14:44-15:39 - 7.9m	9.5	1.0	3	9.3	0.2	1.9
13-Oct	CR02/LOS2	Release 10 15:44-16:29 - 7.9m	25.0	1.3	3	25.4	-0.4	-1.5
13-Oct	CR02/LOS2	Release 11 16:34-17:16 - 3m	23.6	1.6	3	23.9	-0.3	-1.4

Data collected during the controlled release experiment was independently evaluated by each contractor and submitted to SCAQMD in January 2016. After all contractors submitted their results, SCAQMD made the actual release rates known simultaneously to all contractors. Table 3.2 provides a summary of the measured DIAL propane rates and a comparison with the released rates. For each release the difference between the released and DIAL rates was less than the standard deviation of the DIAL measurements. This includes Release 8 that was quite low and close to the DIAL detection limit that during this experiment can be estimated to be between 0.5 kg/hr and 1 kg/hr. The emission rates measured by the DIAL were also linear as shown in Figure 3.1 with an excellent R² value.

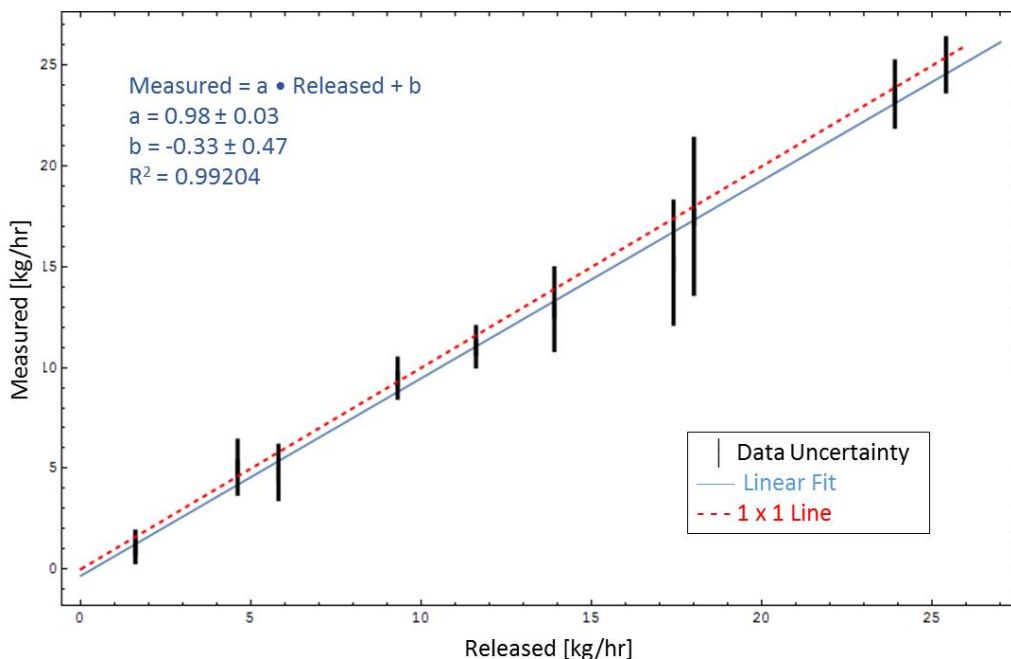


Figure 3.1 Comparison of actual propane release rates with DIAL measurements.

Figure 3.2 shows a histogram of the difference between the DIAL and released rates for each individual DIAL scan measured during the ten controlled releases. Although the number of samples is

fairly low, an inspection of the data shows an approximately normal distribution. Apart for a scan measured during the low emission release (8) all the other individual scans were < 40% off the controlled release values. Also, 89% and 75% of the scans were < 30% and < 20% off the controlled release rates respectively. Excluding the low emission release (8), the differences between the average DIAL and controlled release rates were between -17% (underestimate) and 10% (overestimate) and in four sets of controlled releases this difference was less than 5%. The sum of all the DIAL emission rates and the release rates are 125.7 kg/hr and 131.5 kg/hr respectively, with a difference of only - 4.4%. This is equivalent to an approximately ten hour long controlled release experiment but also it simulates DIAL measurements of different areas on a site that are then summed together to obtain an estimate of the total emission.

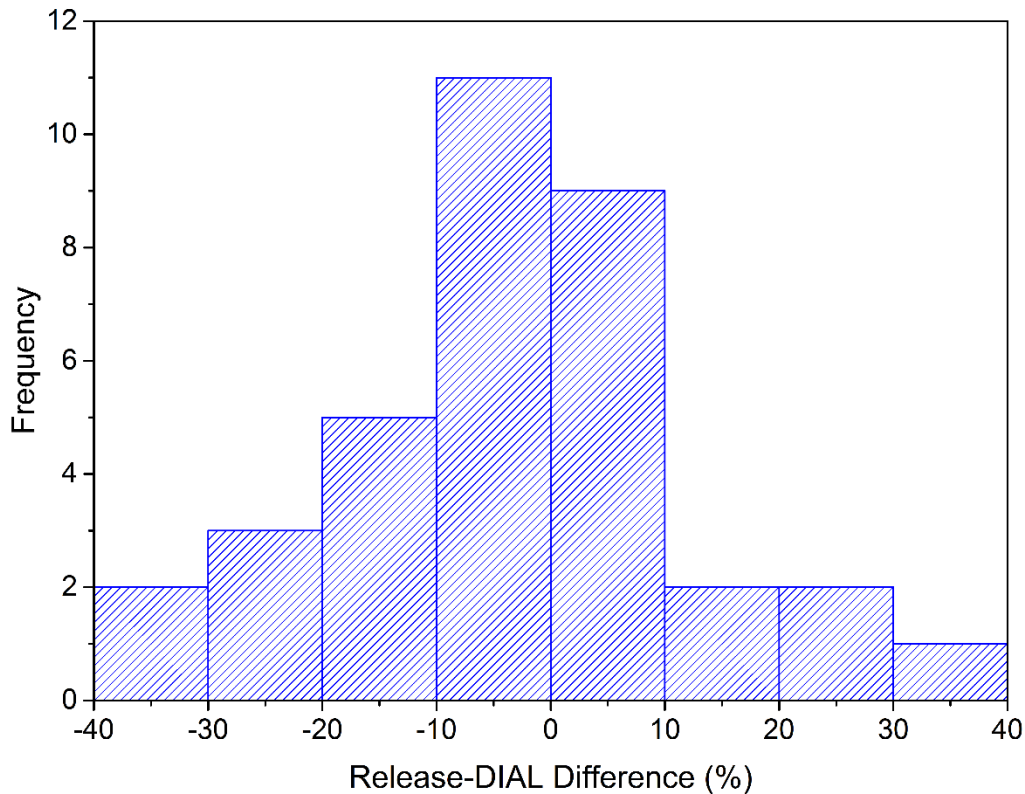


Figure 3.2 Histogram of the DIAL-Release rates difference for each scan.

3.1 CONCLUSION

During the SCAQMD blind controlled release study the DIAL method was demonstrated to be very accurate. The DIAL method was not affected by meteorological conditions and it was able to report emissions from all the test releases, owing to its ability to change scan configuration to match the wind conditions.

4 ANNEX 1: DESCRIPTION OF THE DIAL TECHNIQUE

4.1 OVERVIEW OF THE DIAL TECHNIQUE

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

4.2 DESCRIPTION OF THE THEORY OF DIAL MEASUREMENTS

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

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

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

The equation has three basic components:

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

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

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

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

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

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

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 energy normalisation of the on- and off-resonant signals respectively.

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

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

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

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

4.3 DESCRIPTION OF FACILITY OPERATED BY NPL

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

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

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

The following sections describe the DIAL system in more detail.

Source

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

Detection

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

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

Data Analysis

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

The data analysis process consists of the following steps:

i) Background subtraction

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

ii) Normalisation for variation in transmitted energy

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

iii) Calculation of path-integrated concentration

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

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

iv) Derivation of range-resolved concentrations.

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

v) Calculation of emission rates

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

The emitted rate is calculated using the following mathematical steps:

- (a) The product is formed of the gas concentration measured with the DIAL technique at a given point in space, and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.
- (b) This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.
- (c) This array of results is then integrated over the complete concentration profile to produce a value for the total emitted rate.

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

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

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

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

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

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

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

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

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

Table A1.1 Ultraviolet capability of NPL DIAL Facility

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

Table A1.2 Infrared capability of NPL DIAL Facility

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

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

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

4.4 RELATIONSHIP BETWEEN EMISSION RATE AND CONCENTRATIONS

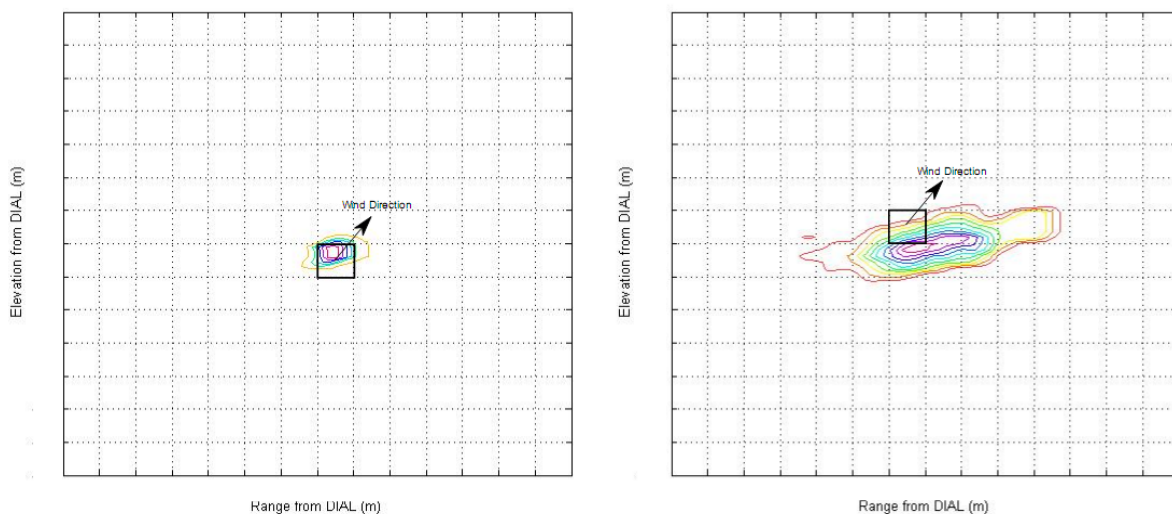


Figure A1.1 Illustration of the emission rate calculation approach

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

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

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

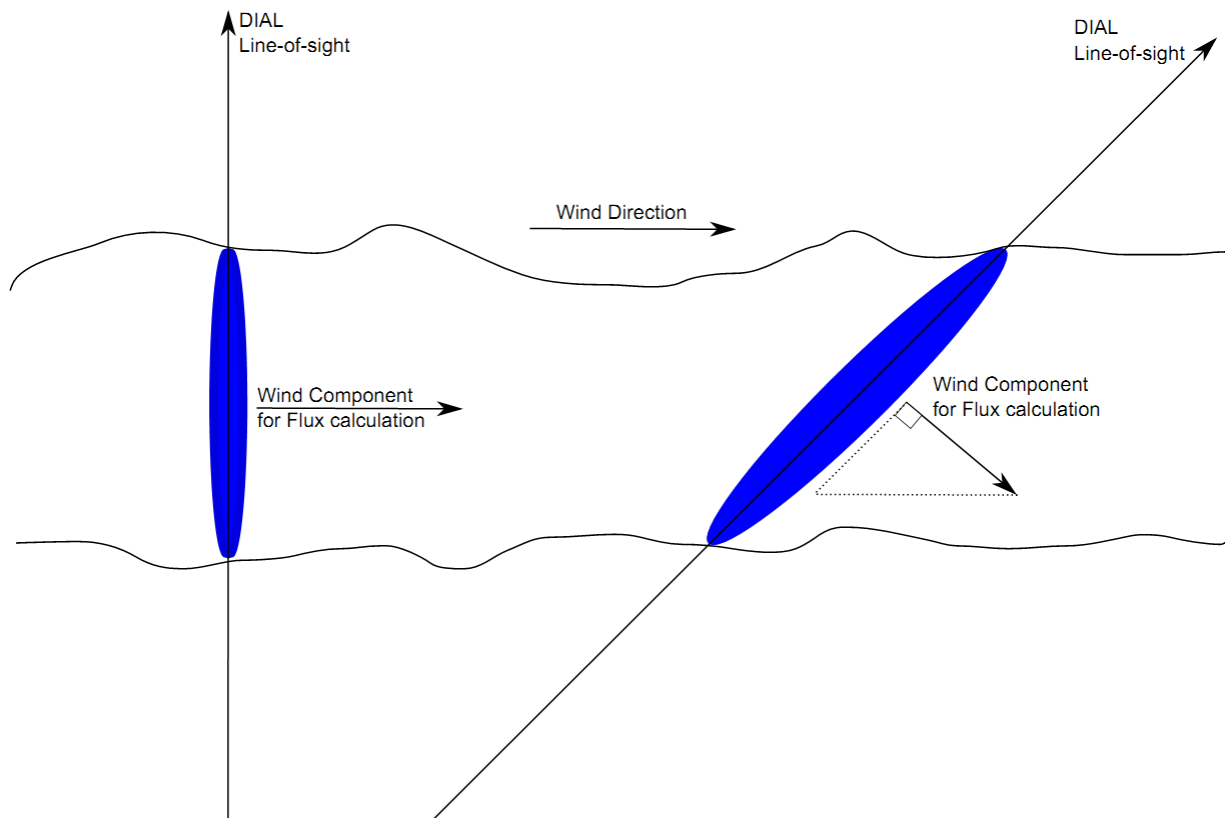


Figure A1.2 Schematic showing relationship between emission rate and wind direction

4.5 CALIBRATION AND VALIDATION

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

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

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

- i) Intercomparisons have been carried out on chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL beam was directed along the same line-of-sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range C₂ - C₈. 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 emission rates and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within $\pm 12\%$.
- iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission rates to within $\pm 15\%$.

5 ANNEX 2: DESCRIPTION OF AREA-SOURCE FACILITY

The Area Source Facility (ASF) is a custom-made controlled gas release system capable of mimicking various emission patterns and rates as encountered in industrial environments. Initially, the system was developed by the NPL in order to validate the emissions measured by NPL's DIAL system. The ASF has been used multiple times for quality-assurance and control of the two DIAL systems designed and operated by NPL. Figure A2.1 shows a picture of the ASF deployed in a tower release configuration for a comparison between NPL DIAL systems (seen in the background).



Figure A2.1 The ASF deployed in a tower release configuration.

The ASF consists of high flow gas blender controlled by custom-made software and distribution and emission system comprised of the release nodes and distribution hoses to connect nodes to the blender.

The high flow blender consists of four main gas channels, each with a mass flow controller (MFCs) with full scale flow equivalent to 500 l/min propane, and two smaller channels (100 l/min nitrogen), which can be blended into each of the four main channels by the control of appropriate valves. These smaller channels are intended to be used for introducing interfering or tracer gases and also for purge gas. Figure A2.2 shows a schematic and photograph of the high flow blender system. The blender unit measures approx. 1.2 x 1.1 x 0.4 m, weighs about 100 kg and is enclosed within a housing similar to a flight case.

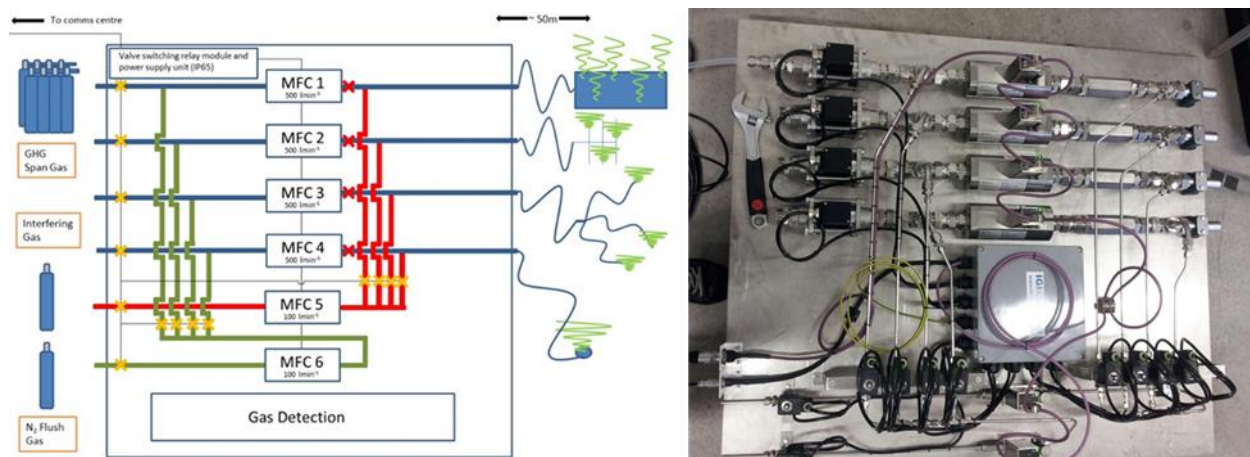


Figure A2.2 Drawing (left) and photograph (right) of the high flow gas blender.

The system is controlled through customized software utilizing the Brooks SMART Interface. The software allows direct control of the MFCs and valves. Execution of a pre-programmed routine is also possible.

The ASF has four primary distribution hoses to connect the high flow blender to the release nodes. The hoses are Swagelok 1" PB rubber hoses that are chemically compatible with most inorganic and non-aromatic organic gases and fluids. An example distribution hose and emission node are depicted in Figure A2.3. This arrangement means that up to four spatially separated and independently controllable release nodes can be set up.



Figure A2.3 Pictures of the distribution hose (left) and emission node (right).