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Carbon dioxide release by industrial processes, such as fossil fuel combustion, is a major anthropogenic contributor to the greenhouse effect. The quantification of this emission is therefore important. There has been very little verification of calculated CO2 emissions by measurements of emitted CO2. We report on the ability of our differential absorption lidar system to directly and remotely measure the mass emission rate of CO2 in the plume from a power station, demonstrating its potential use in the future as a tool to validate reported emissions. Further work is necessary to enable the system to quantify emissions from smaller emitters, for example detection of fugitive emissions where there is wider interest in the application of this technique.

Environmental Science: Processes & Impacts RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

First Measurements of a Carbon Dioxide Plume from an Industrial Source Using a Ground Based Mobile Differential Absorption Lidar

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The emission of carbon dioxide (CO_2) from industrial sources is one of the main anthropogenic contributors to the greenhouse effect. Direct remote sensing of CO_2 emissions using optical methods offers the potential for the identification and quantification of CO_2 emissions. We report the development and demonstration of a ground based mobile differential absorption lidar (DIAL) able to measure the mass emission rate of CO_2 in the plume from a power station. To our knowledge DIAL has not previously been successfully applied to the measurement of emission plumes of CO_2 from industrial sources. A significant challenge in observing industrial CO_2 emission plumes is the ability to discriminate and observe localised concentrations of CO_2 above the locally observed background level. The objectives of the study were to modify our existing mobile infrared DIAL system to enable CO_2 measurements and to demonstrate the system at a power plant to assess the feasibility of the technique for the identification and quantification of CO_2 emissions. The results of this preliminary study showed very good agreement with the expected emissions calculated by the site. The detection limit obtained from the measurements, however, requires further improvement to provide quantification of smaller emitters of CO_2, for example for the detection of fugitive emissions. This study has shown that in principle, remote optical sensing technology will have the potential to provide useful direct data on CO_2 mass emission rates.

Introduction

The emission of carbon dioxide (CO_2) from fossil fuel combustion in power generation and other industrial sources is one of the main anthropogenic contributors to the greenhouse effect (e.g. Figure 2.1(a) in the IPCC's 2007 synthesis report[1]). Current mechanisms for reducing CO_2 emissions through economic instruments, such as the European emissions trading scheme[2], rely on the accurate reporting of mass emissions, as laid out for example in the EU Monitoring and Reporting Regulations (MRR)[3]. These approaches use mainly calculation based techniques, in which the emitted CO_2 is determined from source parameters. For combustion plants, which in 2011 accounted for 80% of the UK's traded CO_2 [4], these source parameters are fuel use, an emission factor based on the carbon content of the fuel and a combustion efficiency factor (to take account of unburnt carbon).

There has been very little direct verification of calculated CO_2 emissions by measurement of the emitted CO_2 and indeed no relevant citations could be found by the authors, searching online reference sources (keywords: emissions trading, CO_2, measurement). Calculation approaches offer a cost effective and accepted approach for many simple combustion processes. Direct measurement of emission flue gas parameters (flow and concentration) provides a means to directly determine CO_2 mass emission rates as described in the MRR, and this could be used to provide an independent validation of reported emissions. However, for complex sites with multiple or distributed emission points and for processes which are handling CO_2 rich streams, for example carbon capture and storage (CCS) facilities where leaks and fugitive emissions may be a significant component of the overall emissions, direct monitoring at release points becomes less cost effective, and input based calculation approaches, or mass balance methods may be subject to higher levels of uncertainty owing to the increased complexity.

Direct remote sensing of CO_2 emissions using optical methods offers the potential for the identification and quantification of CO_2 emissions. This has potential application for the verification of emissions and the identification of fugitive emissions from CO_2 transport and processing infrastructure. In addition, this sort of monitoring can be less intrusive, and may even be carried out from outside the facility.

Differential absorption lidar (DIAL) has long been used for such monitoring of a range of gaseous emissions, for example for quantifying hydrocarbon emissions from petrochemical plants and methane emissions from waste and landfill[5,6] and has been used extensively for measuring industrial emissions plumes, for example Carruthers et al[7] report the use of lidar and DIAL data in validating dispersion models.

The DIAL technique is based on the use of pulsed laser radiation tuned to a specific absorption feature to probe the atmosphere.

Analysis of radiation scattered by the atmosphere enables the spatial distribution of gas concentration to be measured allowing maps of target compounds to be constructed. Such data can be combined with meteorological data to enable emission rates (fluxes) to be determined. More details on the use of DIAL to determine industrial emissions can be found in Robinson[5].

A ground-based CO_2 DIAL profiling system was reported to be under development by NASA[8,9]. It uses 100 mJ energy double pulsed Ho:Tm:YLF laser locked to a CO_2 absorption line and operating from a side-line position. The expected CO_2 profiling capability is from the boundary layer to 5 km, with 0.5-1.0 km resolution and 1-2 ppm precision, operating in the 2000 nm wavelength region with a half hour averaging period. Johnson et al[10] report the development of a micro-pulse DIAL system for identification of leakage of CO_2 from carbon sequestration sites. The configuration for the system is designed for long term monitoring of a large area, and the system has a reported range of up to 2.5 km with range dependent resolution of between 200 m to 750 m, and a temporal averaging period typically of one hour. This makes it potentially suitable for monitoring a CCS storage site but not for measurements of an emission plume from an industrial source, where shorter spatial and temporal resolutions are required. Others (for example, Fabien[11]) have investigated the use of CO_2 DIAL in the 2000 nm region to measure the turbulent flux of CO_2 in the atmospheric boundary layer. This approach is aimed at determining the net transport and exchange of CO_2 between the surface (biosphere) and the atmosphere and it is not targeted at quantifying the emission flux in an elevated plume from an industrial source. Fiorani et al[12] report on the potential application of DIAL to the measurement of CO_2 in plumes from volcanic emissions, and provide a summary of CO_2 DIAL systems in development or use as of 2012. The systems listed either determine path integrated concentrations, or where they do provide range resolved measurements these have resolutions of >200m, and so are not designed to measure individual industrial plumes.

To our knowledge, DIAL has not previously been successfully applied to the measurement of emission plumes of CO_2 from industrial sources.

The objectives of this study were to modify our existing mobile infrared DIAL system to enable measurements of CO_2 and to demonstrate the system at a power plant to assess the potential application of the technique for the identification and quantification of CO_2 emissions.

In this paper we present the DIAL measurements of a CO_2 plume from an industrial source - a coal fired power plant. We describe the modifications needed to an infrared DIAL system to enable it to measure CO_2 and we report on the capabilities of the modified DIAL system. We then present the results of a preliminary field demonstration of the modified DIAL system, in which emission fluxes from a power plant were quantified.

Methodology

Overview of the DIAL technique

The DIAL technique is described in detail in Robinson et al[5], however, for completeness we provide a brief summary in this section. DIAL is an extension of the Lidar (LIght Detection And Ranging) technique, in which short (few nanosecond) pulses of laser light are transmitted into the atmosphere and the time resolved backscattered signal is measured. This gives information on the distribution of the scattering media along the line of the transmitted pulse. In the DIAL technique, the transmitted laser pulses are tuned to two (or more) wavelengths in order to measure a specific compound in the atmosphere. To achieve this one pulse is tuned to an absorption feature of the target compound (the so called on-line wavelength) and the other is tuned to be just off the absorption feature (known as the off-line wavelength), but at a close enough wavelength that differential scattering and absorption due to other atmospheric compounds is kept to a minimum and in many cases can be assumed to be negligible. One signal will therefore be absorbed by the target compound in the atmosphere, the other will not. The concentration of the target species in the atmosphere is determined from the ratio of the two signals following the DIAL equation[13].

Selection of CO_2 wavelengths

In order to measure CO_2, a suitable pair of wavelengths for the DIAL laser pulses was chosen. The selection of the CO_2 infrared absorption feature to use was based on the following considerations:

A) System capability.

A key driver for this study was that the laser pulse generation should be achievable using our current DIAL system without the requirement for major modifications to the laser source which operates around 3000 nm. The availability of a mechanism, described below, to generate the required laser pulses at the CO_2 absorption band around 1500 nm which used the existing non-linear optical stages was a major factor in the selection of the CO_2 lines chosen for use.

B) Absorption strength

The strength of the CO_2 absorption feature at the two wavelengths chosen for the DIAL measurement, and hence the related differential absorption coefficient ($\Delta\alpha$), has a number of consequences. Clearly, a strongly absorbing feature will improve the sensitivity of the measurement. However, because there is a relatively high background level of CO_2 in the atmosphere, there will be a significant attenuation of the on-line laser pulses due to absorption, effectively reducing the range of the DIAL measurements. Conversely, selecting a line which is too weak will reduce the sensitivity, potentially to the point where the emitted CO_2 plume will not be detectable. The atmospheric CO_2 absorption band around 1500 nm contains individual lines which give a predicted absorption, determined from Hitran 2000 [14], of approximately 7% over a 500 m DIAL path-length under typical atmospheric conditions. The use of this line strength is supported by the analysis of the selection of an appropriate differential absorption in the presence of background concentrations given in Measures[15].

C) Spectral interference

The selected absorption feature should be in a region free from interference from other atmospheric species, in particular water vapour. While there are water absorption features in the 1500 nm wavelength region, these are not saturated under typical water vapour mixing ratios, and the narrow bandwidth of the DIAL laser pulses ($0.128\ cm^{-1}$, see the results and discussion section) enables the selection of specific wavelengths which avoid water absorption features.

Based on these selection criteria, the CO_2 absorption band in the region of 1500 nm was chosen for further investigation. Hitran 2000 parameters were used to generate the CO_2 absorption spectra from 1571 nm to 1573 nm. For the purposes of this study a Voigt line profile was used, with a temperature of 296 K and a pressure of 101.3 kPa. The CO_2 peak at a wavelength of 1572.66 nm has a modelled peak absorption, α_{on}, of $2.00\text{x}10^{-4}\ ppmv^{-1}.km^{-1}$. Selecting

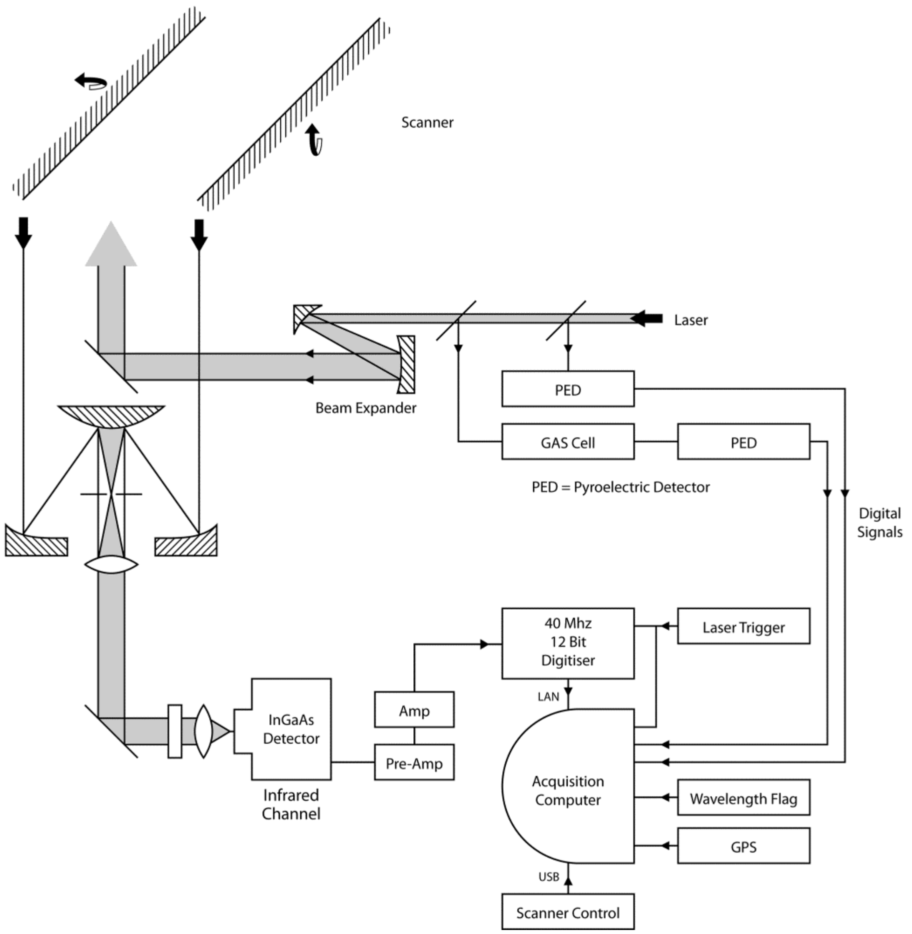

Figure 1. Functional outline of the NPL DIAL system.

Energy	5-10 mJ
Laser repetition rate	10 Hz
Pulse length	4 ns
Telescope diameter	0.5 m
Field of view of telescope	~ 1 mrad
Laser divergence	~ 0.2 mrad

Table 1. Key characteristics of the lidar system.

the second DIAL wavelength to be just off this absorption feature, at 1572.46 nm, gives a differential absorption due to CO_2 between the two wavelengths of $\Delta\alpha = 1.873\times10^{-4}$ $ppmv^{-1}.km^{-1}$.

A significant challenge in observing industrial CO_2 emission plumes in the atmosphere is the ability to discriminate and observe localised concentrations of CO_2 above the atmospheric CO_2 background level. This was measured to be approximately 395 ppmv, determined in this study in the field close to ground level using a Picarro G2301 cavity ringdown spectrometer. The absorption of this background over a 1 km path, given by Eq 1, is 7.21×10^{-2}. This is equivalent to the absorption that would be observed with a 500 m DIAL measurement range, as the laser pulses travel out and back through the atmosphere.

$$\boldsymbol{A = C.L.\Delta\alpha} \qquad \text{Eq 1}$$

Where:

A is the absorption over the path = ln (Initial Intensity/Final Intensity)
C is the concentration ppmv
L is the path in km
Δα is the differential absorption in $ppmv^{-1}.km^{-1}$

Development of infra-red DIAL CO_2 monitoring capability

The infra-red (IR) DIAL system developed and operated at NPL generates wavelength tuneable, narrow bandwidth IR laser pulses required for the spectrally specific detection of IR -active chemicals. The NPL IR DIAL was developed to measure hydrocarbon absorption features at around 3000 nm. It has since been used to monitor a range of pollutants, including HCl, CH_4, C_2H_6 and various other individual hydrocarbons. Methodologies have also been developed and used successfully to determine emission fluxes by combining range-resolved concentration measurements made using the DIAL with measurements of wind speed and direction.

Figure 1 presents a functional schematic of the system. In order to adjust the system to monitor CO_2 it was necessary to modify three key components: the laser source, the infrared detection system and the gas cell used for online diagnostics.

Table 1 gives the key characteristics of the lidar system.

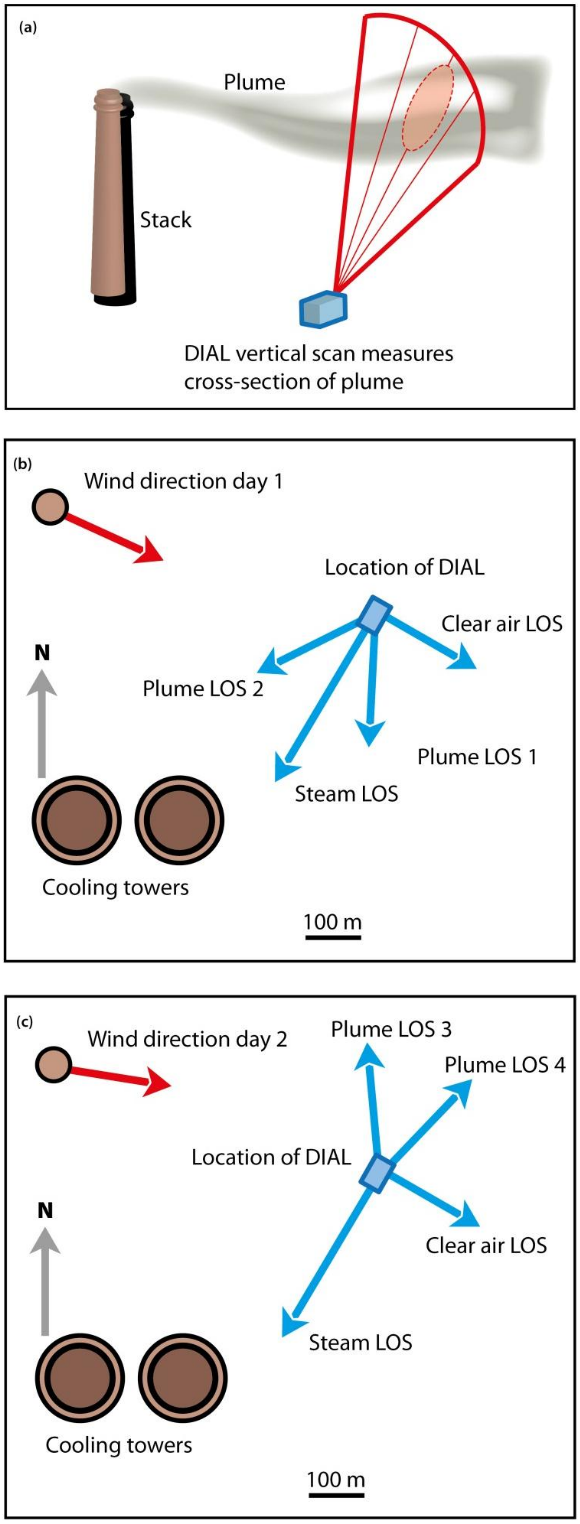

Figure 2. Configuration of DIAL measurements of the CO_2 plume from a power station. a) Conceptual configuration. b) Day one and c) day two aerial view of measurement alignments. Note that the plume was almost above the DIAL for LOS 1 and 2.

Laser source. In its usual configuration the NPL IR DIAL system generates 3000 nm laser pulses using a difference frequency mixing (DFM) stage which mixes the outputs from a tuneable dye laser and an injection seeded Nd-YAG laser in a lithium niobate crystal, and an optical parametric amplification (OPA) stage[16]. Amplification is achieved by mixing a low power 3000 nm pulse with a high power, seeded, Nd-YAG laser pulse within a second lithium niobate crystal. This process results in the generation of an idler beam, which has a wavelength given by Eq 2. In normal operation of the DIAL this beam is not used.

$$\frac{1}{\lambda_i} = \left(\frac{1}{\lambda_p} - \frac{1}{\lambda_s}\right) \qquad \text{Eq 2}$$

Where:
λ_i is the idler wavelength
λ_p is the pump wavelength
λ_s is the signal wavelength

For the CO_2 measurements the Nd-YAG pump wavelength, λ_p, defined by the seed laser, is 1064 nm and the 3000 nm dye laser output was tuned to deliver 3289.5 nm following the DFM stage. The idler wavelength was therefore at 1572.7 nm, and the transmit optics were changed to use this near-IR beam as the output from the laser source.

Detection system. The cryogenically cooled InSb detector used for 3000 nm measurements did not have suitable sensitivity in the 1500 nm region. Therefore an InGaAs detector from OEC GmbH designed to work in the 900 nm to 1700 nm wavelength range was integrated into the system. The detector head housed a 0.78 mm^2 detector and a low noise preamplifier, connected to a main amplifier by a shielded cable. The main amplifier was switchable between 2.4 and 8 MHz, with a controllable gain between 1 and 35. Testing the detector/amplifier package using a calibrated 600 MHz oscilloscope determined the detectivity to be 1.17 (± 0.03) x 10^{11} $cm.Hz^{1/2}.W^{-1}$–. The optimum compromise between performance and noise was found with a 2 MHz bandwidth setting and a gain setting of $10^{1/2}$.

Diagnostic gas cell. Within the DIAL system, online diagnostics are provided by the use of a gas cell. Figure 1 includes a schematic of the diagnostic arrangement. A fraction of each transmitted laser pulse is passed through a reference gas cell, and measured using a pyro-electric detector (PED). Combined with the measurement of the pulse power on a second PED this provides an online shot-by-shot measurement of the absorption strength. The relatively low absorption strength of the selected CO_2 line meant that the normal configuration of a 20 cm gas cell would not have provided sufficient absorption to be measurable. Therefore, a Specac Cyclone C10 gas multi-pass cell was integrated into the system. This cell was configured to provide a path length of 10.6 m, and filled with CO_2 with 99.99% purity.

Field measurement

In order to assess the potential application of the DIAL for CO_2 measurements, the DIAL system was deployed at a coal fired power plant. In order to preserve the anonymity of the site, specific details have been generalised. The DIAL was located approximately 270 m from the base of the emission stack. The stack was over 150 m high. The DIAL measurement beam was scanned through the plume in vertical planes, as shown schematically in Figure 2. A series of measurements were made with different configurations depending on the wind direction. In addition, measurements were made of a clear region of the atmosphere (i.e. not downwind of the emission point) and of the steam plumes from the cooling towers. In total 42 measurement scans were made over 2 days.

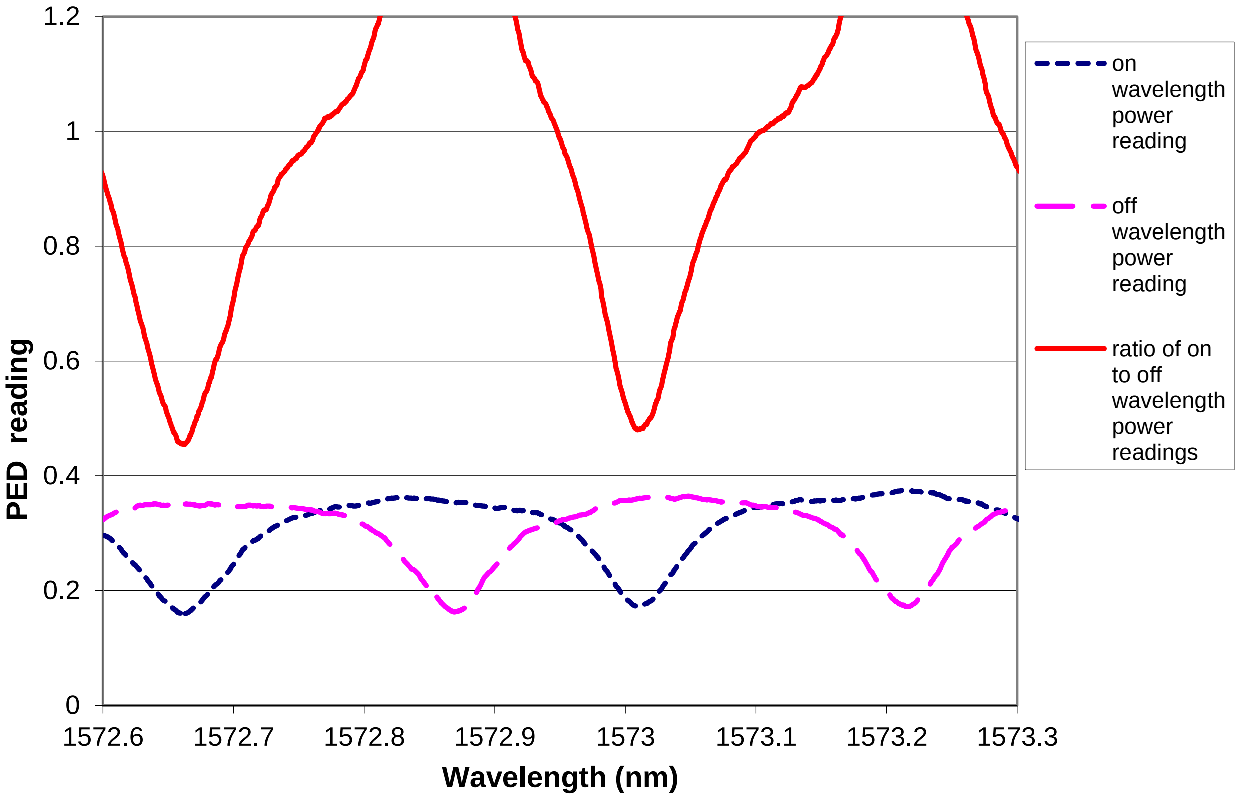

Figure 3. Example wavelength scan through CO_2 gas cell, showing normalised PED readings and the ratio of on- to off-CO_2 line normalised PED readings. Note that the off-line wavelength is equal to the on-line wavelength minus 0.20 nm.

This study was an initial investigation to assess whether the DIAL was able to observe the CO_2 plume. Therefore, limited measurements of the meteorological conditions were made as flux measurements were not the primary objective of this study. Measurements of the wind speed and direction were made using a combination of a cup anemometer and wind vane mounted on the DIAL's integrated 12 m meteorological mast and a portable 2-D sonic wind sensor mounted on a 2 m tripod. These measurements were not ideally located, as there were some upwind obstructions to the measured wind field caused by trees. For this reason wind direction measurements from a meteorological station 30 km from the site were also used, together with observations of the plume location. Despite the lack of optimal wind data, the available data were used to provide an estimate of the wind speed and direction for each measurement scan, and this was used to determine the CO_2 emission flux, using the approach described in Robinson[5]. This emission flux was compared to the emissions calculated by the site; their calculation was based on the amount of power generated.

Results and discussion

Determination of differential absorption

To confirm the spectral sensitivity of the DIAL to CO_2 and to determine the appropriate differential absorption parameter to use, the system was set to scan the on-line off-line pair of wavelengths across the chosen CO_2 spectral feature (maintaining the separation between the two wavelengths). The measured power readings from the PEDs were recorded and Figure 3 shows the results of one of these scans. The scan was over a wavelength range which encompassed two CO_2 absorption features. Examining the CO_2 peak at a wavelength of 1572.66 nm the normalised ratio between the power reading for λ_{on} and λ_{off} was found, from Eq 3, to be 0.4544.

$$\boldsymbol{Power\ Ratio} = \frac{\boldsymbol{NPED_{ON}}}{\boldsymbol{NPED_{OFF}}} \qquad \text{Eq 3}$$

Where:

$$\boldsymbol{NPED_{ON}} = \frac{\boldsymbol{CELL_{ON}}}{\boldsymbol{REF_{ON}}} \quad \text{and} \quad \boldsymbol{NPED_{OFF}} = \frac{\boldsymbol{CELL_{OFF}}}{\boldsymbol{REF_{OFF}}}$$

And:

$CELL_{ON}$ is the average of the power readings of the on-line wavelength pulses after passing through the CO_2 multiple-pass gas cell

$CELL_{OFF}$ is the average of the power readings of the off-line wavelength pulses after passing through the CO_2 cell

REF_{ON} is the average of the power readings of the on-line wavelength pulses

REF_{OFF} is the average of the power readings of the off-line wavelength pulses

For a cell of path length of 10.6 m containing pure CO_2 this is equivalent to a differential absorption, determined from Eq. 1, of 7.442×10^{-5} $ppm^{-1}.km^{-1}$. Comparing this to the theoretical differential absorption determined above of $\Delta\alpha = 1.873 \times 10^{-4}$ $ppm^{-1}.km^{-1}$, the observed differential absorption is significantly smaller.

Two main effects contribute to this observation:

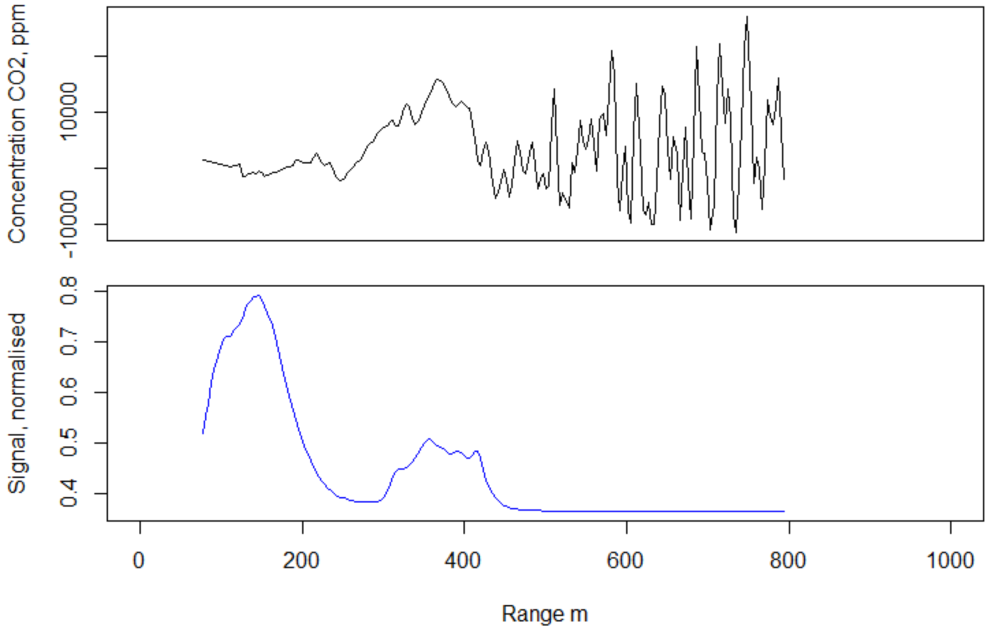

Figure 4. Upper panel: Range resolved concentration of CO_2 determined from on and off-resonant wavelength returns. Lower panel: normalised signal return of the off-resonant wavelength.

1) The theoretical absorption has been calculated with a line shape modelled for atmospheric conditions, however, the cell contains pure CO_2 which will have a spectrum which will be self-broadened, rather than air-broadened.

2) The DIAL system will introduce an instrument line shape (ILS) on the measured spectrum due to the spectral width of the laser pulses.

The effect of the broadened line shape can be taken into account as follows. The theoretical self-broadening width was determined from Hitran 2000 parameters. The observed broadening seen in the gas cell will be due to the combined effect of the ILS and the self-broadening, and so the ILS can be estimated from the additional broadening in excess of the self-broadening. This measured ILS is then applied to the theoretical air-broadened CO_2 line to determine the observed line width from which the system differential absorption to be used for the field measurements can be determined.

The observed full width half maximum (FWHM) for the CO_2 peak from the cell measurement is 0.244 cm^{-1}. This is a convolution of the self-broadened line width and the ILS. From Hitran the FWHMs for this peak are 0.1494 cm^{-1} for air broadening and 0.2064 cm^{-1} for self-broadening. The ILS is determined, assuming a simple relationship between the line widths, from Eq 4.

$$\boldsymbol{FWHM_{ILS}} = \sqrt{\boldsymbol{FWHM_{CELL}}^2 - \boldsymbol{FWHM_{SELF}}^2} \qquad \text{Eq 4}$$

Where:
$FWHM_{ILS}$ is the broadening effect of the selected CO_2 peak due to the ILS function,
$FWHM_{CELL}$ is the observed width of the selected CO_2 peak in the gas cell,
$FWHM_{SELF}$ is the theoretical width of the peak due to self-broadening.

The DIAL ILS determined from Eq. 4 is 0.128 cm^{-1}. Applying this ILS broadening to the HITRAN air broadened CO_2 peak enables us to determine the line width which would be observed when using the DIAL for atmospheric measurements. This predicts a combined air-broadened and ILS-broadened width for the CO_2 line of 0.197 cm^{-1}. The differential absorption observed from the gas cell measurements was then multiplied by the ratio of the observed line width in the cell and the predicted line width for atmospheric measurements, to give a predicted differential absorption for atmospheric measurements which takes account of the DIAL ILS. This gave a value for the differential absorption of 9.179×10^{-5} $ppm^{-1}.km^{-1}$. This value was used in the analysis of DIAL field data to determine the observed CO_2 concentrations and CO_2 fluxes.

CO_2 emission measurements

Figure 4 presents an example measurement of the plume taken at the industrial site. The lower plot displays the normalised return signal of the off-resonant wavelength. This plot shows that there is a region of enhanced backscatter related to the plume. The upper panel shows the range resolved concentration derived from the analysis of the on- and off-resonant wavelength return signals. The CO_2 plume is clearly discernable in the range 250-450m. The concentration data shows an increase in noise with range as expected for a DIAL measurement.

Sequences of DIAL measurements at different elevation angles were made to provide vertical scans. These were analysed to provide two dimensional CO_2 concentration maps of cross sections through the emission plume. Figure 5 shows a composite (average) plot of the plume observed in a series of vertical scans (the LOS4 data set) approximately 600 m downwind from the emission source. These data have been smoothed using a 19 m x 19 m 2D smoothing function. It is clear that the DIAL has been able to detect the extent and structure of the CO_2 in the plume observable above the background.

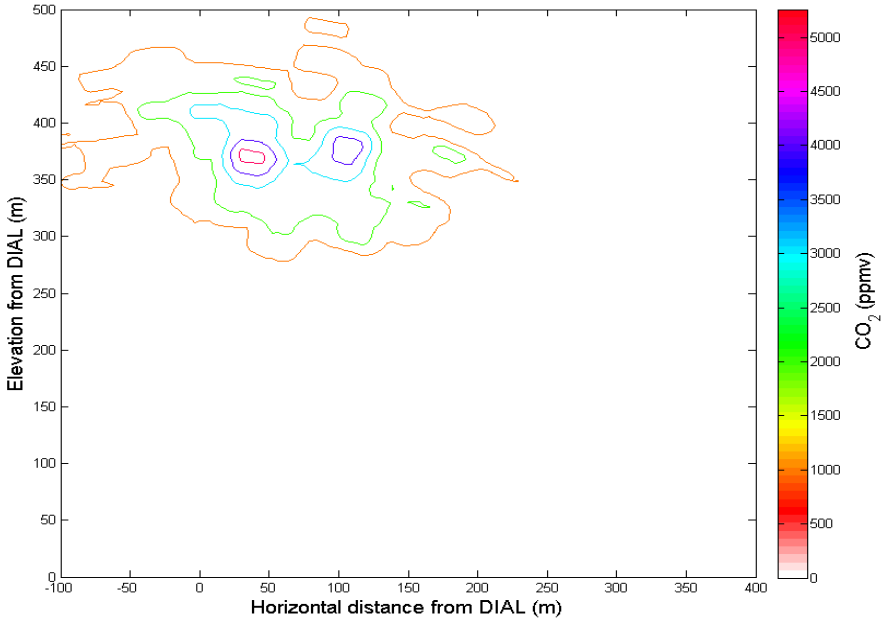

Figure 5. Average CO_2 plume cross section observed by DIAL

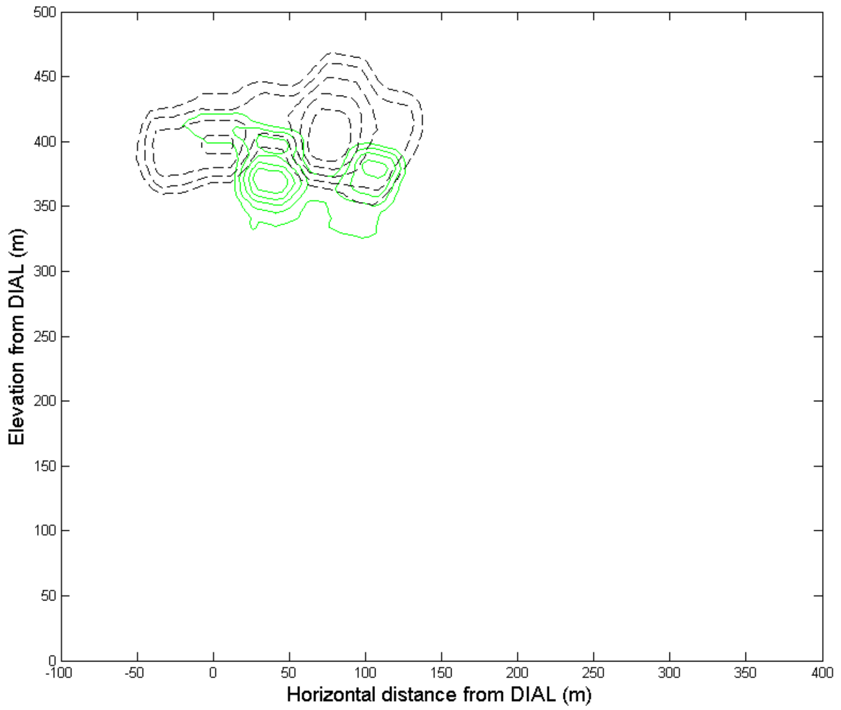

Figure 6. Cross section of CO_2 plume (solid lines) and aerosol backscatter (dotted lines). Contour lines are normalised to the respective maximum to allow comparison between aerosol backscatter and CO_2 concentration.

Data set	Number of Scans	Average Flux Measured by DIAL Tonnes CO_2 /hr	Standard Deviation of DIAL Measurements Tonnes CO_2/hr	Average Site Determined Emission Tonnes CO_2 /hr
Clear	4	52	127	N/A
Steam	4	18	148	N/A
Combined plume measurements (LOS 1-4)	29	2611	489	2723
Combined ‘zero’ measurements (steam + clear)	8	35	129	N/A

Table 2. Summary of DIAL CO_2 emission rate results, including calculated site emissions for the same period as the DIAL was measuring the plume.

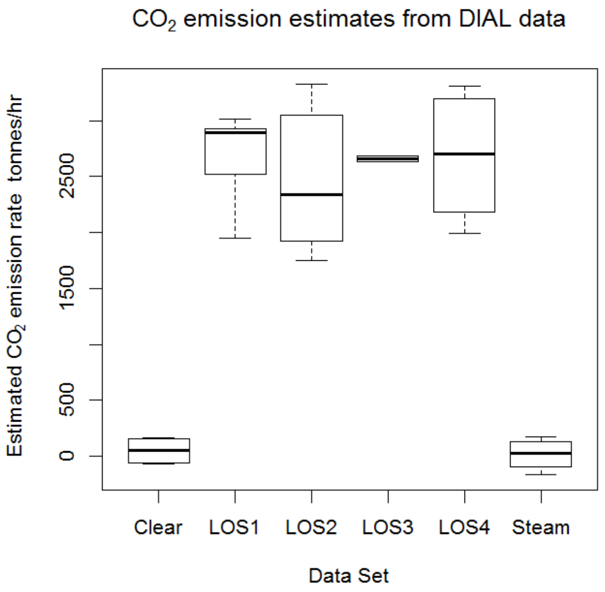

Figure 7. Box plot summary of DIAL CO_2 emission flux results.

The plume cross-section is repeated in Figure 6, with the addition of an indication of the aerosol plume (probably condensed water vapour), plotted as dashed black contour lines. The contour levels are based on normalised values for the two plots, to indicate the relative locations of the aerosol and CO_2 plumes. The aerosol plot has been determined in a basic manner from the absolute backscatter signal in the off-line wavelength channel, after normalisation for the $1/R^2$ fall-off of the DIAL signal and subtraction of a signal offset level. This is not a quantitative measure of the aerosol, but it does give a visual indication of the location of the aerosol plume from the power station stack. The aerosol and CO_2 data have been determined from the same DIAL signal returns, and so are coincident data. It is interesting to observe that the CO_2 plume appears to have separated from the water aerosol plume, presumably due to different buoyancy and dispersion. This is similar to an observation made previously when using the NPL DIAL to measure SO_2 plumes from a cement plant[17], in which for some measurements there appeared to be a similar separation of the gaseous compound from the aerosol. This is a phenomenon which will be the subject of future work.

The emission flux was estimated from the integral of the concentration maps combined with wind speed and direction data as described in Robinson[5]. The wind data were extrapolated from wind speed and direction measurements made at heights of 2m and 12m using a simple logarithmic vertical wind profile model. Different sets of measurements were made at different cuts through the plume at different angles. Table 2 presents a summary of the measurements. Two sets of measurements were not of the plume. The measurement set labelled ‘steam’ was a series of measurements through the cooling tower steam plume. The set labelled ‘clear air’ was a set of measurements of background atmosphere not downwind of the plant. These two measurements are similar implying that there was little interference in the plume measurement due to steam. The site continuously calculated the CO_2 emissions they expected to emit based on the amount of power generated. The measurement labelled ‘average site determined emission’ gives the amount of CO_2 emission that was calculated for the period during which our measurements of the plume were taking place.

It can be seen that the DIAL measurements are remarkably close to the expected emissions, given that the flux determination was not the primary aim of these exploratory measurements. Differences are most likely due to the limited wind direction and velocity data used, and to the relatively high detection limit caused by the use of a CO_2 line with comparatively low absorption cross-section, which will have meant the DIAL could have missed the diluted edges of the plume. Figure 7 is a box plot showing the median, quartiles and extent of the data for each set of measurements.

From the measurements made of steam and background air an estimate of the detection limit, in terms of CO_2 emission flux, can be made. The standard deviation of these ‘zero’ readings is 129 tonnes CO_2 per hour. Using the definition of detection limit from the European standard for instrument type testing, EN 15267-3 [18], which is twice the standard deviation at zero, the limit of detection for these measurements is 258 tonnes CO_2 per hour. This detection limit is based on the observed in-field performance during these preliminary measurements, and is approximately 10% of the CO_2 average observed emission rate from the site.

The standard deviation of the plume measurements is 19% of the average reading. The standard deviation of the plant emission data over the same periods is less than 2%, and so it is reasonable to assign the majority of the observed variability in the DIAL results to the measurement technique.

Conclusions

We have demonstrated for the first time that the DIAL technique can detect and map CO_2 concentrations in a power station plume. It was also possible to directly determine CO_2 emission fluxes using these data, although the measurements taken were not optimised for this.

The flux values obtained in this study used the available meteorological data, which was not optimised for flux measurements as the primary aim of this study was to ascertain whether CO_2 could be detected. Since the variability of the plume flux measurements is significantly higher than the variability of the 'zero' measurements, it is likely that the primary source for the observed variability is the wind data, which will have introduced significant uncertainty into the results. The detection limit obtained is equivalent to the emission of the 23rd ranked power station in terms of annual emission. Therefore, realistically, the system as currently configured for CO_2 would only be applicable to the quantification of the largest 10 to 20 power stations in the UK. Despite this, the results show very good agreement with the expected emissions from the site.

The large uncertainty obtained should not be considered a significant obstacle in the development of the CO_2 DIAL technique. In studies which target flux emission measurements we consistently record significantly improved meteorological data and consequently achieve much better detection limits. For measurements of methane and VOCs, uncertainties of ±15% have been achieved with the NPL DIAL[5] – with further work uncertainties approaching this level may also be achievable for CO_2. Further work would involve the deployment of a more appropriate meteorological monitoring system.

At present this technique could not be used for emission verification or model improvement, but with further development work these kinds of measurements may be possible. These developments will include using optimised meteorological data, which will improve the uncertainties associated with the flux measurements. Employing a stronger CO_2 line will also improve the sensitivity of the technique. A laser source tailored to the generation of the CO_2 wavelengths, rather than a retrofit modification of the existing system will be developed. This work will investigate the use of a laser source based on an Optical Parametric Oscillator, as previously demonstrated for methane measurements at NPL[19].

With these improvements many interesting CO_2 measurements which exploit the capabilities of the DIAL technique could be made. For example, the dispersion of a plume or direct verification of reported emissions could be measured. There is also interest in the use of the technique for the detection of fugitive emissions or leaks from carbon capture and storage facilities.

Acknowledgements

This work was supported by the UK Government National Measurement System Chemistry and Biology metrology research programme. The authors would also like to thank the power station site used in the field measurements, for allowing us access and for providing data on the calculated emissions.

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