# voc emissions from external floating roof tanks: comparison of remote measurements by laser with calculation methods

Prepared for the CONCAWE Air Quality Management Group, based on work carried out by the Special Task Force on DIAL measurement of gasoline tanks (AQ/STF-44):

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## ABSTRACT

Hydrocarbon emissions from storage tanks are normally calculated using procedures published by the American Petroleum Institute.

A laser-based technique has been used to measure remotely the emissions of hydrocarbons from floating roof tanks. The measurements obtained have confirmed the accuracy of the recently updated API estimation method for external floating roof tanks.

The ability of the remote measurement technique was demonstrated by comparison with direct measurements of emissions during the loading of a barge

#### **KEYWORDS**

API, hydrocarbon emissions, laser, measurement, storage tank, VOC.

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CONT	ENTS		Page
SUMMA	ARY		V
1.	INTROI	DUCTION	1
2.	OBJEC	TIVES	3
3.	PLANN	ING	4
	3.1.	SITE SELECTION AND DESCRIPTION	4
	3.2.	WIND DATA	5
4.	REMO	TE MEASUREMENT BY A LASER TECHNIQUE USING DIAL	6
	4.1.	THE TECHNIQUE	6
	4.2.	THE EQUIPMENT	6
5.	BARGE	LOADING	8
	5.1.	BARGE LOADING EMISSION FACTORS	8
	5.2.	BARGE LOADING EMISSION MEASUREMENTS	8
	5.3.	DETAILS OF BARGE LOADING OPERATIONS	9
	5.4.	DIRECT MEASUREMENTS AND RESULTS	9
6.	TANKS		12
	6.1.	THE API 2517 CALCULATION PROCEDURE	12
	<ul> <li>6.2</li> <li>6.2.1.</li> <li>6.2.2.</li> <li>6.2.3.</li> <li>6.2.4.</li> <li>6.2.5</li> <li>6.2.6.</li> <li>6.2.7.</li> <li>6.3.</li> </ul>	INPUT PARAMETERS FOR CALCULATIONS Tank Details Product True Vapour Pressure Product Bulk Temperature Wind Speed Rim Seal Factors Clingage Factor Tank Throughput MEASUREMENT PERIODS	13 14 14 14 15 15 15
	6.4.	DATA OUTPUT	16

	6.5.	ADDENDUM TO API 2517	17
7.	COMPA	RISON OF RESULTS	20
	7.1	BARGE EMISSIONS AND DIAL VALIDATION	20
	7.2	COMPARISON OF MEASURED AND CALCULATED TANK EMISSIONS	20
8.	CONCLU	JSIONS	23
9.	ACKNO	WLEDGEMENTS	24
10	REFERE	ENCES	25
APPEND	DIX		

SPECTRASYNE LTD. TECHNICAL REPORT NO. TR 9413, STUDIES OF VOC EMISSIONS FROM EXTERNAL FLOATING ROOF TANKS AND BARGE LOADING, NOVEMBER 1993 27

#### SUMMARY

Storage tanks are one of the many sources of VOC emissions. In the oil industry, emissions from tanks have traditionally been computed due to the considerable technical difficulties and costs in undertaking individual tank measurements. Calculation procedures derived by the American Petroleum Institute (API), and periodically updated, are used for this purpose world-wide. API Publication 2517 applies to external floating roof (EFR) tanks

Recently a remote measurement technique for VOCs has become available. Known as DIAL, it uses a laser to measure the concentrations of VOCs downwind of a source of emissions. The VOC emissions can then be determined from the concentration and the wind speed.

On the basis of short-term measurements of tank emissions using DIAL for periods of less than an hour, there have been suggestions that the API calculation methods for tanks were in serious error with measurements averaging 2.7 times calculated emissions. For this reason, CONCAWE initiated a comparative study in which continuous long-term emission measurements and calculations were to be undertaken for up to 96 hours for a group of five tanks.

In addition, CONCAWE planned to validate the DIAL output by comparison with the direct measurement of emissions from a vent pipe during the loading of gasoline into a barge. For the barge loading, the emissions measured by DIAL were within 10% of the direct measured value. Also, the value calculated using API Publication 2514A for Marine Vessel Transfer Operations was within 3% of the direct measurement.

In the comparative tank study over 90 hours, the DIAL measurement was 56% greater than the API 2517 calculated emissions. However, API 2517 was amended in May 1994 with the result that the difference between the DIAL measurement and the Addendum to API 2517 was reduced from 56% to 10%. Emissions were mainly from the guide poles which are fitted, one per tank, to prevent the rotation of the EFRs.

A number of short-term differences between measurements and calculations which were observed during the study are discussed. Further studies could consider large tanks with significantly lower height-to-diameter ratios than those involved in this study. Possible reasons for the differences observed in this study could be components of any such future studies.

The preliminary planning and continuous technical liaison were considered essential to the success of this comparative study. In the event, contingency plans aiming for the collection of two sets of comparative data proved vital due to operational problems and adverse meteorology which resulted in only one set of data being useable.

This study indicates that, in the context of the serious concerns which have been raised, API 2517 provided a reasonable estimate of tank emissions over the measurement period. The calculations based on the Addendum to API 2517 compare well with the DIAL measurements. The Addendum is considered to represent adequately the emissions from the various sources associated with the study tanks and their operation.

### 1. INTRODUCTION

Emissions of volatile organic compounds, VOCs, are of concern because together with nitrogen oxides,  $NO_x$ , they form photochemical oxidants, including ozone. The prevention of a build-up of ozone, a so-called secondary pollutant, in the lower part of the atmosphere can only be controlled by means of the two primary pollutants, VOCs and  $NO_x$ .

Over recent years, regulatory pressure to reduce VOC emissions has resulted in controls on both mobile and stationary sources. In the latter case the European Union's Stage I Directive requires vapour recovery in bulk gasoline storage and distribution. It includes controls on barge loading emissions and it sets an efficiency for tankage emission controls.

On a broader European front, the UN-ECE has published a VOC Protocol. This requires each "major VOC-emitting Party" to the Protocol "to reduce its national emissions of VOCs by at least 30% by the year 1999, using 1988 levels as a basis or any other annual level during the period 1984 to 1990, which it may specify upon signature of or accession to the present Protocol".

It is likely that as national emission databases are developed, both for EU and UN-ECE purposes, the pressures on the oil industry to validate its methodology for the assessment of VOC emissions will increase.

Since the storage of volatile products in fixed roof tanks would lead to the displacement of vapours in the tank to the atmosphere during tank filling, such products are normally stored in internal or external floating roof tanks which essentially eliminate the vapour space and hence displacement emissions. However some emissions do occur from external floating roof tanks due to the wind effect on roof to tank wall seals and on various roof fittings.

Whilst it has been reported that the apportionment of refinery oil losses, including emissions from tankage, are too small to be determined by mass balance accounting techniques<sup>1</sup>, others have nevertheless attempted to allocate losses in this manner<sup>2</sup>. Against this background, the measurement of emissions from tankage has been attempted using a remote laser technique known as DIAL (see **Section 4**). On the basis of short term measurements by DIAL <sup>3</sup> it has been suggested that the calculation procedure derived by the American Petroleum Institute in Publication API 2517 <sup>4</sup> is in serious error. The short term measurements were made over periods of 10 to 48 minutes and covered various groups of different tanks. The ratios of measured emissions to calculated emissions ranged from 0.8 to 5.8, averaging 2.7. For CONCAWE this raised important questions of:

- whether API 2517 was adequate for tanks in the conditions covered by the Publication;
- whether API 2517 was being applied to tanks which were outside its scope, not least because the poor condition of the tanks was not recognised or acknowledged;
- whether short-term, highly discontinuous measurements by DIAL were representative bearing in mind the fluctuations in both tank emissions and background emissions. The latter have to be subtracted from total measured emissions to obtain the emissions from tankage.

In the overall consideration of refinery oil losses, the apportionment of emissions between different activities is of particular importance to an operator since it is the operator who has to take appropriate action. The availability of DIAL facilities offered CONCAWE an opportunity to attempt the validation of emission calculations by remote measurement.

It was against this background that CONCAWE initiated the project which is the subject of this report.

## 2. OBJECTIVES

The main objective was to use the DIAL technique to measure emissions continuously from a group of external floating roof gasoline tanks during a full turnover of one tank whilst other tanks remained static and to compare the results with emissions calculated independently using API 2517.

An important complementary objective was to validate the capability of DIAL to measure mass emissions remotely and continuously under the field conditions pertaining. Emissions from a discrete source relative to both space and time, e.g. the vent line of a barge during a loading cycle involving gasoline, were to be measured using DIAL. The results could be compared both with emission data obtained independently using a conventional analytical technique and with the calculation procedure derived by the American Petroleum Institute in Publication API 2514A.<sup>5</sup>

#### 3. PLANNING

From the onset, CONCAWE considered both effective planning and continuous technical liaison throughout the project between the DIAL team and site personnel essential to its success.

In early discussions with Spectrasyne, a company specialising in environmental monitoring, it was confirmed that the DIAL facility could be operated for up to 96 hours continuously. This meant that the site selected must have tanks with a turnover within this period. Also to avoid the frequent and disruptive relocation of the facility during measurements, both the site and the timing of the project needed to be selected on the basis of a suitable record of sequential wind direction data (ideally the wind direction should not veer over more than 90° during the tank turnover period).

A pre-project visit was made to the potential measurement site by the CONCAWE Special Task Force, STF:

- to select the tanks to be studied;
- to assess their physical condition including fittings; and
- to note typical operating patterns.

Barge loading operations were also assessed during the visit.

Spectrasyne also visited the site to ascertain its suitability with respect to access for the DIAL facility (including parking), the availability of services, and the on-site health and safety requirements.

The visits were essential for both site familiarisation and planning purposes.

In the 2 week on-site period, emission measurements during at least 2 tank turnovers and 2 barge loadings were planned. It was recognised that there would need to be a reasonable break between the 2 periods of up to 96 hours of continuous operation. Advantage would be taken of this break to assess progress in the first trial, any lessons for the second trial, and to carry out any short-term studies of specific events.

During the on-site measurement period it was planned to have STF members available as necessary round the clock to ensure that a comprehensive log of all events was maintained at all times even if the DIAL measurements were disrupted for any reason. Hourly project schedules covering all the information to be collected were prepared. A PC program based on API 2517 would be available throughout the project to perform provisional calculations at any appropriate opportunity.

In the case of the barge loading exercise, STF members were to be responsible for the in situ measurement of hydrocarbon content of the vent gas and for its sampling for subsequent laboratory compositional analysis.

Finally, the achievement of the primary objective depended to a large extent on the prevailing meteorological conditions which could be forecast but not guaranteed. Therefore some risk was involved but planning for two measurement periods reduced this risk.

#### 3.1. SITE SELECTION AND DESCRIPTION

The preferred test site was to be a non-coastal site in continental Europe with barge loading facilities. An initial screening of a number of possible sites was undertaken based on photographs and plot plans. The site selected by CONCAWE was based on the ideal measurement criteria defined by Spectrasyne in its report (see **Appendix**, **Figure 1**).

The site, although not ideal, was considered to be best suited because of its level topography with a relatively well segregated group of 5 gasoline tanks and consistent wind conditions during a period when the study could be scheduled. The relatively few tanks adjacent to the five "study" tanks hold non-volatile products. There was also an operational possibility of main-taining products in 4 of the 5 study tanks at low levels during the measurement period.

The terminal is fed by pipeline. The tanks are used for the temporary storage of products prior to barge loading. It is also possible to load barges directly by pipeline.

Adjacent facilities include a number of other terminals for petroleum products fed by barge and/or pipeline, and other industrial facilities.

#### 3.2. WIND DATA

An important factor in considering long-term continuous measurements by DIAL was the meteorological situation at the site. In the absence of multi-year average data, hourly wind and precipitation records for October to December in the previous year were plotted and examined. These showed that winds mainly tended to blow either up or down the river with very variable speeds. Within the other timing constraints, a window of 4 weeks from the second week in November to the first week in December was chosen to avoid prolonged periods of calm. However during this period it was accepted that wind speeds could be intermittently high for a relatively large number of hours.

In the event, for the period of the second measurement period it was reported in the press that "an early winter causes havoc in Europe" due to the development of a giant anticyclone over Russia. The impact of this is referred to in **Section 6.3**.

# 4. REMOTE MEASUREMENT BY A LASER TECHNIQUE USING DIAL

Two DIAL facilities are available in Europe. One is operated by the UK National Physical Laboratory and one by Spectrasyne, an independent environmental surveying company.

Spectrasyne was selected for the CONCAWE project with a contractual responsibility for the remote measurement of emissions.

The following description of the technique and the equipment is reproduced with kind permission from the Spectrasyne brochure.

#### 4.1. THE TECHNIQUE

The remote sensing method used by Spectrasyne is a laser based technique known as DIAL, or Differential Absorption LIDAR. LIDAR is itself an acronym for light detection and ranging, and is the optical analogue of the better known radar. Over the last 15 years the technique has been developed and refined in a project involving the UK National Physical Laboratory (NPL) and BP, and is now available as a commercial tool through Spectrasyne.

The Spectrasyne DIAL system is single-ended; this means that the light used to make the measurement is sent out from the mobile Environmental Monitoring Unit (EMU) and returned for detection back at the EMU by backscattering of the light from particles in the air. In this sense, the dust particles and aerosols are being used as backreflectors, albeit rather weak ones.

DIAL relies on a differential return signal from two closely spaced wavelengths one of which is absorbed more strongly by the molecule being detected. The size of the differential signal indicates the concentration of the absorbing pollutant molecules along the path being monitored. The laser light is in short pulses and time resolution of the backscattered light gives the range resolution needed in the measurement. Scanning the laser beam across the site allows range resolved concentration measurements to be made across the whole area and 2 and 3 dimensional maps of emissions to be generated. This is one of the few ways of tracing the source of leaks or "fugitive" emissions.

Spectrasyne's DIAL system is one of only two worldwide with the capability of using tuneable infrared light to measure hydrocarbons. It also has visible and ultraviolet sources for measuring other airborne molecules.

#### 4.2. THE EQUIPMENT

Built in 1990, the Spectrasyne Environmental Monitoring Unit (EMU) is a 12 metre long mobile unit containing all the equipment necessary to make the measurements and process the data collected.

#### Lasers

The EMU contains two complete Nd: YAG pumped, dual wavelength dye lasers (see **Appendix**, **Section A3**) to provide a multi-wavelength tuneable source for DIAL measurements. Both systems are based around 1.4 Joule, 10 Hz, Nd: YAG lasers. One of the systems is used to generate tuneable ultraviolet and visible radiation and is equipped with frequency doubling and tripling crystals to achieve this. The second system generates a beam of narrow band, tuneable infrared radiation by means of a unique infrared source assembly.

#### Telescope

The output beams from the laser systems are directed into the area being monitored by means of a computer controlled steering mirror system which rotates in two planes. Collection is via a Cassegrain-type receiving telescope.

#### Data processing

Data processing is performed via a sophisticated, high speed data communication network which has been developed in parallel with a unique Micro Vax based software package.

The EMU is equipped with an extendable meteorological mast and a number of mobile, telemetric stations which are used to measure wind speed and direction, temperature and humidity. These are used in conjunction with the DIAL concentration measurements to calculate mass emission fluxes.

## 5. BARGE LOADING

#### 5.1. BARGE LOADING EMISSION FACTORS

Inland barges transporting gasoline within Europe are designed to the ADNR<sup>6</sup> regulations. These require that the vapours displaced from all of the cargo tanks during loading operations are collected in a common vapour pipe and either passed to a shore-side vapour recovery system or released to atmosphere through a high velocity vent. The latter is designed to give the vapours sufficient momentum to ensure that they are dispersed well above the barge deck level.

The concentration and composition of the vapours displaced will be dependent on both the residual vapours from the previous cargo left in the empty tank and from the vapours generated from the cargo being loaded. Residual vapours will not be present if the tanks have been cleaned or gas-freed prior to loading. Where residual vapours exist they will be dominant in the vented vapour during about the first 75% of the full loading period into each cargo tank. <sup>5</sup>

Emission factors for barge loading are given in CONCAWE Report 85/54<sup>7</sup>, derived from API 2514A.<sup>5</sup> These factors are shown in **Table 1.** 

Previous Cargo	Cargo Tank Condition	Average Filling Emissions (liquid equivalent) % of	
		liquid volume loaded	liquid weight loaded
Volatile	Uncleaned	0.078	0.064
Volatile Non-volatile	Cleaned, Gas-Freed Cleaned or Uncleaned	0.04	0.033
Non-volatile	Cleaned of Uncleaned	0.04	0.033

 Table 1
 VOC Emission Factors for Barge Loading Operations

#### 5.2. BARGE LOADING EMISSION MEASUREMENTS

Barge vapour collection systems are designed so that all of the vapours displaced during loading are emitted from a single vent. Thus the total volume of hydrocarbons emitted during loading can be determined by measuring the hydrocarbon concentration of the vapours vented and making the assumption that the volume discharged equals the volume of product loaded. To calculate the mass of vapours emitted, the composition of the vapours can be analysed to derive the average molecular weight.

The validation of the DIAL was undertaken during a complete barge loading operation by comparing the mass of vapours vented, calculated from direct measurements, with DIAL flux measurements. This is discussed in **Section 7.1**.

#### 5.3. DETAILS OF BARGE LOADING OPERATIONS

Measurements of emissions were undertaken during the loading of a barge with a cargo of 950 m<sup>3</sup> of gasoline into the cargo tanks over a period of about 220 minutes. Generally two cargo tanks were filled at a time. Loading was continuous except for one interruption. The previous cargo carried by the barge had also been gasoline. No cleaning or gas-freeing of the barge had been undertaken after the discharge of the previous cargo.

#### 5.4. DIRECT MEASUREMENTS AND RESULTS

Measurements of the hydrocarbon concentration of the vapour being vented were made every five minutes using an oxygen depletion technique. The measured values are given in **Table 2** overpage. The concentration varied during the loading cycle as different cargo tanks were filled or topped up, the resultant vapour being a mix of the residual vapour from the previous cargo and the vapour generated from the gasoline being loaded. The residual vapour concentration was of the order of 9% by volume, whereas the concentration of the saturated vapour generated by the gasoline loaded was about 26% by volume. The average vent concentration was 15.3% by volume.

Time	Hydrocarbon Concentration		Operation	Cumulative Emissions
	% vol			kg
05:25			Loading started	Ŭ
05:30	9.5		5	
05:35	9.5	*		8
05:40	11.4			16
05:45	12.9			26
05:50	13.8			36
05:55	14.3			47
06:00	13.8	*		59
06:05	14.3			70
06:10	14.8			82
06:15	14.8			94
06:20	15.2			105
06:25	15.2			117
06:30	15.2	*		129
06:35	16.2			142
06:40	16.7			154
06:45	15.7			168
06:50	15.7			180
06:55	8.6		Changeover of cargo tanks	190
07:00	8.6	*		197
07:05	8.6			203
07:10	9.5			211
07:15	12.4			219
07:20	13.3			229
07:25	12.9			240
07:30	12.9	*		251
07:35	12.9			261
07:40	21.0			274
07:45	21.4			291
07:50	16.7	*	Changeover of cargo tanks	307
07:55	16.7			320
08:00	16.7			334
08:05	19.5			348
08:10			Loading stopped	356
08:40			Loading restarted	356
08:45	19.0			363
08:50	20.0	*		378
08:55	24.8			395
09:00	26.2			413
09:05	26.2	*		430
09:10			Loading completed	435

#### Table 2 Barge Loading - Direct Vent Emission Measurements

\* vapour sample taken for subsequent analysis

Eight vapour samples were taken during the loading operations and subsequently analysed for composition. The average vapour composition is shown in **Table 3**.

Compound	% Hydrocarbon by volume
C1	0.0
C2	0.0
C3	1.3
C4	50.1
C5	15.3
C6+	33.3

Table 3Average Vapour Composition

The average molecular weight of the hydrocarbons was 69. As the molecular weight of gasoline vapour is normally between 64 and 66, the higher value from the barge vent indicated the influence of the residual vapour that would have correspondingly fewer light ends than freshly evaporated vapour due to "weathering".

From **Table 1** the average emission factor for loading an uncleaned barge with volatile cargo is 0.078% as volume liquid equivalent of the volume loaded. This is equivalent to a factor of 0.064% by weight, assuming the density of the condensed vapour is 0.6 kg/l.

Using the average molecular weight of 69, the calculated total mass of hydrocarbons emitted during the loading of 950  $m^3$  of gasoline was 435 kg. With a gasoline density of 0.733 kg/l this gives an emission of :

(435x100)/(950x0.733x1000) = 0.062% by weight

The result of this test shows good agreement with the published API emission factor of 0.064% by weight.

## 6. TANKS

### 6.1. THE API 2517 CALCULATION PROCEDURE

The API 2517 procedure was selected for the calculation of hydrocarbon emissions from external floating roof tanks. Although API 2517 is normally applied to calculate annual emissions, in this case a spreadsheet was devised to enable hourly calculations to be performed. **Table 4** below shows the form of the spreadsheet.

#### Table 4API 2517 Input Data Requirements

Item	Unit	Acronym
Product Characteristics		
RVP S - Slope of distillation curve at 10% recovered Bulk storage temperature TVP @ storage temperature	kPa degrees F per percent degrees C kPa	
Standing storage emissions:		
TVP Atmospheric pressure Average wind speed Pressure function Tank diameter Molecular weight of vapour Product factor Rim seal factor Seal-related wind exponent Rim seal emissions Roof fitting emissions	kPa kPa abs m/s dimensionless m kg/kmole dimensionless dimensionless dimensionless kg/h kg/h	TVP Pa V P* Dt Mv Kc Kr n Lr
Standing storage emissions	kg/h	Lr+Lf=Ls
Wet wall emissions:		
Clingage factor Clingage factor Pump out rate Average liquid density Wet wall emissions	bbl/1000ft <sup>2</sup> m <sup>3</sup> /1000m <sup>2</sup> m <sup>3</sup> /h kg/m <sup>3</sup> kg/h	Cf Cf' Tp DI Kgw
Total emissions	kg/h	Ls + Kgw

#### 6.2. INPUT PARAMETERS FOR CALCULATIONS

#### 6.2.1. Tank Details

The gasoline tank farm, which was selected for the comparative hydrocarbon emissions study, contained 5 external floating roof tanks for the handling of various grades of gasoline. The particulars for these tanks which are relevant to the API 2517 emission calculation are:

- external floating roof seal types
- roof fittings: types and number

Tank dimensions, external floating roof seal types and their condition, and the number and type of roof fittings are listed in **Table 5** below.

Four tanks were provided with liquid mounted resilient material primary seals plus weather shields (X). In one of these tanks the resilient material of the primary seal was partly missing and considered below average condition (B). The condition of the primary seals plus weather shields for two external floating roof tanks was considered to be average (A), and for one external floating roof tanks was a tight-fit (T). The fifth tank was provided with a wiper type primary and secondary seal (Y). The primary seal was vapour mounted and provided with a liquid skirt. The seal had been recently installed and was in a tight-fit condition (T).

Tank No.	40	41	42	43	46
Diameter [m]	19.5	19.5	19.5	19.5	17.0
Height [m]	18.4	18.4	18.4	18.4	12.9
External Floating Roof Seal type	Y	Х	Х	Х	Х
Seal Condition	Т	А	В	Α	Т
Access Hatch, bolted, gasketed	3	3	3	2	2
Slotted Guide-pole, gasketed sliding cover,					
without float	1	1	1	1	1
Gauge-well, unbolted, ungasketed	1	1	1	1	1
Gauge-hatch/Sample Well, bolted cover,					
gasketed	3	3	3	3	3
Vacuum Breaker	1	1	1	1	1
Roof Legs (3-inch diameter)					
Pontoon area	6	6	6	6	5
Centre area	4	4	4	4	3
Rim Vent (6-inch diameter)	1	1	1	1	1



A Product Quality Log provided essential product quality details and an hourly printout of tank movements was available from the control room computer for entry onto a spreadsheet. A Movements Log provided information on all oil movements in and out of the terminal by pipeline and barge which was important in monitoring likely changes in emissions from different sources.

#### 6.2.2. Product True Vapour Pressure

The RVP, reported from the product quality certificate, has been used to calculate the product true vapour pressure (TVP).

#### 6.2.3. Product Bulk Temperature

Product bulk storage temperatures were available from the tank readout in the site control room.

#### 6.2.4. Wind Speed

The hourly average wind speed, in m/sec, was used in the emission calculation. API 2517 advises that the wind speed be user-specified or else taken from meteorological records. It contains tabulated data for a range of locations in the US. Outside the US, it is usual for wind data to be obtained from the nearest meteorological station. In accord with this practice, for this study data were obtained from an official automatic environmental monitoring station located a distance of some 7 km from the terminal. The wind speed and direction monitor is calibrated monthly. This location was selected as being representative for the area. The data are shown in **Figure 1**.





The DIAL facility provided a local source of wind data and overall the two data sets showed reasonable agreement. For the study period the average wind speeds were 4.4 and 4.5 m/s for the remote and local measurements respectively.

#### 6.2.5. Rim Seal Factors

The rim seal loss factors (Kr) and the rim seal related wind speed exponent (n) which were selected from Table 3 in API 2517 for use in the emission calculations are shown in **Table 6.** 

Table 6 Tank Rim Seal Detail
------------------------------

Tank No.	Rim Seal Loss Factor Kr	Wind Related Exponent n	Rim Seal Type and Condition
40 41 42 43 46	0.2 0.8 1.0 0.8 0.5	0.9 0.9 1.0 0.9 1.0	Double Wiper/ Liquid Skirt/ Tight Fit Liquid Mounted Resilient Filled/ Weather Shield/Average Fit Liquid Mounted Resilient Filled/ Weather Shield/Below Average Condition Liquid Mounted Resilient Filled/ Weather Shield/Average Fit Liquid Mounted Resilient Filled/ Weather Shield/Tight Fit

#### 6.2.6. Clingage Factor

The clingage factors (C) used in the emission calculation, derived from Table 11 in the API 2517, are shown in **Table 7**.

<b>Table /</b> Tank Wall Details	Table 7	Tank Wall Details
----------------------------------	---------	-------------------

Tank No.	Condition of Tank Wall	Clingage Factor C
40	lines of dense rust	0.0045
41	good	0.0015
42	good	0.0015
43	1/3 circumference dense rust	0.0045
46	medium rust	0.0045

#### 6.2.7. Tank Throughput

For the throughput, the tank pumpout rate (Tp) was calculated from hourly liquid level changes and used as input for the wet wall emission calculation.

### 6.3. MEASUREMENT PERIODS

Data were collected over two measurement periods. The first period forms the basis for the comparison between measured and calculated emissions. Unfortunately, the second period coincided with extremely adverse meteorological conditions involving very low temperatures with freezing fog and calm air. As a consequence data collection was intermittent.

#### 6.4. DATA OUTPUT

The consecutive hourly input data entered onto the spreadsheet enabled the calculation of hourly emission data to be made. In view of the large amount of both input and output data contained in the spreadsheet it is not included in this report in its digital form but rather in graphical form. This has the advantage of facilitating an understanding of the extensive data.

Figure 2 shows the total calculated emissions. It can be seen that the emissions follow a similar pattern to the wind speed in Figure 1.

kg/h ...... Time (h)

*Figure 2* Total Emissions - API 2517

The output data included standing storage emissions, comprising rim seal emissions and roof fitting emissions, and wet wall emissions during tank emptying. **Figure 3** shows these calculated component emissions which indicate that the roof fittings were by far the major source for the tanks being studied. The wet wall emissions, which occur when the tank roof descends as product is pumped from the tank, were insignificant.



Figure 3 Component Emissions - API 2517

#### 6.5. ADDENDUM TO API 2517

During the report drafting stage of the project, an Addendum to API 2517<sup>8</sup> was published. It is based on the most recent API-sponsored programme that includes laboratory testing to validate emission loss factors for roof fittings previously tested and to test new equipment configurations to establish loss factors; the programme also included testing to establish the effect of wind speed on evaporative losses. The foreword to the Publication advises that "The fourth edition of API Publication 2517 is forthcoming. In the interim, API is publishing this addendum to the third edition of Publication 2517 to release new, pertinent information regarding evaporative losses from .... guide poles". A guide pole is a device used in external floating roof tanks to prevent the floating roof from rotating and guide the roof as it rises during tank filling. This new information is included in this report.

The roof fitting loss factor, Kf, for each type of fitting is estimated as follows:

$$Kf = Kfa + KfbV^{n}$$

where;

Kfa = loss factor for a particular type of roof fitting, in pound-moles per year Kfb = loss factor for a particular type of roof fitting, in pound-moles per (miles per hour)<sup>m</sup> - year

- V = wind speed, miles per hour
- m = loss factor for a particular type of roof fitting (dimensionless)

The changes in the factors for the study tanks in this report are shown in Table 8.

Table 8 Comparison of Previous and Revised API Factors

	Kfa	Kfb	m
API 2517	0	260	1.20
Addendum to API 2517	40.7	311	1.29

The apparently large impact of the Addendum is shown in **Figure 4** which plots the Addendum data together with the original data shown in **Figure 2**. **Figure 5** shows the component emissions from which, by comparison with **Figure 3**, it can be seen that the increase is associated with the roof fittings. The reasons for the increase are discussed in **Section 7.2**. Individual total emissions for each of the 5 study tanks are shown in **Figure 6**. It can be seen that the emissions are fairly evenly spread amongst all of the tanks.

Figure 4 Total Emissions - API 2517 vs Addendum to API2517





Figure 5 Component Emissions - Addendum to API 2517





## 7. COMPARISON OF RESULTS

The Spectrasyne report is included as the **Appendix.** 

#### 7.1. BARGE EMISSIONS AND DIAL VALIDATION

DIAL scans were taken sequentially some 36 m downwind during the whole of the barge loading operations and for a short period afterwards (see **Appendix**, **Table 1**).

The DIAL data were plotted in 5 minute periods to match the directly measured data. The two data sets are compared in **Figure 7**.

## *Figure 7* Barge Loading - Comparison Between Direct (Vent) and Remote (DIAL) Measurements.



During the period of interruption of loading when no vapour was emitted from the vent the DIAL still indicated some emissions. This was probably due to the slow dispersion of the emissions from the barge across the DIAL scan line in the low wind speed.

The total hydrocarbon emissions as calculated using DIAL were 390 kg. This compares to 435 kg from the direct measurements. The relatively close agreement, approximately 10%, demonstrates that the DIAL could measure the total flux from an emission source under the field conditions pertaining at the time.

#### 7.2. COMPARISON OF MEASURED AND CALCULATED TANK EMISSIONS

To facilitate the comparison between the DIAL measurements and the calculated emissions both data sets were processed into 15 minute intervals expressed on kg/h basis. In the case of DIAL, the tabulated data from the Spectrasyne report were used to derive the 15 minute data; the calculated hourly data were simply plotted in 15 minute intervals.

**Figure 8** shows the DIAL emissions plotted at 15 minute intervals over the whole measurement period of some 90 hours; the emissions calculated by API 2517 and by the Addendum to API 2517 are shown as line plots.



Figure 8 Emissions - DIAL vs API 2517 and Addendum to API 2517

On comparing the calculated data for the periods when DIAL data were available, the DIAL measurement was 56% greater than the API 2517 calculated emission. However the Addendum to 2517 refers to an error in the wind speed measurement in the test programme to derive some of the factors for API 2517. The result is that for the CONCAWE study, the difference should have been 26% rather than 56%. For the Addendum to API 2517, which in any event introduces factors which supersede API 2517, the DIAL measurement was 10% greater than that for the Addendum to API 2517.

In spite of the relatively good agreement between the measured and calculated data sets, particularly for the Addendum to API 2517, there were periods when differences between the two were more pronounced.

In the early part of the study, during a period of relatively high average wind speeds, gusting wind conditions were experienced over one period of 4 hours and a second period of 2 hours (hours 2-6 and 14-16). API 2517 states that the emission equations were developed for average wind speeds ranging from 2-15 mph and should only be used within this range. The Addendum to API 2517 advises "due to a lack of test data at higher wind speeds it is recommended that table of factors not be used for wind speeds above 15 mph" (6.7 m/s). Wind speeds above this value were experienced during the early part of the study as can be seen from Figure 1. However in the absence of any alternative, the factors were used and resulted in the good overall agreement between measured and calculated losses as referred above. Some of the short-term differences between the measured and calculated emissions may have reflected a gusting effect. In view of the non-linear dependence of emissions on wind speed, the sum of the individual hourly calculated data was compared with the product of an hourly calculated loss based on the average wind speed and the total number of hours. The latter loss was within 10% of the total for the individual hourly data. It is emphasised that the reasons for, and the sources of, the differences coincident with these periods of gusting winds were not resolved in this study.

Further differences are apparent in **Figure 8** particularly where the measured emissions show an increase whilst the calculated emissions remain relatively steady. In the investigation of the differences the DIAL emissions were plotted against the roof height of Tank 41, which was subject to controlled movements during the test period, and a partial plot of the roof height of Tank 42; other tanks were static.



Figure 9 Emissions (DIAL) vs Roof Heights of Tank 41 and Tank 42 (partial plot)

Reference to **Figure 9** shows that the increased emissions occurred during the filling of Tank 41 from half full to full (hours 55-62). This effect was not observed during the initial filling of the tank from essentially empty to half full over a total period of some 12 hours (hours 21-33). However a partial plot of Tank 42 indicates that the "topping up" of this tank from close to top dip to top dip (hour 19-20) may also have been responsible for an increase in measured emissions.

One further peak (during hour 69) was considered to be due to operations not directly associated with the tanks themselves.

A period where it had been anticipated that high emissions may be sustained was when the tank was held at its full position (hours 62-76). In fact on completion of filling the emissions decreased.

The comparative measurements by direct and indirect methods during barge loading clearly demonstrate the capability of DIAL to measure emissions with reasonable accuracy. Whilst the tank emission data reinforce the concerns regarding the use of short-term measurements by DIAL to validate a long-term calculation procedure, the value of DIAL in this longer term comparative study has been clearly demonstrated.

Finally, it is important to emphasise the overall difference between the measured and calculated losses using the Addendum to API 2517 was only 10%.

## 8. CONCLUSIONS

- 1 The validation of DIAL measurements under field conditions was an important objective. The direct measurement of emissions during barge loading and the calculation of emissions using an established factor were in close agreement; the remote measurement by DIAL was within 10% of the measured value.
- 2 For tank emissions, the overall agreement between the API 2517 calculated emissions and DIAL measurements was considered reasonable. There were a number of incidences where spikes occurred in the measured emissions. In some instances there were possible operational reasons which could explain these but since they could not be quantified the data were plotted "as measured".
- 3 The Addendum to API 2517 resulted in good agreement between measured and calculated emissions.
- 4 The discrepancies incurred during periods of gusting winds were only partially offset by the revised emission factors in the Addendum. The reasons for, and the sources of, the differences coincident with these periods of gusting winds were not resolved in this study.
- 5 The indicated emissions which occurred during the latter half of tank filling and possibly during topping up were unexpected. This is an area for possible further investigation.
- 6 The emissions arising from the exposure of the wet wall as the tank roof was lowered were insignificant.
- 7 It is considered unequivocally that the detailed initial planning for the relatively long term, continuous measurements and the technical liaison provided throughout were fundamental to the success of the project.
- 8 In view of the high costs involved in the project and the acknowledged risk of it not being successful, the planning for both two barge loading operations and two tank studies was important. In the event, only one barge loading operation was covered for operational reasons and only one tank study for meteorological reasons.
- 9 Any future work could be directed at large tanks having significantly different height-to-diameter ratios. Emissions during filling could be a component of such studies.
- 10 This study indicated that, in the context of the serious concerns which have been raised, API 2517 provided a reasonable estimate of emissions over the measurement period.
- 11 The Addendum to API 2517 was considered to represent adequately the emissions from the various sources associated with the tanks and their operation.

## 9. ACKNOWLEDGEMENTS

CONCAWE gratefully acknowledges the considerable assistance given by the staff associated with the test site during all phases of the measurement programme and without which this comparative study would not have been possible.

## 10. **REFERENCES**

- 1. Schmitt, R.E. et al (1993) Amoco got involved at Yorktown Joint Amoco/USEPA Pollution Prevention Project. Report AM-93-32. Washington, DC: National Petroleum Refiners Association
- 2. Robinson, E.R.(1991) A survey of losses in UK oil refineries. Paper presented at Fourth Oil Loss Conference. London: Institute of Petroleum
- 3. Woods, P.T. et al (1993) A determination of the emissions of volatile organic compounds from oil refinery storage tanks. NPL Report DQM(A)96. Middlesex: National Physical Laboratory
- 4. API (1989) Evaporative loss from external floating roof tanks. Publication 2517. Third Edition. Washington, DC: American Petroleum Institute
- 5. API (1987) Atmospheric hydrocarbon emissions from marine vessel transfer operations. Publication 2514A. Second Edition 1981, reaffirmed 1987. Washington, DC: American Petroleum Institute
- 6. ADNR (1993) Accord Européen relatif en Transport International des Merchandises Dangereuses par Voie de Navigation Interieur/Rhin. Geneva: UN
- 7. CONCAWE (1985) Hydrocarbon emissions from gasoline storage and distribution systems. Report 85/54. Brussels: CONCAWE
- 8. API (1994) Addendum to Publication 2517 Evaporative loss from external floating roof tanks. Publication 2517. Third Edition. Washington, DC: American Petroleum Institute

## APPENDIX

SPECTRASYNE LTD. TECHNICAL REPORT NO. TR 9413, STUDIES OF VOC EMISSIONS FROM EXTERNAL FLOATING ROOF TANKS AND BARGE LOADING, NOVEMBER 1993.



ISSUE DATE: 13th June 1994 TECHNICAL REPORT NO.: TR9413

## STUDIES OF VOC EMISSIONS FROM EXTERNAL FLOATING ROOF TANKS AND BARGE LOADING NOVEMBER 1993

WORK BY: COMMISSIONED BY: SPECTRASYNE / CONCAWE CONCAWE

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## Contents

1.	Intro	duction	1
<b>2</b> .	Test	Site	2
З.	Survey Objectives 4		4
4.	Expe	Experimental Programme	
	4.1	Barge Loading	5
	4.2	Tank Studies	6
		4.2.1 First Study	6
		4.2.2 Second Study	
		4.2.3 Upwind Subtractions	8
<i>5</i> .	Resu	Ilts And Discussion1	1
	5.1	Barge Loading Comparison 1	1
	5.2	First Tank Study 1	2
	5.3	Second Tank Study (Tank 46) 1	3
6.	Cond	2 <i>lusions</i> 1	4
<b>A</b> .	1 Ba	ckground 1	5
	A.1.	1 History 1	5
<b>A</b> .:	2 Eq	uipment 1	6
	A.2.	1 DIAL 1	6
	A.2.	2 In-stack Emission Measurement 1	17
A.:	3 Ab	breviations1	8

## 1. Introduction

Since the early 1960s the petroleum industry has relied upon methods of calculation for estimating the losses from storage tanks. In the case of external floating roof tanks, the American Petroleum Institute (API) have issued three bulletins in 1962, 1980 and 1989 setting out procedures for the calculation of emissions. The method of calculation relies upon input data relating to the physical properties of both the product stored and the storage tank, meteorological conditions and tank operational data. The calculations have been designed to provide annualised loss data on tanks, or groups of tanks, by the use of annual tank turnover information and annual average wind speed. The use of these API correlations have provided the industry, for over 30 years, with a relatively simple means of estimating losses from floating roof tanks and, through other API bulletins, fixed and internal floating roof tanks.

The API calculation methods were derived empirically from the use of a small test tank in an enclosed laboratory. Because of the extreme difficulty, until recently, of directly measuring losses in the atmosphere from tankage, no definitive validation of the calculation methods has been undertaken. It has long been recognised that the calculation, particularly if applied to single tanks over short operating periods, might not accurately reflect the real losses.

The advent of infra-red DIAL technology (Appendix A) has, for the first time, provided a means of directly measuring, in the atmosphere, mass emission of hydrocarbons from tankage or other plant. The Spectrasyne DIAL team have been operating this technology routinely since 1990, during which time data from many tankage areas have been accumulated. These data have demonstrated that emissions from floating roof tanks appear to be especially dependent upon tank roof level in relation to the tank top, ambient wind speed and tank seal condition. The first of these issues is not addressed in the API calculation, the assumption being that over a long period tank turnover will average out the effect of roof level. The average roof position of the tank, relative to top dip, will, however, depend upon many factors such as tank aspect ratio, for clearly a large diameter short tank, for a given turnover schedule, will operate closer to top dip level than a smaller diameter taller tank of the same capacity. Wind speed is taken into account as a function in the API calculation measured by an anemometer which could be located at some distance from the tanks. There are some indications from DIAL studies that wind speed effects apply according to a power law, at least over part of the wind speed range. Insofar as short term calculations are concerned, wind speeds must be applied which are well in excess of the limits drawn by API for the average, "extended period" wind speeds used in the calculation. The tank rim seal losses in the API correlation are calculated from a rim-seal loss factor derived from the type of seal, its condition and the average wind speed. This factor is then multiplied by the average wind speed with an exponent based again on the condition and type of seal. The condition related input is, however, to either 'average' or 'tight fitting' seals. Some definition of 'tight fitting' seals is given, but anything outside this criterion is taken to be 'average'. It is clear that seal condition ranging from almost tight to very poor will fall under the same classification and this could give rise to errors in the calculation for tanks with poor condition seals. It has been suggested that the API correlation was never intended to be applied to tanks with poor condition seals since these should routinely be replaced as part of on-going maintenance programmes.

## 2. Test Site

Spectrasyne were requested by CONCAWE to provide a description of an ideal site arrangement for detailed DIAL studies. Figure 1 is Spectrasyne's response to this request in a sketch showing a close to ideal arrangement for the measurements, bearing in mind that the ideal situation of a single tank in an open isolated site which provided complete tank movement flexibility was unlikely to be achieved. This was used by CONCAWE as a pattern for selecting a test site. Their selection criteria were thus,

- 1. Minimum number of floating roof gasoline tanks in the group containing the study tank.
- 2. Maximum spacing between the tanks in the group to minimise the problem of discrimination between plumes.
- 3. Clear space around the group containing the study tank to provide sufficient downwind clearance to avoid wind shadow effects. Four diameters of downwind space was considered to be the ideal arrangement, but less space than this could be accommodated by careful wind station positioning. Space all around the tank would also provide the DIAL with near-field room in the event of wind direction changes.
- 4. Flexibility in the operation of, particularly, the non-test tanks to enable these to run down to a low level for the test sequence in order to minimise interference.
- 5. No, or few, other hydrocarbon sources around the site to minimise the necessity of upwind subtraction from the measured data.
- 6. Barge loading facilities to provide correlation opportunity.
- 7. Stable wind conditions.

These criteria, of course, presented a difficult challenge and it was recognised at the outset that some compromises would, in fact, be inevitable. An inland / continental site was preferred as this was felt to offer a better choice of stable wind conditions than a coastal site. Eventually a site was found which CONCAWE considered met as many of the criteria as they were likely to achieve. The site was a barge loading terminal thus providing the opportunity of a correlation exercise during a barge loading operation. The site contained 5 gasoline / light spirit tanks with separation for some wind directions between the group and other tankage plant. On the debit side, the tanks were quite small (18 m diameter) and rather closely spaced for DIAL measurements thus requiring co-operation from the site owners in running down the tanks adjacent to the test tank. The site was constrained for S - SW wind directions by an adjacent storage installation. Additionally, there were fuel oil and gas oil tanks on the site as well as slops tanks together with water treatment facilities which would provide upwind sources with N - NE and Westerly wind directions respectively. Barge loading operations, which were intermittent, could also provide upwind sources with an approximately NW wind direction. Wind directions, almost continuously, from about 210° through 360°, to about 50° thus provided potential upwind source difficulties.

A historical meteorological data study was initiated by CONCAWE for the site which showed stable conditions for the month of November. Wind speeds for the month averaged over  $3 \text{ m.s}^{-1}$  whilst the direction was mostly S - SW with occasional N - NE periods. These S - SW wind directions would provide a substantially contamination free upwind path to the

test tanks whilst a N - NE direction would apparently only have significant upwind sources when the wind was close to the NE cardinal point.

The site is essentially a barge loading terminal with storage facilities for fuel oils, gas oils and gasolines. The site had the facility for loading barges directly by pipeline as an alternative to loading via the terminal's storage tanks. This provided additional flexibility which, it was hoped, would prove useful in securing a complete turnover cycle for the study.

Bearing in mind all these factors, CONCAWE decided to undertake the study at the site in November 1993. The elements of risk on wind direction, especially, were counterbalanced by the perceived site advantages of its operating flexibility, the barge loading facility and the downwind measurement space available with the anticipated wind direction.

The group of tanks designated as the subject of the study consisted of 4 tanks (T40, 41, 42 & 46) containing various specification gasolines and one tank (T43) containing Naptha (Light Boiling Fuel). Tank 40 was equipped with a secondary seal whilst the other four tanks had single seals with weather shields. On tank 42 a short length of the rim seal was damaged where part of the seal packing had become detached causing the weather shield to distort and open a gap between the shield and the tank wall. Other than this area of damaged seal, all the tank seals were determined by CONCAWE to be in good condition.
## 3. Survey Objectives

The defined objectives for the survey were, firstly, to undertake measurements of VOC emissions from a barge throughout its loading schedule. These measurements were to be made simultaneously with barge vent VOC concentration measurements to be undertaken by a CONCAWE team. From the vent measurements and a knowledge of the loading rate and thus vapour displacement rate, the CONCAWE team were to calculate the mass hydrocarbon emission levels throughout the loading, for correlation with the Spectrasyne DIAL measurements to be made some distance downwind of the barge. A barge loading motor spirit product was to be chosen for this exercise in order to represent a discrete emission source. The correlation exercise was to be carried out during one or two complete loading schedules. The sequential measurement data derived from the two methods were to be integrated over the loadings to provide total mass emission figures for each measurement technique. These correlation data, it was hoped, would provide additional accreditation<sup>\*</sup> to the use of DIAL technology for measurement of hydrocarbon losses from gasoline or other light hydrocarbon storage areas.

This preliminary objective was seen as a paving exercise for the main purpose of the visit. This was to undertake studies of the emission from floating roof tankage over extended periods covering a range of tank level and movement conditions. Two measurement exercises were planned to take place during continuous periods of up to 96 hours each. During this time the DIAL would be deployed to make sequential measurements of the emission downwind of, ideally, a single gasoline tank operating over a complete turnover cycle.

The tank study objective was to compare, over an extended period, the measured emission from a single or group of floating roof tanks with the corresponding calculated emission data using the appropriate API formulae.

Insofar as the tank studies are concerned, this report deals only with the measurements made using the DIAL system; the corresponding API emission calculations and comparison with the DIAL data is the responsibility of the CONCAWE team and this will be the subject of a separate report. The concerns of this report are therefore, firstly to describe and discuss the barge loading correlation exercise and secondly, in relation to the tank studies, to describe the measurements made, present the data collected and discuss the implications of these figures in relation to the operational or meteorological factors pertaining during the study.

It should be emphasised that the purpose of the programme, as revised by circumstances, was to provide a comparison between measured and calculated emissions which would be applicable for those *specific tanks under the meteorological and operational conditions experienced*. Clearly, the wider relevance of the comparison cannot be assumed without further work.

<sup>\*</sup> A number of mass emission correlation exercises between DIAL and other measurement techniques have been carried out during recent years. The other methods include SF6, calibrated releases of methane from a point source and marine tanker vent measurements similar to that used by CONCAWE. In all of these exercises the maximum divergence from the DIAL measurements recorded was 15%. In all cases the reports are client confidential.

# 4. Experimental Programme

Data from many refineries have shown refinery non-methane, non-aromatic, hydrocarbon (NMNAHC) fugitive emissions to be a cocktail of mainly alkane species with a mean carbon number of ~4.5 which is very similar to the non-aromatic VOC emission from gasoline. Toluene normally represents about 90% of the total aromatic content of gasoline fugitive emissions and is, therefore, a good indicator for total aromatics. During the tank studies, the measurements of these non-methane, non-aromatic, refinery cocktail hydrocarbons (NMNARCHCs) were occasionally complimented by simultaneous toluene measurements.

Experience has shown that the NMNARCHC emission, alone, from gasoline tankage typically represents approximately 88% to 90% of the total VOC emission. The majority of the remaining 10% to 12% is aromatic hydrocarbon with the occasional very small fraction of other species such as alkenes. The intermittent toluene measurements made at the site confirmed these historical aromatic/NMNARCHC ratios. A reasonably accurate estimate of the total HC emission from the tanks may, therefore, be deduced by dividing the DIAL NM-NARCHC figures by 0.9.

### 4.1 Barge Loading

The barge loading correlation exercise was planned for one or two complete loading operations on gasoline. CONCAWE were to make measurements of the hydrocarbon concentration (by direct measurement and by oxygen depletion) in the tank exit vent. Vapour displacement through the vent was assumed to be equivalent to loading rates. These recorded loading rates at the time of the measurement were then used, together with the measured vent gas hydrocarbon concentration and composition, to give a mass hydrocarbon emission. These data, integrated over the entire loading period, would give the total hydrocarbon losses during the operation. Simultaneously, sequential DIAL scans would be made at some distance downwind of the barge to determine the mass hydrocarbon emission.

Arrangements were made to undertake the first barge loading correlation exercise on the first measurement day at the site (12th November). A barge was scheduled to take on a consignment of gasoline beginning at about 12:00. For the duration of these measurements, all other barge loading operations were to be terminated in order to obviate any interference with the DIAL measurements.

Unfortunately, the loading operation for this barge coincided with a period of relative calm. The plume from the barge vent under these zero, or light, wind conditions could not be consistently located and thus DIAL flux measurements could not be made. Although the CONCAWE team monitored the barge vent throughout the loading, the emission concentrations were very much lower than expected. Hydrocarbon concentrations were only of the order of 2%, thus limiting the accuracy of the measurement. It was subsequently discovered that the barge had previously taken on a cargo of gas oil; for the second barge loading exercise efforts were to be made to secure a barge which had previously loaded gasoline.

The second barge measuring exercise was scheduled to take place immediately following the first tank study. The barge selected was to uplift 950 m<sup>3</sup> of gasoline, having previously carried gasoline. Again, all other barge loadings were suspended to prevent plume interfer-

ence. Sequential DIAL scans, approximately 36 m downwind of the barge vent were taken throughout the loading operation whilst the CONCAWE team undertook vent gas hydrocarbon concentration measurements. Figure 2 shows the DIAL position throughout this exercise and the scan line taken in relation to the barge. The wind speeds prevailing during this exercise were low, but fortunately just about sufficient at 1.0 to 2.5 m.s<sup>-1</sup> to give a consistent enough wind direction (20° to 50°) to enable meaningful data to be obtained. Table 1 contains the data collected by Spectrasyne and Figure 3 shows the sequential data points and the comparative cumulative losses from Spectrasyne and CONCAWE data.

#### 4.2 Tank Studies

#### 4.2.1 First Study

The original objective of the planned tank studies was to measure VOC emission during a complete turnover cycle on a single tank. Because of the close proximity of the tanks at the site, it was recognised that focusing on a single tank would require that the remaining four tanks would have to be run down to a low level in order to minimise interference. For the first tank study CONCAWE had arranged that the study would be undertaken on Tank 41 for which a 96 hour filling, stabilising and emptying schedule was agreed. The remaining four tanks were all to be run down to close to bottom dip levels before the exercise began and maintained at these low levels throughout the 96 hour period.

When the Spectrasyne and CONCAWE teams arrived on site on 14th November to begin the study, it was discovered that, although the intended test tank was empty as required, operations had required the introduction of product into three of the other four tanks. Discussions disclosed that the use of these tanks would be required throughout the test period and at least one further tank movement was anticipated (in addition to the test tank movements). In view of this, it was decided to revise the trial objectives from a single tank study to a combined study of all five tanks in the group. The cycle schedule for the original test tank would remain, but segregation of the emission from this tank and the other four in the group would not be possible. It was recognised at the time that this imperative would, at least, impair the possibility of relating emission to specific tank operational conditions. Nevertheless, it was still anticipated that the study would provide valuable information on tankage losses over an extended period encompassing different weather conditions and day and night time operation. Some attempt might also be devoted to relating combined tank levels to total emissions.

The study began at 10:30 on 14th November and continued until 03:30 on 17th November when the tank study was discontinued to enable barge loading measurements to be undertaken. Throughout the 89 hours of the tank study, sequential DIAL scans were made downwind of the 5 gasoline tanks, interspersed with upwind scans to provide information on incoming hydrocarbon fluxes. During the course of this exercise, some large changes in wind direction occurred which necessitated relocation of the DIAL system to facilitate measurements on a line approximately orthogonal to the wind direction. In fact, the DIAL was located in 7 different positions at various points of the site, three of which were solely for downwind scans, one for upwind scans and the remaining three were locations from which both upwind and downwind scans could be achieved. The DIAL location and the scan lines taken from these positions are shown on Figures 4 and 5. During the 89 hours a total of 116 scans were completed with a mean scan time of about 30 minutes. A small number of the scans (16) were subsequently rejected for reasons such as intermittent upwind site operation, where the external upwind source could not be resolved due to wide short term fluctuations, or where an external agent interfered with the measurements (e.g. clouds of dust on the scan line or torrential rain). Excluding these scans and those 27 scans made upwind of the study tanks, a total of 73 downwind scans were available from the study for analyses. Data from these scans were processed taking into account the appropriate upwind subtraction derived from the upwind measurements. The gross downwind measured flux, the corresponding upwind flux for subtraction and the resulting net hydrocarbon fluxes due to the study tanks alone are shown in Tables 2a to 2d. Figure 6a shows the time sequence emission levels compared with wind speed, rainfall / solar illuminance and tanks levels on Figures 6b, 6c and 6d respectively. Figures 7 and 8 show the emission fluxes plotted against wind speed and a combined wind speed / tank dip factor.

#### 4.2.2 Second Study

The second study exercise was also devised with the primary objective of segregating a single tank and monitoring its emission over a turnover cycle. Discussion between CONCAWE and the site concerning likely operating schedules over the 4 day study period led to the selection of Tank 46 as the study tank. This tank, being the smallest of the group of five, provided the best opportunity for a full turnover range. The 4 day study period was to begin on the morning of 20th November when the test tank level was to be at about 4 metres. A period of measurement at this low level would begin the study. Pumping and barge loading operations were arranged to provide subsequent tank filling, stabilisation and emptying sequences over the next four days. Some of the other tanks would also contain product, but on the other hand Tank 46 was the unpaired tank in the group of five and thus interference from the adjacent tanks would, it was hoped, be minimised.

On arrival at site on the morning of Saturday the 20th November it was discovered that, mistakenly, T46 was being filled, but more seriously the DIAL acquisition computer failed to boot and, in addition, the wind speed was again below a reliable flux measuring threshold. Fault diagnosis and arrangements to secure a replacement computer hard disk from the UK occupied Sunday and Monday 21st & 22nd November throughout most of which time calm meteorological weather conditions prevailed. On Tuesday morning 23rd November the DIAL system was again operational but calm weather conditions still prevented the commencement of the study. A revised operational schedule for Tank 46 was devised based upon an anticipated test commencement of approximately 11:00 on 24th November. This starting time was in fact the operational start point deadline for the CONCAWE team to enable them to vacate the site by Saturday 27th November at the latest. This allowed approximately 3½ days to complete the second study provided that a start could be made as planned on the 24th November.

On the morning of 24th November the prevailing wind although slightly better was again very light at about  $1 - 1.5 \text{ m.s}^{-1}$ ;  $1.5 \text{ m.s}^{-1}$  normally being considered the threshold for DIAL measurements. Unusually, however, under this wind speed the wind direction was quite stable so in view of the operational deadline, the study was begun. Over the next, approximately, 24 hours measurements were made upwind and downwind of Tank 46, positions and scan lines are shown on Figure 9. Intermittently, depending upon wind direction, it was not possible to segregate Tank 46 from its neighbours and these scans have been excluded

from the results. Throughout this period the wind speed was very low and towards the end of the period died almost completely when a thick blanket of fog descended; because of this the scan rate was lower than normal owing to stoppages when the wind speed or direction varied beyond an acceptable level. Some of the scans completed during this low wind speed period were subsequently rejected because the wind speed or direction had drifted outside the acceptable limits during the scan.

Despite repeated attempts to resume the measurements, for the next 24 hours, up to 11:30 on 26th November, no satisfactory measurements were completed. Measurements were resumed again at 11:30 on 26th November when wind conditions were good with a speed of 3 - 4 m.s<sup>-1</sup>. Throughout the day the wind slowly abated until at 21:30 calm unsuitable conditions again prevailed. At this point CONCAWE decided to terminate the second tank study.

The Spectrasyne team stayed on for a further two days to undertake some dispersion studies for developing upwind subtractions. Some of the measurements taken on the second of these days provided scans covering Tank 46; these have been included in the second tank study data.

During the 100 hours which elapsed between the start of the exercise and the completion of the dispersion tests, a total of 49 scans were possible. Of these, 19 were discarded owing to unsatisfactory wind conditions, which became apparent during the data processing, and a further 6 were upwind scans. Thus 24 downwind scans were usable as data for the second tank study. However, much of these data were obtained at very low wind speeds in the region 1 to  $2 \text{ m.s}^{-1}$ . Wind speed and direction measurements in this low speed region are less reliable than at higher speed and this in turn could lead to less precision in the flux calculations.

The results from the second study and including appropriate scans made during the subsequent dispersion tests are shown in Table 3 and in Figure 10a, plotted on a mid-scan time basis. Figures 10b - 10d show the corresponding mean wind speeds during each scan, the solar illuminance readings / rain index, and the tank roof levels for Tank 46 on the same time basis. The net hydrocarbon fluxes are shown plotted against wind speed and a combined tank level / wind speed factor in Figures 11 and 12 respectively.

#### 4.2.3 Upwind Subtractions

The requirement for the subtraction of upwind fluxes from the downwind measurements was mentioned in the sections on the two tank studies. The methodology for taking off the various and frequently varying sources was complicated. As wind directions changed the source of the upwind fluxes often changed. In some measurement locations, even small wind changes altered the degree to which an upwind source impinged on the downwind plume from the tanks.

For most measurement positions the DIAL was located to facilitate upwind and downwind scans without the need to move the truck. In these positions upwind scans were interspersed between the downwind scans at a average frequency of approximately 25% of the total. These data thus provided information on the incoming hydrocarbons but clearly some interpolation was necessary in accordance with both the wind direction and wind speed as every combination of these which occurred in the downwind scans could not be covered in the upwind scans. In addition to the difficulties associated with the wind changes a further complication when considering upwind subtractions is the variability of the upwind source. In this

context one of the factors which needed to be considered were product movements where fixed roof tanks were in the upwind area, where there were no movements and thus only breathing losses were occurring then the emissions would be reasonably stable. The occasions when the adjacent petroleum product storage site was in the upwind region occurred only during the weekends and since this site is non-operational during the weekends no tank movements took place. Thus only breathing losses from fixed roof tanks and weather related losses from floating roof tanks were relevant. Interpolation between upwind scans was therefore relatively straightforward. The occasions when loading barges were in the upwind region were fortunately few, but the magnitude of these emissions and their variability prevented any meaningful upwind subtractions being derived. Emissions from the slops tankage and water treatment area were seen to vary significantly only when movements to the sumps and tanks were occurring. During the course of the survey the sumps were temporarily covered in an effort to minimise this source. For the most part, during transfer periods, when high emissions occurred, satisfactory upwind subtractions could not be obtained and therefore the corresponding downwind data was discounted.

On some occasions the road loading facility on the other side of the basin was in the upwind region. Upwind scans showed these to be, as expected, largely independent of the wind speed. The emissions were, of course, correlated with activities at the loading bays, which were about 200m away from the upwind scan line, and also with wind direction. When the wind direction presented the loading bays in the upwind field and this corresponded with loading operational periods the upwind scans were plotted against wind direction. This situation occurred throughout most of the position 6 scans. Upwind measurements from the period showed the decline in loading activities between the morning and the afternoon periods. Reasonably accurate interpolations between the upwind scans were therefore possible throughout this period.

With a North Easterly wind direction the upwind region contained not only the other site fixed roof tankage which was accounted for as mentioned above but also two other sources. The first of these was the hot oil heater complex immediately upwind of the tanks. Small and reasonably constant emissions were seen from this area which were independent of wind speed. The second source was thought to come from an industrial site located several hundred metres from the test tanks. These emissions appeared at a higher elevation than the plume from the tanks on the downwind scan lines and these were able to be segregated directly from the downwind tank plumes.

It will be immediately apparent that the presence of these various upwind sources, at least one of which was in evidence for every scan made, have added significantly to the complexity of processing the data. Normally when Spectrasyne undertake survey work, a number of measurement objectives are required and the study area is chosen on a daily basis in order to avoid or minimise upwind contributions. In the case of the CONCAWE programme, the prime objective was to conduct 4 day continuous measurements on one group of tanks. The various upwind sources which at some time came into play during the two studies are depicted on Figure 13 which is a map of the whole basin area.

The final factor which had to be taken into account in so far as the upwind contributions were concerned, was the degree of dispersion of the upwind source between the upwind scan line and the downwind scan line. Whilst formulae and programmes exist for estimating dispersion effects over distances, very little validation work has been done on these and their reliability has yet to be demonstrated. It was recognised at the time of the measurements that upwind subtractions would be necessary. The final two days of work at the site were devoted to making DIAL measurements along a series of downwind scan lines in order to provide a better estimate of the plume dispersions characteristics. This was achieved by measuring the *upwind and downwind fluxes*, over plume areas similar to those of the "area being measured", along the scan lines just in front of and/or just behind the "area being measured", in a region where there was no intervening emission source. The ratio of these *upwind and downwind fluxes* was then used to estimate the dispersion. Clearly, in the time available, dispersion measurements for every combination of wind speed direction (upwind source) was not possible. Enough measurements were made, however, to derive a reasonable approximation of the dispersion characteristic for most conditions encountered. In circumstances where the upwind source was close to the study tanks (e.g. the slops tankage area) and when the wind direction was such that the projected upwind plume was well within the boundaries of the study tanks, then no dispersion was applied as the whole of the upwind source would have been captured by the downwind scans.

# 5. Results And Discussion

### 5.1 Barge Loading Comparison

The DIAL / CONCAWE barge loading losses comparison took place on the 18th November 1993. Losses were recorded from a 950 m<sup>3</sup> gasoline load delivered to a barge which had carried gasoline immediately prior to the comparison test.

A CONCAWE team member made oxygen depletion and HC concentration measurements in the vent gas; the loading rate and gasoline loading temperature were also recorded throughout the loading period. In addition some samples were taken from the gas emitted from the vent; these were subsequently analysed for specific hydrocarbon content. DIAL data were collected some 36 m downwind of the vent, aiming the measurement beams through a gate (see Figure 2) and scanning vertically from the water level to beyond the top of the plume from the vent.

CONCAWE data were collected every 5 minutes throughout the loading period and 10 DIAL scans were completed between 05:20 and 09:10 am. The DIAL was set up to measure NMNARCHC as described above, which is typical of fresh gasoline emissions. However, as it was necessary to make measurements throughout the load, it was not possible to perform any DIAL spectral scans to determine the specific composition of the emitted gas and the sample data were therefore used to compensate the DIAL data for the aromatic and alkene content of the emitted gas which was not detected on this occasion by DIAL. The individual scan DIAL emission measurements for the barge loading are listed in Table 1 and the total loss for the loading period (including alkenes and aromatics) is also given.

The emission variation with time for both the DIAL and CONCAWE data sets is shown in Figure 3 along with the cumulative losses for both data sets. There was an interruption in the loading operation between ~08:00 and 08:40. As no pumping to the barge was taking place, the calculated CONCAWE emission fluxes dropped to zero during this period, but the DIAL was still recording some residual emissions as they dispersed downwind. Allowing for the fact that the DIAL data, which consisted of fewer data points, necessarily has a "smoothed" emission trace, the time related trends from the two data sets are very similar, as are the cumulative loss trends. The CONCAWE team recorded a total loss of 435 kg and Spectrasyne a total loss of 390 kg; the total CONCAWE derived loss was 11.5% higher than the DIAL recorded loss. This small difference between the two results is well within the errors of these two quite dissimilar techniques; the agreement can, therefore, be considered to be excellent. The Spectrasyne DIAL system has now been involved in many VOC emission correlation exercises with other dissimilar techniques throughout mainland Europe, Scandinavia and the U.K. and on no occasion have the mean differences been greater than 15%<sup>\*</sup>.

For the gasoline product loaded, with a density 0.733 kg.1<sup>-1</sup>, the DIAL VOC loss recorded from the barge loading represented 0.057% by mass of the complete consignment.

<sup>\*</sup> See footnote on page 4

### 5.2 First Tank Study

As discussed earlier, the choice of site for the CONCAWE tank studies was based upon a number of factors:

- inland location
- barge loading
- a small group of 5 relatively isolated, floating roof, gasoline tanks
- operational flexibility

and

• historical wind data.

This historical wind data indicated that the prevailing wind for November would result in there being few if any significant hydrocarbon sources upwind of the site. Figure 14 shows the time related wind directions actually experienced during the first study compared with those predicted. It can readily be seen that the two wind roses only overlap for a brief periods mostly around South-West. As a result of these "abnormal" November wind directions all the downwind measurements taken required an upwind subtraction process.

The flexibility of the gasoline tanks was, unfortunately, rather restricted because of unusual operational requirements and it was not possible to fill and empty one of the five gasoline tanks keeping all the others at stable low levels. The first test objectives were therefore revised to encompass all five tanks.

A number of operational and maintenance activities occurred on the site itself during the study period. These served to reduce the effective isolation of the tanks, creating intermittent upwind sources which were sometimes observed in the downwind measurements, but, because of their intermittent nature, not always quantifiable in the subsequent upwind measurements.

Whilst every effort was made by the Spectrasyne and CONCAWE site teams to identify and avoid possible interferences from local operations, it is possible that some of the measurement data were subject to additional errors from these operations although it is believed that in most instances the scans affected have been identified and deleted from the data.

The upwind sources emanating from outside the site were also to some extent intermittent and certainly variable. These have been closely scrutinised in the data processing routines and have been allowed for as precisely as possible. However, in many cases the measured upwind fluxes exceeded the VOC contribution from the tanks; small percentage changes in the upwind source (caused by wind direction changes or upwind source modulation) could thus have a disproportionate affect on the calculated net fluxes. Quantification of the errors associated with these "large upwind" measurements is extremely difficult because of the unknown extent of the instantaneous upwind variations. These additional uncertainties apply to individual data points and will, in some cases, have a positive effect and in others a negative effect. Although this does create some scatter of data points, the general levels and trends should be reliable. The main scans affected by these "large upwind" uncertainties were Positions 3 and 5 and the early scans in Position 6 (see Tables 2a and 2b).

Figures 6a, b, and d compare the sequential net flux data with the corresponding wind speed and tank level data. There is a clear general correlation between wind speed and emission, but the amplitudes and timing of the variations in the two traces do not correspond precisely. One particular difference between the two occurs in position 7; the flux trace rises between scans 7.12 and 7.25, but during this period the wind speed is reasonably constant at 4 to 5 m.s<sup>-1</sup>. However, these scans correspond with the latter part of an increase in the level of Tank 41 from 8.4 m to close to top dip (~16 m); scan 7.12 started some 2 hours after the filling operation commenced and the emission peaked during scan 7.25 about 2 hours after the filling ceased. This flux peak during scan 7.25 also corresponded with the maximum wind speed in the scan 7.12 to 7.25 period. Immediately after scan 7.25, the emission level fell dramatically and the wind speed dropped over the corresponding period from 5 to 3.5 m.s<sup>-1</sup>. However, the cessation of filling and/or tank mixing could also have contrived to reduce the emission level. This aspect calls for further investigation.

It is apparent from Figure 6 (a and b) that the correlation between wind speed and emission is very strong. This is demonstrated clearly by the measurements made from positions 2, 3, and 5 where high wind speeds corresponded with higher emission levels, despite a lower overall product inventory in the five tanks.

During the high wind speed period spanning scans 2, 3, and 5, there were a number of rain showers (Figure 6c) with periods of much heavier rain during scans 3.3, 5.12, 5.13 and 6.2 to 6.5. All of these specific scans had significantly reduced emissions and all except 3.3 showed no wind speed correlation which could have accounted for the reduced emission levels. It is, therefore, probable that heavy rain also has a significant effect on the VOC emission rate. Rain effects on emissions from tankage and other emission sources have been observed previously by Spectrasyne. It is believed that rain droplets may act as condensation centres for hydrocarbons in the air thus directly 'washing out' these hydrocarbons. Other effects probably include direct cooling to the tanks and possibly even assisting sealing.

High speed, gusting winds dominated during scans 3.1 to 3.4, 5.7 to 5.9 and the arithmetic mean of the wind speeds during the scan, under such conditions, will probably not be representative of the true wind effect on the tank emissions. The points on Figure 7 from these scans (marked G), which are emissions plotted against arithmetic mean wind speed, would probably be displaced towards the higher mean wind speeds were their true effect to be represented.

### 5.3 Second Tank Study (Tank 46)

The introductory observations made in Section 5.2 are generally also applicable here with an additional caveat relating to the extremely unfavourable meteorological conditions which prevailed throughout the test period (see Figure 15 for a comparison of actual and previous wind directions). The data are included for completeness. However, in view of the sparsity of the data and the very low levels of measured emissions, CONCAWE advised that detailed discussion was not warranted.

# 6. Conclusions

- 1. Sequential DIAL scans downwind of a barge loading gasoline provided flux data which closely correlated with simultaneous emission rates determined by a CONCAWE team from vent concentration and loading rate information. The integrated total emission figures for the whole loading period derived from the CONCAWE method was 12% higher than the DIAL scan integrated figure.
- 2. The two tank studies undertaken at the site provided a total of 165 scans of which 33 were upwind scans and a further 35 could not be used owing to unfavourable wind conditions or intermittent upwind sources. A total of 97 downwind scans after appropriate upwind subtractions are available for comparison with emissions to be calculated from API data by CONCAWE.
- 3. The first tank study undertaken during a continuous period of 89 hours provided data on the combined emissions from the five gasoline / naptha floating roof tanks. Despite the fact that each measured downwind flux required a significant upwind subtraction, the net downwind fluxes were broadly consistent with prevailing wind speed. Wind speeds were seen to be the predominant emission driving force, the emissions ranging up to 45 kg.h<sup>-1</sup> at wind speeds of over 9 m.s<sup>-1</sup>. Over and above the wind speed effect an influence on emissions of increasing tank roof level was observed as the tank in question approached top dip which subsequently diminished at a static top dip. This observation warrants further investigation.
- 4. The second tank study which focused upon the emissions from a single tank was severely constrained by weather conditions.

## **APPENDIX**

## A.1 Background.

### A.1.1 History

Over a decade and a half, a combined industry/government (BP/NPL) project has been operating to develop light/laser based technology systems for the remote monitoring of gaseous species in the atmosphere. The flagship of these developments is a Differential Absorption LIDAR or DIAL system. DIAL is a development of LIDAR, a light based range finding system similar to RADAR. If a laser is used as the LIDAR light source, the collimated, coherent light emitted can be used to define the range of specific small objects with great precision. A tunable laser source can give LIDAR an additional spectroscopic capability as the source laser can alternately be tuned onto then off an absorption feature in the known 'spectral fingerprint' of a specific gas. Measurement of concentration in the path between the laser and the detector can then be made by comparing the energies in the two return signals  $(\lambda_1 \& \lambda_2, \text{ see Figure A-1})$ .

Until 1986 the joint development programme had concentrated on the UV and visible spectral regions where gases such as sulphur dioxide, nitric oxide, nitrogen dioxide and ozone have specific absorption features. Many other gases including the majority of the hydrocarbons have strong absorption features in the infrared region. The significance and potential of a system which could operate in the infrared was realised by all concerned and a further research programme was established to enable the technology development for DIAL hydrocarbon species monitoring. This programme involved a number of British companies, a laser manufacturer and the creation of a unique infrared source assembly which with the customised laser system, provided tunable infrared laser radiation.

During the prototype testing phase, and subsequently, the "DIAL Team" were engaged in the design and construction of a more commercially orientated DIAL system. This system was built on the experience of the prototype and incorporated many recent technological improvements in optics, laser equipment, fast data transfer and communications hardware. Two parallel laser systems were installed to enable simultaneous measurement in the UV, visible, and IR spectral regions. Additionally with assistance from computing specialists, the acquisition software was improved, and fast data handling programs were designed to speed up the processing of the vast amount of data generated by the system. This data processing development is continuing to provide, ultimately, a real-time read-out capability.

The construction of the new DIAL was completed, installed in the 12 metre mobile Environmental Monitoring Unit (EMU, Figure A-2), in September 1990, 6 months ahead of the original schedule.

Subsequently, the technology was licensed to SPECTRASYNE Ltd. which purchased the Environmental Monitoring Unit outright from BP. The EMU also houses a unique in-stack, emissions monitoring system, which along with its current Spectrasyne operating team has

been engaged by a number of national authorities to make emission measurements from various refinery sources.

Throughout the 1980s and early 90s, at various critical development stages, validation and correlation work was carried out with the DIAL. This work ranged from making measurements through gas cells which had been filled with gravimetric standard gas mixtures to correlation exercises between DIAL concentration measurements and stack gas analyses collected using conventional gas analysers and gas chromatography equipment. Concentration correlations at ambient/environmental levels against accredited thermal sorption tube data were also undertaken. In all cases the DIAL measured concentrations were within 10-15% of the standard or the data generated by the more conventional technologies. However, since 1988, DIAL concentration data have been used with wind speed and direction to produce mass emission fluxes (kg,h<sup>-1</sup>) and some further validation work on the production of mass emission fluxes was considered necessary. The most effective method of achieving this was to use DIAL and its associated meteorological equipment to measure a "known" gas release calibrated to a traceable standard gas mixture. The BP/SPECTRASYNE DIAL was invited to participate in an EC funded programme, hosted by British Gas (BG), to measure and model plume dispersion. The work was to be carried out at the British Gas Spadeadam site in Cumbria where calibrated amounts of methane gas were to be released into the atmosphere over 10 minute periods. In July 1991 this "flux measurement" validation exercise was undertaken at the Spadeadam test site. The mean percentage difference between the BG calculated and DIAL measured release rates was 10%. This remarkably close agreement between the DIAL measured fluxes and the calibrated BG emission rates and the previous DIAL concentration correlation/ validation results are a testament to the reliability of the DIAL technique for both determination of gaseous emission fluxes and for remote measurement of gaseous concentrations in the atmosphere.

## A.2 Equipment

#### A.2.1 DIAL

The Spectrasyne DIAL is based on two high energy (1.4J), 10Hz pulsed Nd:YAG pumped dye lasers. Tunable ultraviolet and visible radiation is generated in one of the laser sets by selective use of frequency doubling and tripling crystals. The second laser set, which has an injection seeded Nd:YAG, is used to generate tunable infrared radiation by means of the unique infrared source assembly. The DIAL is single ended and its output beam is directed by means of a mirror steering system which rotates in two planes. The backscattered light, which returns along the same path, is collected in a cassegrain-type receiving telescope and delivered to the appropriate detector through a multi-dichroic, beam splitting, collimating and focusing system. In order to collect, store, handle and process the DIAL signals a sophisticated, high speed data communication network has been developed in parallel with a unique MicroVax based software package. The MicroVax is also used to perform a number of ancillary control functions and to store essential spectroscopic and other databases. The vehicle is also equipped with an extendible meteorological mast and a number of portable telemetric stations which are used along the DIAL scan lines to measure wind speed and direction, temperature and humidity. These data are displayed in real time and digitally logged for subsequent use with DIAL concentration data to produce mass emission fluxes. A sophisticated 3D computational fluid dynamics (CFD) model is also connected to the processing system; this is used to provide interpolation between measured wind speed data points for flux calculation and to assist in the definition of suitable measurement positions where the wind fields are complex. Telephoto and wide angle TV cameras are used on the steering system to facilitate beam pointing, the wide angle image is recorded on a time-lapse video recorder to be used if necessary to identify problems visually during subsequent data analysis.

#### A.2.2 In-stack Emission Measurement

The gaseous emission measurements are carried out on-line in the EMU; a PTFE lined heated sample line (up to 200 ft. long) is connected into the flue gas ducting by means of sample points installed in the duct or stack. Flue gases are then transferred to the EMU by means of heated head pumps. Within the EMU the gases are split into two streams: one stream is kept hot and wet and fed to a comprehensive multi-column, multi-detector gas chromatography system where various trace compounds, CO, speciated hydrocarbons, sulphur gases nitrogen compounds (including  $N_2O$ , but not NO or  $NO_2$ ) are determined. The second gas steam is cooled in a peltier cooler and dried in perma-pure driers then analysed as follows:

- Oxides of nitrogen : Chemiluminescence
- Sulphur dioxide : Non dispersive infrared
- Carbon monoxide : Non dispersive infrared
- Carbon dioxide : Non dispersive infrared
- Total Hydrocarbons : Flame Ionisation
- Oxygen : Paramagnetic.

# A.3 Abbreviations

API	American Petroleum Institute
DIAL	Differential Absorption Lidar
EMU	Environmental Monitoring Unit (DIAL Van)
HCs	Non-Methane, Non-Aromatic, Refinery Cocktail Hydrocarbons
Nd:YAG	Neodymium : Yttrium Aluminium Garnet
LIDAR	Light Detection And Ranging
NMNAHC	Non-Methane, Non-Aromatic, Hydrocarbon
NMNARCHC	Non-Methane, Non-Aromatic, Refinery Cocktail Hydrocarbon
TWM	Time Weighted Mean
VOC	Volatile Organic Compound

### Table 1 Barge Loading.

SCAN No.	TIME	HC* FLUX (kg.h⁻¹)
9.1	05:20 - 05:27	28.3
9.2	05:30 - 05:53	93.1
9.3	05:55 - 06:12	103.6
9.4	06:17 - 06:56	106.0
9.5	06:58 - 07:16	91.7
9.6	07:18 - 07:50	99.5
9.7	07:52 - 08:10	110.4
9.8	08:11 - 08:26	59.2
9.9	08:31 - 08:39	49.4
9.10	08:42 - 09:10	173.2
9.11	09:10 - 09:30 (Background)	1.6

## **CUMULATIVE TOTAL\*\***

### <u>390 kg</u>

- \* Non-methane, non-aromatic, alkane cocktail
- \*\* Including aromatics & alkenes

Scan	Scan Date	Scan	u	M	Wind	Upwind		Flux (kg/h)		Notes
No.		Start/End Time	d Time	Speed Dir	Direction	Sources	Ma	NNN *	MO	
				(m/s)	(deg)		(Gross)		(Net)	
2.1	14/11	10:25	11:07	7.0	200	H (DW)	41.6	6.6	35.0	
2.2	14/11	11:12	11:59	7.0	196	H (DW)	37.3	6.6	30.7	
3.1	14/11	12:54	13:41	9.4	243	д_	63.4	17.1	46.3	
3.2	14/11	14:22	15:22	6.1	230	۵.	54.3	11.8	<b>42.5</b>	
ຕ. ເ	14/11	15:34	16:21	6.2	230	ፈ	44.7	12.0	32.7	
3.4	14/11	16:28	17:12	5.8	232	۵.	48.1	11.4	36.7	
5.1	14/11	20:23	20:59	7.2	236	٩	38.8	13.6	25.2	
5.2	14/11	21:05	21:35	7.3	228	а.	32.5	13.7	18.8	
5.3	14/11	21:51	22:44	8.5	234	٩.	41.3	15.5	ଝୁଁଝୁ	
5.4	14/11	22:31	23:02	6.9	235	۵.	31.0	16.3	14.7	
5.5	14/11	23:09	23:43	6.9	235	Ф.	33.2	14.7	18.5	
5.6	14/11	23:53	00:40	7.9	235	۵.	39.0	14.6	24.4	
5.7	15/11	00:49	01:26	7.0	243	ፈ	47.7	13.3	34.4	
5.8 .8	15/11	01:28	02:04	6.7	234	ፈ	49.7	12.8	36.9	
<del>5</del> .9	15/11	02:10	02:43	6.8	250	ፈ	54.0	12.9	41.1	
5.10	15/11	02:50	03:35	6.0	245	ፈ	32.6	11.8	20.8	
5.11	15/11	03:36	04:19	6.0	245	ፈ	34.6	11.8	22.8	
5.12	15/11	04:23	05:05	5.8	249	ፈ	31.8	11.4	20.4	
5.13	15/11	05:21	05:57	5.8	245	ር.	30.3	1.4	18.9	
5.14	15/11	06:12	07:14	5.0	260	P + S	38.3	10.3	28.0	

Table 2a. First Tank Study. Positions 2,3 & 5

KEY: [H]eater area / [P]etroleum product storage / [S]lops area
DW - Downwind / UW - Upwind
\* Upwind sources dispersed to downwind scan line

Notes			Heavy rain	Heavy rain				Wind speed too low	Wind speed too low							
	MO	Net)	< 0.1	< 0.1	4 4	4.4	с. Г	k 0.1	< 0.1	3.5	3.4	4. 2	3.0	4.2	4.6	6.6
E	uw *	)	43.4	42.8	41.1	41.4	8.5			4.1	15.3	5.4	3.2	2.4	2.4	2.4
	MQ	(Gross)	43.3	42.9	42.2	45.8	9.7			7.6	18.7	7.8	6.2	6.6	7.0	9 <sup>.</sup> 0
Upwind	Sources		S + B	S + B	S+В	S + B	S + B	S + B	S+В	ш	S + B	Ш	В+Ј	D+J	В+J	B + J
Wind	Direction	(deg)	285	288	298	296	315	296	310	305	301	320	346	350	348	356
M	Speed 1	(m/s)	3.3	4.3	4.4	3.9	2.5	0.6	0.5	2.5	ດ. ເບ	2.3	2.5	3.7	4.0	4.0
	d Time		10:14	10:39	11:09	12:53	19:47	23:24	23:58	03:29	03:54	04:23	07:12	07:27	08:00	08:32
Scan	Start/End Time		09:39	10:17	10:42	12:22	19:06	22:42	23:28	02:55	03:29	04:10	06:38	07:13	07:28	08:02
Scan Date			15/11	15/11	15/11	15/11	15/11	15/11	15/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11
Scan	No.		6.2	6.3	6.4	6.6	6.13	6.19	6.20	6.26	6.27	6.28	6.31	6.32	6.33	6.34

Table 2b. First Tank Study. Position 6.

KEY: [S]lops area / storage area across [B]asin / [J]etties DW - Downwind / UW - Upwind
\* Upwind sources dispersed to downwind scan line
(Jetties excluded from upwind figure in processing)

Notes																										
	DW	(Net)	4.3	0.0	<b>*</b>	6.8	<b>%</b>	4,1	ດ. ເວ	6.1	<del>0</del> .5	10.4	19.3	13.9	18.7	16.0	17.2	24.6	25.5	6.5	7.1	0.9 0	18.0	6.0	ູ ບໍ່ເວ	8.7
Flux (kg/h)			9.1	9.0	10.0	8.1	9.4	10.5	6.9	7.3	7.0	6.0	5.5 .5	5.5	5.4	6.9	6.6	5.9	5.8 .8	8.9	6.3	6.1	5.2	5.9	<u>5</u> .5	1.8
	DW	(Gross)	13.4	18.6		14.9	17.3	14.6	12.8	16.4	15.5	16.4	24.8	19.4	24.1	22.9	23.8	30.5	31.3	15.4	13.4	15.0	23.2	11.9	11.1	10.5
Upwind	Sources		-+ L + T	-+ -+ + + -+ 	H+ T+ H		H + F + H	 + L + H	+ L+ + T	H+ H	-+ + + + T	+ + + + H	+ + + + + + + + +	H + F +	H + F + H	+ +++ ++ T	Ц + Ц + Ц	H + F +	H + F + H	+ L+ H	_+ _+ _+ _+ _+ _+	H + F + I	+ + + + + +	H + T + L	H + F + H	H + –
Wind	Direction	(deg)		20	14	24	18	42	ŝ	8	32	4	44	44	46	4	35	41	42	5	38	39	49	44	45	56
Wi	Speed L	(m/s)	4.8	4.9	5.0	4.5	4.4	3.5	4.9	4.0	5.0	4.6	4.1	4.0	4.4	4.2	4.5	4.8	5.1	3.5	3.6	4.6	4.4	4.3	3.9	3.5
u	d Time		12:26	13:07	15:32	17:34	18:59	19:31	20:22	20:49	21:30	22:51	23:36	23:58	00:44	01:10	01:52	02:26	03:56	06:01	07:10	07:48	08:21	09:01	09:37	11:52
Scan	Start/End Time		11:51	12:29	15:03	17:12	18:27	19:01	19:43	20:25	20:55	22:16	22:55	23:37	60:00	00:47	01:11	01:59	03:30	05:33	06:35	07:12	07:50	08:25	09:05	11:17
Date			16/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11	16/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11
Scan	No.		7.2	7.3	7.7	7.9	7,11	7,12	7,13	7,14	7,15	7,17	7.18	7.19	7.20	7.21	7.22	7.23	7.25	7.28	7.30	7.31	7.32	7.33	7.34	7.36

Table 2c. First Tank Study. Position 7.

KEY: [H]eater area / [F]ixed roof tanks (gas/fuel oil) / [I]ndustrial site DW - Downwind / UW - Upwind
\* Upwind sources dispersed to downwind scan line (Industrial site excluded from upwind figure in processing)

Notes																
	DW	1.e 8.1	3.4	5.6	9.4	1.6	10.8	3.8	4.0	7.2	2.6	4.6	5.6	3.5	1.6	4.8
lux (kg/h)	NW *	1.8	1.8	1.8	1.8	1.8	1.8	1.8	<del>1</del> .	1.8	1.8	5.9	1.8	1.8	1.8	1.8 6
U.	DW (22050)	0.0	5.2	7.4	11.2	3.4	12.6	5.6	5.8	0 <sup>.</sup> 0	4.4	10.5	7.4	5.3	3.4	6.6
Upwind	Sources			 + T	-+ + T	-+ T	-+ -+ T		-+ + T		-+ T	H + F + H		+ -+	+ -+	– + H
Wind	Direction	59 59	55	53	57	55	54	52	56	51	50	45	53	54	41	9
M	Speed Dire	4.7	4.1	4.4	4.8	3.7	3.3	2.8	3.0	3.3	3.8 0.8	3.4	3.2	3.0	2.7	2.0
an	d Time	14:19	15:21	15:44	16:07	16:27	17:48	19:11	20:15	20:44	21:21	21:38	22:18	22:49	00:37	01:49
Scan	Start/End Time	13:54	14:50	15:24	15:45	16:09	17:08	18:40	19:35	20:16	20:49	21:23	21:49	22:20	23:53	01:15
Scan Date		17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	17/11	18/11
Scan	No.	8.1	<u>ເ</u>	8.4	8.5 9.5	8.6	8.8	8.10	8.11	8.12	8.13	8.14	8.15	8.16	8.18	8.19

Table 2d. First Tank Study. Position 8.

KEY: [H]eater area / [I]ndustrial site / [F]ixed roof tanks (gas/fuel oil)
DW - Downwind / UW - Upwind
Upwind sources dispersed to downwind scan line
(Industrial site excluded from upwind figure in processing)

Notes																									
	DW (Net)	< 0.1	0.S	0.4	<b>0</b>	1.2	< 0.1	0.8	0.5	0.4	< 0.1	0.5	0.5	< 0.1	0.5	ŝ	0.8	<del>م</del> ه جب	0.4	0.9	0.8	1.6	1.7		1.3
Flux (kg/h)	* WU	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.3	0.3	0.6	0.2	0.4	0.6	0.6	0.2	0.6	0.6	0.6	0.2	0.6	1.7	1.7	1.7	1.7
	DW (Gross)	0.1	0.0	0.5	 -	1.3	0.0	0.9	0.8	0.7	0.6	0.7	1.0	0.0	<del>.</del> ۲	1.5	1.4	1.6	1.0	+ +-	1.4	3.3	3.4	2.8	3.0
Upwind	Sources	I	- <b></b>	Ŧ	T	« <b>-79-11</b>		Т						]						T				ц. + Т	للہ ج-
	)irection (deg)		20	50	34 1	- 6 8	4	9	345	345	336 ,	352 1	343	337	339 ,	349	340	337 ,	335 ,		335 .	21	7	14	1 61
Wii	Speed D (m/s)	<del>.</del> .	1:2	1.0	1.6	2.1	<u></u>	1.1	3.2	3.2	2.4	3.1	2.5	2.7	2.1	2.6	2.5	2.5	1.9	1.7	1.9	5.6	5.4	4.0	4.3
L	Time	12:14	12:52	13:50	15:28	15:54	16:57	20:28	11:54	12:49	13:50	14:40	15:29	16:36	17:12	17:41	18:33	19:07	19:48	20:21	21:13	11:42	12:22	14:19	15:10
Scan	Start/End Time	11:46	12:19	13:18	14:59	15:32	16:27	18:57	11.25	11:57	13:35	14:21	15:03	16:10	16:38	17:16	18:04	18:42	19:19	19:54	20:48	11:17	12:02	13:50	14:34
Date		24/11	24/11	24/11	24/11	24/11	24/11	24/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	26/11	28/11	28/11	28/11	28/11
Scan	So.	10.2	10.3	10.4	10.6	10.7	10.8	10.9	13.1	13.2	13.6	13.8	13.10	13.12	13.13	13.14	13.16	13.17	13.18	13.19	13.20	16.1	16.3	16.6	16.7

Table 3. Second Tank Study. Positions 10, 13 & 16

KEY: [H]eater area, [J]etties, [F]ixed roof tanks (gas/fuel oil)
DW - Downwind, UW- Upwind
\* Upwind sources dispersed to downwind scan line



Figure 1 Preferred DIAL Measurement Position





Figure 3 Barge Loading. Comparative Cumulative Losses.



T BOT TANK STG Environmental Survey

SPECTRASY







Figure 7 First Tank Study. Wind Speed vs Flux.



0.25 0.20 Ő Wind Speed (m/s) / Tank Dip (m) First Tank Study , \_\_\_\_\_ 0.15 e ش ů Ů ů Ď Ъ, 0.10 0.05 Gusting wind Mixers in use Tank Filling SPECIFICSYNE Environmental Surveying Flux (kg/h) U ₽ \_\_\_\_\_0 50 20 40 30 0

Figure 8 First Tank Study. Wind Speed/Tank Level Factor vs Flux







Figure 10 Second Tank Study. a) Flux, b) Wind Speed, c) Light Level, d) Tank Level.



Figure 11 Second Tank Study. Wind Speed vs Flux.

Figure 12 Second Tank Study. Wind Speed/Tank Level Factor vs Flux.







Figure 14 Wind Rose - First Tank Study.



Figure 15 Wind Rose - Second Tank Study.



