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## A dial method to estimate VOC emissions

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## Summary

The Dutch Ministry of Housing, Physical Planning and the Environment commissioned TNO to evaluate the practical application of a differential-absorption lidar (DIAL) system in the measurements of the emissions of volatile organic compounds (VOCs). The evaluation took place by carrying out a measurement campaign (of about one week duration) in which the mobile DIAL facility was used simultaneously with a more conventional TNO-based method in the evaluation of the VOC emission of a tank storage in the “Rijnmond” area. The TNO method was based on downwind concentration measurements and these measurements were used to back calculate the source emissions, using a gaussian-plume dispersion model. These measurements were also extended by using passive hydrocarbon measurements at the tanks to facilitate the gaussian-plume calculations.

The measurements were carried out at and in the vicinity of the tank farm “van Ommeren Tank Terminal Europoort BV”. The measurement were carried with permission and cooperation with Van Ommeren Tank Terminal Europoort. At this site it was possible to make emission measurements when various wind directions were present.

During the first few days of the campaign the meteorology was unfavourable, with a wind from the east with low wind speeds. Later in the campaign the wind turned more to the south-west side, with increasing wind speeds. There was very little rain during the campaign, but some fog was present during the first days.

### (i) Summary of the Results

The results of the TNO and NPL measurements given in Table 1 are for the measurements where comparisons could be made between the two methods.

Table 1 Emissions of total hydrocarbons during the measurements.

| Date  | Start | Stop  | TNO measured emission (kg/hour) | NPL measured emissions |
|-------|-------|-------|---------------------------------|------------------------|
| 30/10 | 14.35 | 15.40 | 3 E2                            | 4.80 E2                |
| 30/10 | 16.00 | 17.00 | 3 E2                            | 3.20 E2                |
| 30/10 | 17.20 | 18.20 | 2 E2                            | 1.70 E2                |
| 03/11 | 14.12 | 15.15 | 2 E2                            | 0.90 E2                |
| 03/11 | 15.45 | 16.45 | 1 E2                            | 1.20 E2                |
| 05/11 | 12.15 | 13.15 | 5 E2                            | 5.00 E2                |
| 05/11 | 13.30 | 14.30 | 5 E2                            | 2.80 E2                |
| 06/11 | 10.30 | 11.30 | 4 E2                            | 1.70 E2                |
| 06/11 | 13.00 | 14.00 | 2 E2                            | 2.00 E2                |
| 06/11 | 14.20 | 15.15 | 1 E2                            | 2.20 E2                |

The two sets of results show a good correlation. On average the TNO measurements lead to a slightly higher emission value than the NPL measurements, although this difference is not significant. The total hydrocarbon flux averaged over

all the simultaneous measurements was 280 kg/hour for the TNO measurements. The NPL measurements lead to an average emission flux rate of 260 kg/hour.

The results also show, however, that an individual measurement may differ by significantly more (the highest difference is a factor of 2.3).

Additional passive hydrocarbon measurements, carried out at the storage tanks by TNO, indicated that the main emissions originate from a few tanks, and that the emissions from the majority of the tanks were low. An explanation for this could not be found on the basis of available data.

### **(ii) Comparison of the Two Measurement Methods**

The DIAL measurements give a more or less a direct estimate of the emissions, without many assumptions. Though for the determination of the emission of individual tanks with the DIAL technique measurement of the local wind field becomes a problem, which requires additional measurements. The TNO method relies more heavily on dispersion models and therefore has a lower practicability. In this particular case, additional measurements on the site were carried out by TNO in order to obtain a better emission estimate. (The additional site measurements are not essential, however, for the estimate).

The costs of the conventional measurements are lower than the DIAL measurements. The TNO measurements cost about 50 - 60 % of the cost of the DIAL measurements for the same number of measurement days.

### **(iii) Comparison with the data from Emission Registration**

Only a limited number of hourly averaged measurements were made and these hourly emissions may differ significantly from the long term average values. Therefore the measurements probably provide no more than an indication of the annual emissions. Given this restriction, a valid comparison with the annual emission estimation and registration system cannot be made with any accuracy. Nevertheless such measurements when combined with longer-term data on the representativeness of the measurement period, can provide valuable data on the validity of emission inventories for such industrial plant. When the hourly measurements are used to calculate an annual emission this would lead to an emission of approximately 3000 tonnes/year given these restrictions.

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- 2 Characteristics of optical measurement methods
- 3 Description of the DIAL method
- 4 Description of the conventional method

## 1. Introduction

### 1.1 Background

The Dutch Ministry of Housing, Physical Planning and the Environment commissioned TNO to evaluate the practical application of a variant of the Light Detection and Ranging (Lidar) principle known as Differential Absorption Lidar (DIAL) in the measurement of volatile organic compound (VOC) emissions.

Optical methods have great potential in the measurement of hydrocarbons and are used commercially by different groups (for instance the National Physical Laboratory in England, Spectrasyn, Siemens, Shell and others). There is a tendency for a wider spread use of optical techniques in the measurement of emissions of different compounds amongst which hydrocarbons. Different optical techniques are in use, the most important techniques are:

- Differential Absorption Light Detection And Ranging (DIAL-LIDAR or as an abbreviation DIAL)
- Differential Absorption Spectroscopy (DOAS)
- Fourier -transform Infra-red Spectroscopy (FTIR)
- Tunable Diode-Laser Spectroscopy (TDLAS)

Some characteristics of the different methods are given in appendix 2.

In this project the practical application of a DIAL in emission measurements was evaluated by carrying out a measurement campaign in which the DIAL system was used simultaneously with a more conventional technique. The conventional technique was based on downwind concentration measurements and back calculating the concentrations to emissions by using a Gaussian Plume model. The conventional technique was used by TNO.

Current DIAL systems are used for the measurement of a number of compounds. The most important are ozone, nitrogen dioxide, sulphur dioxide, total volatile organic compounds (VOCs), benzene, toluene, methane and a wide range of other specific VOCs, ethanol, ammonia and chlorinated solvents.

Typical emitted mass flux detection limits for DIAL systems are 1 - 10 kg/hr. The detection limits for (total) VOC concentrations are relatively high, in the order of magnitude of 20 ppb.

An appropriate site was selected for the evaluation of the optical technique. A measurement campaign of about one week was carried out at the site, with the emphasis of the measurements put on the (total) VOC emissions from the site. This gave the opportunity to also evaluate the results of the measurements within the framework of the so called "Koolwaterstoffen 2000" (the hydrocarbon 2000 proj-

ect in which emission decreases are taken up for specific base years, ending in the year 2000).

It should be stressed that the project was planned to be a demonstration project, and that it was not meant to give a specific annual average emission value for the selected site.

## **1.2 Overview of the Report**

A description of the site is given in chapter 2. In chapter three a description is given of the meteorology which occurred during the measurements. The conventional measurements are described in chapter 4 and the DIAL measurements are described in chapter 5. In chapter 6 the different methods are compared and a comparison of the measured emissions and the data in the emission registration system is made. Finally in chapter 7 the conclusions are given.

## 2. The site

### 2.1 Selection of the Site

A suitable site to perform the comparative measurements had to meet a number of specific criteria. The most important of these were that:

1. The VOC-emissions of the site must be in the Emission Registration (ER) system of the Netherlands;
2. It had to be possible to measure simultaneously with the DIAL system and the conventional method;
3. The site had to be accessible by a truck;
4. The people involved at the site had to be willing to cooperate with the measurements;
5. The site should have a significant level of VOC emissions;
6. There were suitable locations for the measurement of the concentration profiles downwind from the site using the conventional technique;
7. There were no other large VOC-emission sources in the direct vicinity of the site.

For practical reasons the site had to be situated in the so called “Rijnmond area” or in the province of Zeeland. TNO made a first selection of a shortlist of sites based on the Emission Registration data. A number of sites were identified which had suitable levels of hydrocarbon emissions. These sites were then viewed to see whether or not they could meet the criteria mentioned above.

The tank farm “van Ommeren Tank Terminal Europoort BV” met nearly all of the measurement criteria, and its location meant that emission measurements could be made under a variety of wind conditions. The only potential problem was that emissions from another tank farm lying close by might cause difficulty in the evaluation of the measurements. The total VOC emissions (according to the ER) was estimated to be 922 tons per year.

### 2.2 Description of the site

The site consists of 26 major storage tanks and 10 smaller storage tanks. The tanks contain:

- gasoline
- diesel
- gas-condensate
- kerosene
- naphta

The largest tank has a diameter of 60 metres and has a maximum capacity of about 85.000 m<sup>3</sup>. A schematic view of the site is shown in Figure 2.1, with the individual



tanks identified. A table of the contents of the tanks and the variation in their contents during the measurements is given in appendix 1.

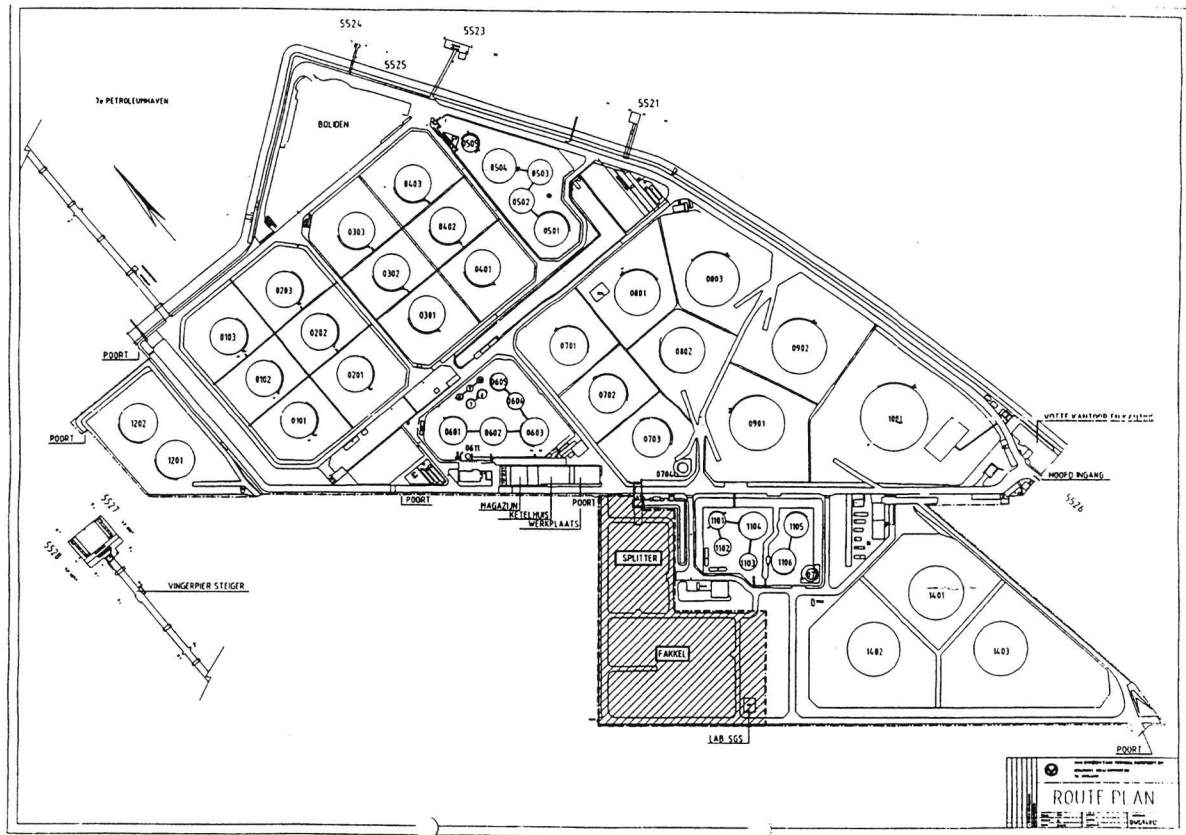
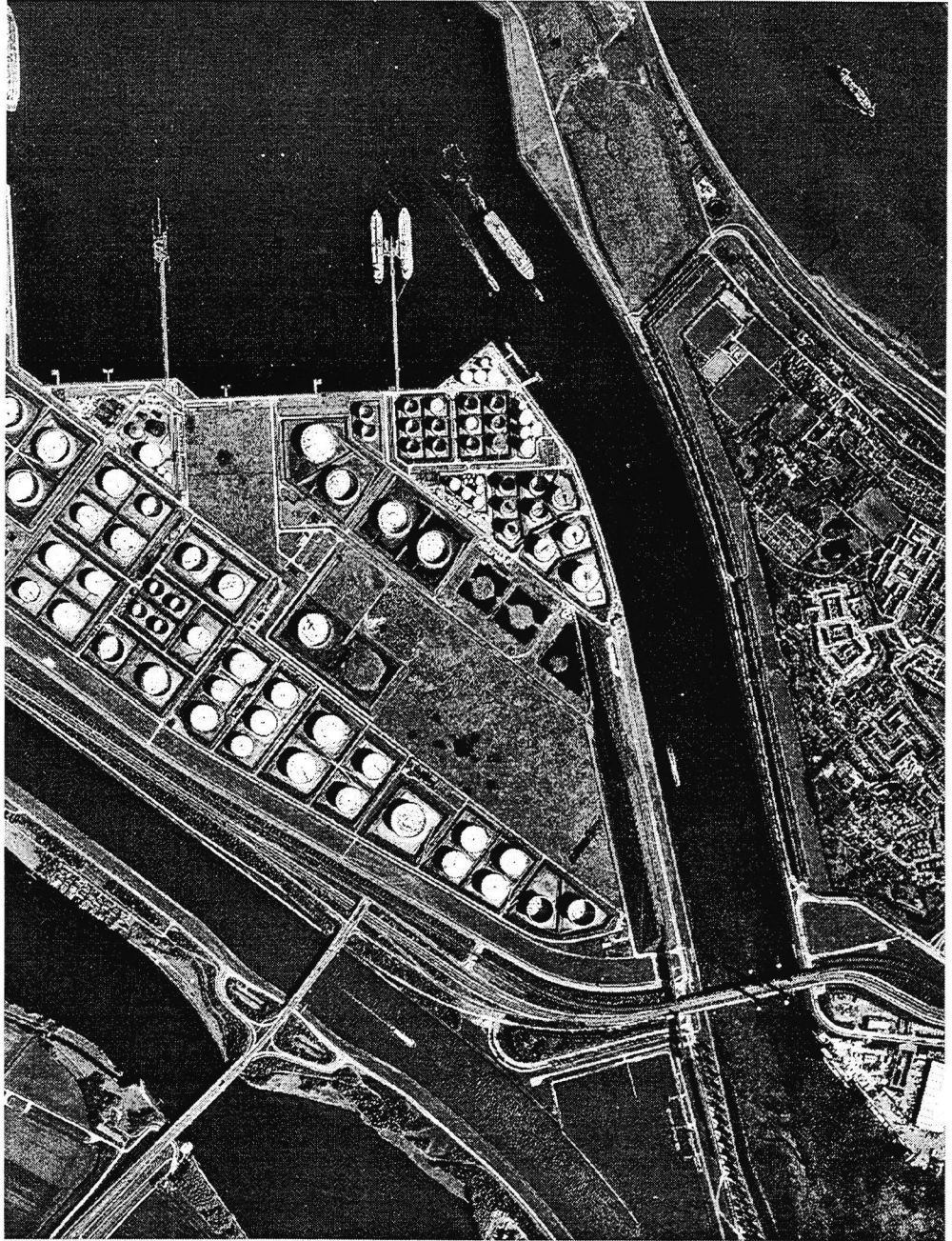


Figure 2.1 The site van Ommeren Tank Terminal Europoort BV Europoort.

The tank storage is bordered by the Calland canal along its eastern edge. On the north side there is the Petroleum port and the western and the southern borders of the site lie next to the Paktank tank storage site. Emissions from this site might lead to high background concentrations of hydrocarbons.

Figure 2.2 is a map showing both the van Ommeren and Paktank sites. This figure also indicates the roof type of each tank - which is either fixed roof with an internal floating roof or a single floating roof.



*Figure 2.2 The tank storage of van Ommeren and it's direct surroundings.*

The whole site was accessible for the measurements. The process installation on the site (ie the splitter and the flare) were not operating during the measurements.

### 3. Meteorology during the measurements

The measurements were carried out between Friday the 31st of October and Thursday the 6th of November. From Friday until Tuesday the wind direction was generally Easterly, with low, variable wind speeds ( $< 3$  m/s). On Wednesday and Thursday the wind was from the South West, with higher wind speeds ( $> 5$  m/s) and therefore better defined wind conditions. There was no rain during the measurement period, However, there was some fog on Saturday and Sunday which restricted but did not prevent the measurements.

The meteorology which occurred later in the week provided a good opportunity to carry out simultaneous DIAL and standard measurements. With the Eastern winds earlier in the campaign the location to perform the standard measurements was less favourable. In addition, the low wind speeds led to a very variable wind direction, which led to some difficulties for both the measurement techniques.

During the first few days of the measurements the temperatures were around zero, with clear skies and some sunshine. Later in the week (during the period of westerly winds) the temperatures rose to about  $10$  °C, and it was more overcast.

## 4. Optical method

This chapter provides an overview of the measurement technique known as differential absorption lidar (DIAL). An extended description of the optical method is given in appendix 2.

### 4.1 General

The NPL DIAL facility was used to measure the VOC emissions from the Van Ommeren site on six of the seven measurement days. The majority of this period was spent measuring downwind of the entire site, so that the total site emissions could be determined. There was regular communication between the NPL and TNO personnel to ensure that the timing of these total emission measurements were coordinated with the TNO measurement schedule.

During periods when conditions were not suitable for the standard measurements, some time was spent using the DIAL facility to measure within the site in order to locate the major emission sources. Measurements were also made upwind of the site, in order to quantify the contribution of any sources external to the Van Ommeren site. No significant emission sources were detected in these upwind scans.

One day of the campaign (4/11/97) was used specifically for benzene measurements, where DIAL measurements were made from various locations in order to locate and quantify any significant sources of benzene emissions in the site.

### 4.2 Results

An extended review of the results of the DIAL measurements can be found in appendix 2. A brief summary of the measurements is given in table 4.1 below.

Table 4.1 Daily mean VOC fluxes obtained by the DIAL technique.

| Date         | Number of Flux Measurements | Mean VOC Flux (kg/hr) | % Uncertainty (95% conf. level) |
|--------------|-----------------------------|-----------------------|---------------------------------|
| 31/10/97     | 29                          | 330                   | 10                              |
| 1/11/97      | 10                          | 170                   | 35                              |
| 2/11/97      | 3                           | 230                   | 30                              |
| 3/11/97      | 10                          | 100                   | 40                              |
| 4/11/97      | -                           | -                     | -                               |
| 5/11/97      | 13                          | 390                   | 25                              |
| 6/11/97      | 14                          | 200                   | 20                              |
| <b>TOTAL</b> | <b>79 scans</b>             | <b>260</b>            | <b>10</b>                       |

On measurement day (4/11/97) which was used to measure benzene specifically, the peak benzene concentrations (averaged over a 20 meter path) varied between less than 50 and 440 ppb.

### 4.3 Discussion

The VOC fluxes emitted from the Van Ommeren site was successfully measured on six of the seven days of the campaign. The mean flux for each day is shown in table 4.1. A total of 79 flux measurements were made, and the overall mean value is also shown in the table. It should be noted that poor meteorological conditions (unstable wind conditions) meant that the data obtained on the 2<sup>nd</sup> and 3<sup>rd</sup> November had a larger estimated uncertainty than that obtained on other days.

The individual flux results showed a much larger variability than the individual measurement uncertainty (~20%). This indicated that the source was varying significantly over periods of around 15 minutes. This source variability is confirmed by the variations in the daily averages.

Simultaneous site flux data was obtained by the DIAL technique during ten of the sixteen TNO measurement periods, and comparisons between the results obtained are given in section 6.1.

## **5. TNO method**

### **5.1 General**

The method that is used by TNO consists of upwind and downwind concentration measurements, which are then used to calculate the emissions from the selected site by using Gaussian plume dispersion models. Usually a tracer gas is also released and measured, from which the actual dispersion parameters are calculated. In this way more accurate results can be obtained. A detailed description of this method is given in appendix 3.

### **5.2 Results of the measurements**

#### **5.2.1 Concentration measurements**

The measured total hydrocarbon concentrations downwind from the source differed from day to day and even from hour to hour during one measurement day. Butane, pentane, 3-methyl-pentane and hexane had the highest concentrations. Concentrations of aromatic compounds were much lower downwind of the site.

#### **5.2.2 Results of the passive measurements at the different tanks**

High hydrocarbon concentrations were measured from nine out of the 29 tanks studied. In some cases there might have been some influence of neighbouring tanks, especially for the fixed roof tanks.

When these measurements are compared to the data gathered by van Ommeren about the contents of the storage tanks, there is no correlation of the fluctuations of the contents of the tanks and the measured concentrations on the tanks. Also the tank constructions or maintenance schedule was comparable for the different tanks. So an explanation for these differences could not be found. More research is needed to find out the reason for these differences.

#### **5.2.3 Emission estimates obtained using the TNO Method**

The total emissions of the tank storage were using the technique described in appendix 3. During the first days of the measurement (Friday 30 October 1997 and Monday 3 November 1997) only a part of the complete storage tank area could be measured. For the other days (Wednesday 5 November and Thursday 6 November) the emission of the whole storage area could be measured satisfactorily.

Because of the unfavourable meteorological conditions during the first days it was difficult to consistently measure downwind of the site, using the TNO method. Therefore the VOC emission estimates for these days have a higher degree of uncertainty than the estimates for the days later in the week, when the wind came from the South West. These emission estimates are summarised in table 5.1.

Table 5.1 Emission of total hydrocarbons during the measurements.

| Day   | Start | Stop  | emission<br>hourly average<br>(kg/hour) |
|-------|-------|-------|---|
| 30/10 | 14.35 | 15.40 | 3 E2                                    |
| 30/10 | 16.00 | 17.00 | 3 E2                                    |
| 30/10 | 17.20 | 18.20 | 2 E2                                    |
| 03/11 | 14.12 | 15.15 | 2 E2                                    |
| 03/11 | 15.45 | 16.45 | 1 E2                                    |
| 05/11 | 11.00 | 12.00 | 8 E2                                    |
| 05/11 | 12.15 | 13.15 | 5 E2                                    |
| 05/11 | 13.30 | 14.30 | 5 E2                                    |
| 05/11 | 15.00 | 16.00 | 7 E2                                    |
| 05/11 | 16.15 | 17.15 | 2 E2                                    |
| 05/11 | 17.30 | 18.30 | -                                       |
| 06/11 | 10.30 | 11.30 | 4 E2                                    |
| 06/11 | 11.45 | 12.50 | -                                       |
| 06/11 | 13.00 | 14.00 | 2 E2                                    |
| 06/11 | 14.20 | 15.15 | 1 E2                                    |
| 06/11 | 15.30 | 16.30 | 4 E2                                    |

### 5.3 Discussion

The meteorological conditions during the first two measurement days were somewhat unfavourable, with low wind speeds and a variable wind direction. This led to a relatively large uncertainty in the measured concentrations. The conditions for the last measurement days were better, which also allowed a better estimate of the emissions of the site as a whole to be obtained.

It is estimated that the measured emissions during the first two days by the TNO method has an uncertainty of about a factor 2. The emissions measured using the TNO method during the last two measurement days is estimated to have an uncertainty of a factor between 1.5 - 2.

During the first days the measurements were carried out relatively close to the individual tanks (about 100 metres for the nearest tank). It should be noted that when measurements are made close to the source the method is sensitive to where the

emission is assumed to take place. However, the results of the passive samplers were used to support the hypothesis that the majority of the emissions were produced by the tanks closest to the measurement plane.

When the distance between the measurements and the source becomes larger the exact location of the emission becomes less relevant. This is another reason why the measurements carried out on Wednesday and Thursday are considered to be more accurate.



## 6. Evaluation

### 6.1 Comparison of the results

In table 6.1 the results of the TNO and NPL measurements are given for the periods where a direct comparison could be made. NPL also carried out some measurements on the 1st and 2nd of November, however, since the conditions were very unfavourable TNO did not carry out measurements on these days. The results obtained by the NPL were therefore not included in this table.

Table 6.1 Emission of total hydrocarbons during the measurements.

| Day   | Start | Stop  | TNO-emission<br>(kg/hour) | NPL-emission<br>(kg/hour) |
|-------|-------|-------|---------------------------|---------------------------|
| 30/10 | 14.35 | 15.40 | 3 E2                      | 4.80 E2                   |
| 30/10 | 16.00 | 17.00 | 3 E2                      | 3.20 E2                   |
| 30/10 | 17.20 | 18.20 | 2 E2                      | 1.70 E2                   |
| 03/11 | 14.12 | 15.15 | 2 E2                      | 0.90 E2                   |
| 03/11 | 15.45 | 16.45 | 1 E2                      | 1.20 E2                   |
| 05/11 | 11.00 | 12.00 | 8 E2                      | 1.70 E2 <sup>1</sup>      |
| 05/11 | 12.15 | 13.15 | 5 E2                      | 5.00 E2                   |
| 05/11 | 13.30 | 14.30 | 5 E2                      | 2.80 E2                   |
| 05/11 | 16.15 | 17.15 | 2 E2                      | 0.20 E2 <sup>1</sup>      |
| 06/11 | 10.30 | 11.30 | 4 E2                      | 1.70 E2                   |
| 06/11 | 13.00 | 14.00 | 2 E2                      | 2.00 E2                   |
| 06/11 | 14.20 | 15.15 | 1 E2                      | 2.20 E2                   |
| 06/11 | 15.30 | 16.30 | 4 E2                      | 0.50 E2 <sup>1</sup>      |

<sup>1</sup> The emission of a part of the site was measured.

The measurements show a very good correlation. On average the TNO measurements lead to a slightly higher emission than the NPL measurements, though the difference is not significant. The total hydrocarbon flux averaged over the measurements based on the TNO measurements equals 280 kg/hour. The NPL measurements lead to an average emission of 260 kg/hour.

The results show that the comparisons of individual measurements often have quite large variations (highest difference a factor of 2.3). This might be caused by unfavourable meteorological conditions leading to the measurement of only a part of the plume. This shows that, when emission estimates like this are carried out it is advisable to do several measurements in order to obtain a reliable result.

## 6.2 Comparisons of both methods

### 6.2.1 Principle of the methods

The DIAL measurements give a more or less direct estimate of the emission, without a large number of assumptions. The more conventional TNO method relies more heavily on dispersion models and therefore has a lower practicability. With the TNO-measurements more assumptions are made and the use of dispersion models is important. The use of a tracer gas enables the modelled concentrations to be fitted to the measured concentrations. However, the measurements are still extrapolated to an emission flux by dispersion modelling. In this particular campaign additional measurements were done on the site in order to produce a better emission estimate.

One important advantage of the DIAL measurement is that it intersects and measures the atmospheric profile of the pollutant, irrespective of its height above ground, since the DIAL system measures the flux through a vertical plane in the atmosphere. The technique also, however, requires the correct measurement of the meteorology which is equally as important as a correct measurement of the VOC concentrations. When the meteorological measurements are carried out in the vicinity of the site care should be taken to have a really free wind field for the meteorological measurements. This is done by making DIAL measurements at suitable distances downwind of the plant. It should be noted that the sensitivity to wind direction is proportional to the sine of the angle between the DIAL measurement plane and the wind direction. This angle is generally chosen to be as close to  $90^\circ$  as possible in order to minimise this sensitivity.

### 6.2.2 Sensitivity

The conventional method is more sensitive than the DIAL method. The better sensitivity of the conventional measurements enabled the concentrations of individual hydrocarbons to be determined. The fingerprints of the individual hydrocarbon measurements can be used to get a better picture of the processes going on at the site. However, such an analysis was not within the scope of this project.

The conventional (passive) samplers showed very high localised hydrocarbon concentrations (several  $\text{mg}/\text{m}^3$  near the water treatment). The peak concentrations observed by the DIAL system were significantly lower than this due to the 10 m range-resolution of the system..

Detection limits for flux measurements (expressed in  $\text{kg}/\text{hr}$ ) are comparable. The TNO method is also capable of measuring lower emissions ( $0.05 \text{ kg}/\text{hr}$ ), but usu-

ally not with large industrial sources particularly in situations where there are high background concentrations.

### 6.2.3 Background concentrations

For both methods background emissions may cause problems. When, e.g. in the case of van Ommeren, a source of hydrocarbons lies in the near vicinity of the site, the background concentrations (for the TNO method) or the background emissions (for the DIAL measurements) has to be measured and somehow subtracted from the actual measurements.

In the case of van Ommeren, TNO did this by measuring background concentrations at four locations and by using dispersion models the background concentration at the actual measurements was calculated.

Two methods were used to assess the effects of background emissions on the DIAL results. Some upwind measurements were made, none of which detected emissions above the DIAL detection limit. In addition, the main lines-of-sight chosen for the site emission measurements enabled the emissions from van Ommeren to be isolated from any emissions from Paktank. During the period of easterly winds the DIAL measurements were made between the two sites (from locations 1 to 5). During the period of southerly winds any emissions from the Paktank site would have been to the west of the van Ommeren emissions, and therefore the range-resolved DIAL measurements from location 10 could have separate the two sources. No such emissions were detected (see Figure 8 for an example of these measurements).

### 6.2.4 Practicability of the methods

In general the DIAL measurements have less constraints regarding the practicability of the method. It is relatively easy to make measurements in surroundings with a lot of industrial activity. For the more conventional method it is usually more difficult to find a suitable place where the measurements can be carried out and it might take some time before a suitable wind direction may occur.

The DIAL technique can be used to measure very large industrial areas (eg oil refineries) since it can capture and measure concentrations at high elevations which may not be determined by the TNO method if it is close to the plant. If the TNO measurements are made further downwind so that all the plume from the extended area comes to ground level, then there is a possibility that the concentrations may be too low to be determined accurately.

For the measurement of a part of the plant (e.g. in the finding of emission sources) the TNO method will not be suitable in most cases, where for DIAL measurements this is a relatively easy task since the laser beam can be directed in any direction

that is thought necessary. The quantification of the emission may prove more difficult, however, due to disturbances of the local wind field. In this case the passive samplers that were also used in this investigation also offer an elegant solution to pinpoint the location of emissions. However, a quantification of the emission will be difficult to make based on results obtained passive samplers, although this is not always necessary.

### **6.2.5 Measurement Uncertainty**

The TNO measurements are lower in signal-to-noise ratio and, therefore their emission estimates have a higher uncertainty than the DIAL measurements. The TNO measurements at the most favourable days have an uncertainty of a factor of 1.5 - 2. The uncertainty in an individual DIAL measurement is dependant upon a large number of factors. A series of validation experiments have shown that a typical uncertainty is of the order of 20% for an industrial area. However, due to the variable nature of the source, the uncertainty in the daily average was generally higher than this (see Table 4.7 - 30% average uncertainty) during this campaign. The correct measurement of a suitable wind field is essential for this kind of results.

### **6.2.6 Costs**

The TNO measurement campaign costs about 35 % of the DIAL measurement campaign. However, the DIAL measurements contained more individual results. When a comparable amount of measurement days is considered the TNO measurements cost about 50 - 60 % of the DIAL measurements.

## **6.3 Annual emission and comparison with the data from Emission Registration**

The measurements described in this report represent a limited sample of the site emissions. Only a limited number of hourly averaged measurements were made and the hourly emission rates differed quite considerably with time. Therefore, no firm conclusions should be drawn about the difference between the measured emission rate and the estimated annual rate. For a realistic comparison to be made between the measured emission and the emission in the emission registration system a longer measurement period would be necessary. This should ideally be coupled with a long-term evaluation of the operations which occurred at the industrial site.

When the measured emissions are extrapolated to an annual emission, this would lead to approximately 3000 tonnes/year.

## 7. Conclusions

A comparison of hydrocarbon emission estimates, using a DIAL system and a method using inverse modelling led to the conclusion, that both methods are suitable for the measurements of VOC emissions. The emission estimates are very similar, with the average rates over the measurement campaign having a difference of less than 10 %. However, the differences in the individual measurements were generally higher, with the largest difference being a factor of 2.3. The sensitivity of both methods (expressed in kg/hour) is also comparable for emissions originating from large industrial sites.

Both methods have specific advantages and disadvantages. The power of the DIAL technique lies in its very good practicability. This technique is able to identify the major sources of emissions of a site in a short period of time, without making a large number of assumptions though the measurement of a correct wind field might be difficult when the emission has to be quantified. The conventional method relies more heavily on dispersion models and usually distinct wind directions can be used for the measurements. It may therefore take some time before a suitable wind direction occurs. The main advantages of the conventional method are its price, and the ability to measure the emission of individual (speciated) hydrocarbons.

A comparison of the measurement results with the estimate of the Emission Registration system indicated that, during the measurement period, the measured emissions were higher than the annual average emissions. However, the measurements were only carried out during one week and the emission registration data are based on a yearly average. Therefore no firm conclusions could be drawn as to whether the difference was significant.

## 8. Literature

- [1] P T Woods, Remote and Open-path Techniques for Fugitive Loss Monitoring, Gas Detection and Air Pollution Measurements. Proc. Seminar on Process Fugitive Emissions, IBC Ltd, London, November 1993.
- [2] P T Woods, Remote Sensing Techniques for Gas Detection, Air Pollution and Fugitive Loss Monitoring, Jour. Air and Waste Management Association, Special Publication 81, 3-29, 1992.

## 9. Authentication

Name and address of the principal:

Ministry of Housing, Physical Planning and Environment

Names and functions of the cooperators:

-


Names and establishments to which part of the research was put out to contract:

-

Date upon which, or period in which, the research took place:

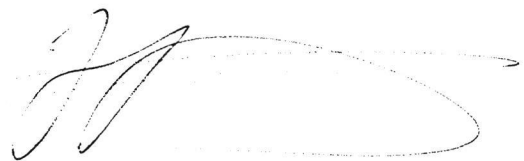
May 1997 - June 1998

Signature:



Jan Baas

Approved by:



H.G. Bours

## Appendix 1 Contents of the tanks

Table 1 Average tank content in cm from Friday 31/10/97 - Friday 7/11/97.

| tankno | content          | tank type  | level<br>(cm) | s.d.<br>(cm) | rel s.d.<br>(%) |
|--------|------------------|------------|---------------|--------------|-----------------|
| 0101   | condensate       |            | 21.242        | 0.015        | 0               |
| 0102   | naphta -> jet A1 |            | 8.605         | 4.295        | 50              |
| 0103   | condensate       |            | 21.124        | 0.014        | 0               |
| 0201   | naphta           |            | 3.387         | 1.825        | 54              |
| 0202   | naphta -> jet A1 |            | 13.272        | 8.294        | 63              |
| 0203   | naphta           |            | 9.990         | 1.755        | 18              |
| 0301   | gasoline         |            | 18.259        | 2.386        | 13              |
| 0302   | gasoline         |            | 13.605        | 2.596        | 19              |
| 0303   | gasoline         |            | 2.203         | 0.010        | 0               |
| 0401   | naphta           |            | 6.112         | 4.045        | 66              |
| 0402   | naphta           |            | 10.390        | 3.645        | 35              |
| 0403   | naphta           |            | 4.310         | 3.100        | 72              |
| 0501   | gas oil <0.05    | fixed roof | 27.389        | 2.429        | 9               |
| 0502   | middledestillate | fixed roof | 28.286        | 0.015        | 0               |
| 0503   | middledestillate | fixed roof | 30.270        | 0.012        | 0               |
| 0504   | gas oil <0.2     | fixed roof | 25.143        | 0.126        | 0               |
| 0505   | fuel oil         | fixed roof | 0.218         | 0.000        | 0               |
| 0601   | jet A1           | fixed roof | 10.817        | 5.872        | 54              |
| 0602   | jet A1           | fixed roof | 19.178        | 0.713        | 4               |
| 0603   | jet A1           | fixed roof | 10.684        | 7.901        | 74              |
| 0604   | gas oil < 0.05   | fixed roof | 15.072        | 9.066        | 60              |
| 0605   | naphta           | fixed roof | 9.926         | 7.543        | 76              |
| 0606   | contam. water    | fixed roof | 8.953         | 0.663        | 7               |
| 0607   | slob oil         | fixed roof | 0.075         | 0.000        | 0               |
| 0608   | water slob       | fixed roof | 7.896         | 0.583        | 7               |
| 0609   | water slob       | fixed roof | 0.770         | 0.684        | 89              |
| 0610   | water slob       | fixed roof | 0.219         | 0.000        | 0               |
| 0701   | condensate       |            | 28.947        | 0.017        | 0               |
| 0702   | condensate       |            | 27.394        | 0.069        | 0               |
| 0703   | naphta empty     |            | 7.388         | 0.090        | 1               |



Table 1 *continue Average tank content in cm from Friday 31/10/97 - Friday 7/11/97.*

| tankno | content       | tank type  | content<br>(cm) | s.d.<br>(cm) | rel s.d.<br>(%) |
|--------|---------------|------------|-----------------|--------------|-----------------|
| 0801   | condensate    |            | 29.425          | 0.013        | 0               |
| 0802   | gas oil <0.05 |            | 26.638          | 0.484        | 2               |
| 0803   | naphta        |            | 22.827          | 5.622        | 25              |
| 0901   | condensate    |            | 29.202          | 0.014        | 0               |
| 0902   | condensate    |            | 29.287          | 0.016        | 0               |
| 1001   | gasoline      |            | 28.811          | 0.015        | 0               |
| 1101   | gasoil empty  | fixed roof | 12.343          | 0.000        | 0               |
| 1102   | gas oil <0.05 | fixed roof | 10.393          | 0.413        | 4               |
| 1103   | gas oil <0.05 | fixed roof | 10.455          | 0.451        | 4               |
| 1104   | gasoil empty  | fixed roof | 2.397           | 0.000        | 0               |
| 1105   | py gas C6-C7  | fixed roof | 12.199          | 0.006        | 0               |
| 1106   | gasoil empty  | fixed roof | 3.376           | 0.000        | 0               |
| 1107   | gasoil empty  | fixed roof | 4.145           | 2.455        | 59              |
| 1201   | gas oil < 0.2 |            | 13.131          | 6.947        | 53              |
| 1202   | gas oil < 0.2 |            | 20.846          | 0.009        | 0               |
| 1401   | gasoline      | fixed roof | 20.116          | 0.011        | 0               |
| 1402   | gasoline      | fixed roof | 20.176          | 0.011        | 0               |
| 1403   | gasoline      | fixed roof | 20.116          | 0.011        | 0               |

## Appendix 2 Some characteristics of optical measurement techniques

| Technique | Site specific | Selectivity | Sensitivity <sup>1</sup> | Costs | Sampling speed |
|-----------|---------------|-------------|--------------------------|-------|----------------|
| DIAL      | yes           | +/-         | -                        | >>>   | ++             |
| DOAS      | no            | +           | ++                       | >     | +              |
| TDLAS     | no            | ++          | ++                       | >>    | ++             |
| FTIR      | no            | ++          | -                        | >     | +              |

1 + indicates the possibility to make immission measurements.

## Appendix 3 Description of the DIAL method

### Content

- 1 Remote Atmospheric Measurements Using the DIAL technique
  - 1.1 General
  - 1.2 Principles of the Differential Absorption Lidar Technique
  - 1.3 The NPL DIAL Facility
  - 1.4 Meteorological Measurements
  - 1.5 Ambient Air Samples
  - 1.6 Method for Measuring Gas Flux using the DIAL Technique
- 2 Validation and Uncertainty of the NPL DIAL Measurements
- 3 Application of the DIAL technique at the Van Ommeren Site
  - 3.1 Measurement Objectives
  - 3.2 Measurement Methodology
  - 3.3 Measurement Locations
  - 3.4 Measurement Resolution and Sensitivity
- 4 Results
  - 4.1 DIAL Measurements on 31/10/97
  - 4.2 DIAL Measurements on 1/11/97
  - 4.3 DIAL Measurements on 2/11/97
  - 4.4 DIAL Measurements on 3/11/97
  - 4.5 DIAL Measurements on 4/11/97
  - 4.6 DIAL Measurements on 5/11/97
  - 4.7 DIAL Measurements on 6/11/97

# **1. Remote Atmospheric Measurements Using the DIAL technique**

## **1.1 General**

The National Physical Laboratory (NPL) has, for a number of years, been involved with the development of new techniques for remote measurements of industrial and urban pollution, and for monitoring air quality [1, 2]. These techniques operate on spectroscopic principles using wavelength-tunable sources. They rely on the fact that each gaseous species in the atmosphere has a characteristic absorption spectrum, and that the wavelength of the source can be chosen so that it coincides with one feature of this spectrum. Then, the concentration of the selected species can be determined by tuning the source wavelength on and off the spectral absorption feature and measuring the absorption that occurs. The performance of these remote techniques have been extended continually at NPL, particularly in terms of the number of gaseous species that are detectable, their detection sensitivities, and the measurement range. Field trials have been carried out regularly to demonstrate the extending capabilities of these new measurement techniques.

## **1.2 Principles of the Differential Absorption Lidar Technique**

One of these remote monitoring facilities uses a principle similar to optical radar, known as differential-absorption lidar (DIAL). Figure 1 illustrates the principle of the technique. In this technique, pulses of tunable laser radiation are launched into the atmosphere over the paths to be monitored. A small fraction of this energy is scattered from the atmosphere itself and from any aerosols and particulates that may also be present, back towards the laser source. This is collected by a telescope close to the source, and measured on a detection system.

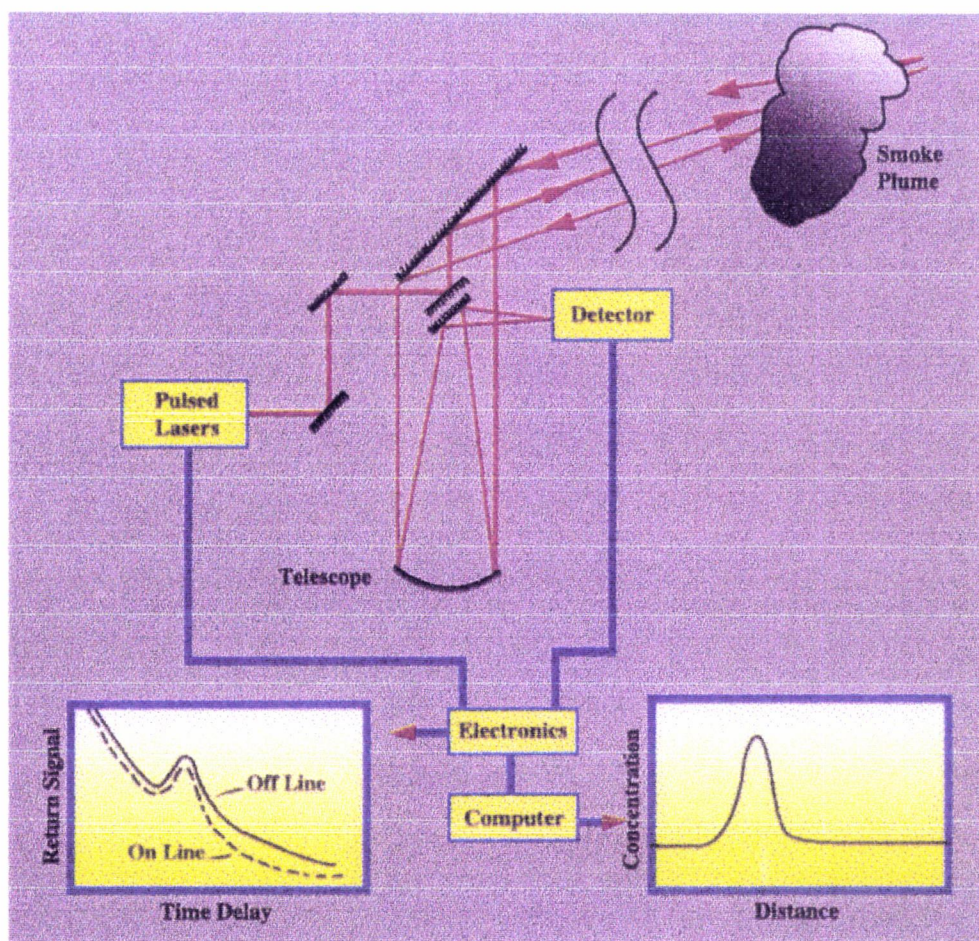


Figure 1 The DIAL Measurement Technique.

Since the atmospheric scattering medium acts as an extended reflector and produces backscattered radiation at all distances from the source, the time of arrival of the returning signal is range dependent. If a short duration pulse of laser radiation is launched into the atmosphere and the amount of backscattered radiation is measured as a function of time from the launch of the pulse, the recorded signal at a particular time relates to radiation scattered at a calculable distance from the source. Then the gas concentration can be measured as a function of range from the source by tuning the laser wavelength on and off the spectral absorption feature of the target gas.

### 1.3 The NPL DIAL Facility

The NPL DIAL facility operates using these principles in the infrared, visible, and ultraviolet spectral regions. This enables a wide range of gases including  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , higher molecular weight alkanes and alkenes, and aromatics such as toluene and benzene, to be monitored specifically and sensitively [1].

A two-dimensional scanning system directs the launched laser beam in any chosen direction and allows the backscattered radiation from that direction to be collected by the receiving telescope and measured. This scanning system covers nearly all horizontal and vertical directions and therefore enables two or three-dimensional concentration profiles of the target gases to be measured directly in the atmosphere. The laser transmitter, the scanning optical telescope, and all the electronic and computer-control system necessary for the measurements is mounted in a dedicated mobile laboratory. This is shown in Figure 2.



Figure 2 The NPL Mobile DIAL Facility.

#### 1.4 Meteorological Measurements

Meteorological measurements of wind speed and direction were made throughout the period. Continuous measurements were made throughout the campaign at two elevations (8 metres and 15 metres) on a meteorological mast located in an area of clear ground to the south-west of the site. Two portable anemometers mounted on tripods (2 metre elevation) were located at the northern and eastern edges of the site. The precise location of each of the fixed meteorological measurement locations are shown in Figure 5.

A fourth anemometer, installed on a 15 m mast attached to the DIAL facility, was also used whenever DIAL measurements were being made.

The results of these meteorological measurements were used to estimate the wind field in the area of each DIAL concentration measurement, and then combined with the concentration results to determine the mass fluxes.

## 1.5 Ambient Air Samples

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

The results of these measurements were used to confirm the spectroscopic parameters that are used in the analysis of DIAL data. NPL holds a spectroscopic database which contains the absorption spectra of over thirty different hydrocarbons. The relative amounts of the different hydrocarbons measured at the site were combined with the absorption parameters for each species on the database. The combined result determines the overall mass absorption coefficient for the hydrocarbon cocktail present at the site. It is important to note that the on- and off-resonant wavelengths used for the VOC measurements are selected for their relative insensitivity to the exact hydrocarbon distribution. The purpose of the ambient air analysis was to determine if there is anything particularly unusual about the hydrocarbon distribution at the site being studied.

## 1.6 Method for Measuring Gas Flux using the DIAL Technique

As noted above, the DIAL technique measures directly the concentrations of the selected gas(es) as a function of range along any selected direction up to the maximum range ( $\sim 1$  km). By scanning the direction in which the transmitted laser beam and the receiving telescope is pointed, the spatial profile of the gas is obtained. The total amount of gas between any two points in the measurement direction can also be determined. If the direction in which the laser beam and the telescope are pointed is scanned in a vertical plane downwind of an industrial plant the total amount of the selected gas(es) passing through the plane can be measured. If similar measurements are carried out upwind, the total flux of gas emitted by the

site can be determined, provided there are no large changes in wind velocity between the downwind and upwind measurements.

Emission fluxes are then determined by combining DIAL measurements of the concentration distributions with meteorological data. For each measurement the emitted flux is calculated using the following mathematical steps:-

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

Considerable care is needed in applying the meteorological data, particularly when the concentration profile measured by the DIAL technique has large and complex spatial variations since, for example, errors in the wind speed in regions where large concentrations are present will significantly affect the accuracy of the results. In such cases, a more complex procedure is used which employs a further software package to combine the data from the set of anemometers with that of an additional meteorological model, to generate the complete wind field over the concentration profile. This model calculates the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain and the atmospheric stability). The calculated wind field is then combined with the measured gas concentration profile using the procedure described above.

## **2. Validation and Uncertainty of the NPL DIAL Measurements**

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

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

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



A number of flux validation experiments have been undertaken with the NPL DIAL facility. These experiments have indicated an accuracy of between 10% and 20% for flux measurements made with the NPL DIAL facility. Specific example of these intercomparison exercises are given below :

- i) Intercomparisons have been carried out in the vicinity of chemical and petrochemical plants where a large number of different volatile organic species are present. In these intercomparisons, the DIAL radiation was directed along the same line of sight as a line of point samplers. The point samplers were operated either by drawing air into internally-passivated, evacuated gas cylinders or by pumping air at a known rate, for a specified time, through a series of absorption tubes which efficiently absorb all hydrocarbon species in the range C<sub>2</sub> - C<sub>8</sub>. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within  $\pm 15\%$ . The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within  $\pm 20\%$ .
- ii) The ultraviolet DIAL system was used to monitor the fluxes and concentrations of sulphur dioxide produced from combustion and emitted by industrial stacks. These stacks were instrumented with calibrated in-stack sampling instruments. The results of the two sets of measurements agreed to within  $\pm 12\%$ .
- iii) DIAL Measurements of controlled releases of methane from a stack agreed with the known emission fluxes to within  $\pm 15\%$ .

### **3. Application of the DIAL technique at the van Ommeren Site**

#### **3.1 Measurement Objectives**

The main objective of the DIAL measurement campaign was to determine the mass flux of volatile organic hydrocarbons (VOCs) from the van Ommeren site, and to compare these results to the values determined using the TNO measurement technique.

Two secondary objectives were :

- to locate the main sources of the VOC emissions.
- to locate and quantify any sources of benzene.

### 3.2 Measurement Methodology

The NPL DIAL facility was used to measure the VOC emissions from the van Ommeren site on six of the seven measurement days. The majority of this period was spent measuring downwind of the entire site, so that the total site emissions could be determined. There was regular communication between the NPL and TNO personnel to ensure that the timing of these total emission measurements were coordinated with the TNO measurement schedule.

During periods when conditions were not suitable for the standard measurements, some time was spent using the DIAL facility to measure within the site in order to locate the main emission sources. Measurements were also made upwind of the site, to quantify the contribution of any sources external to the Van Ommeren site. No significant emission sources were detected in these upwind scans.

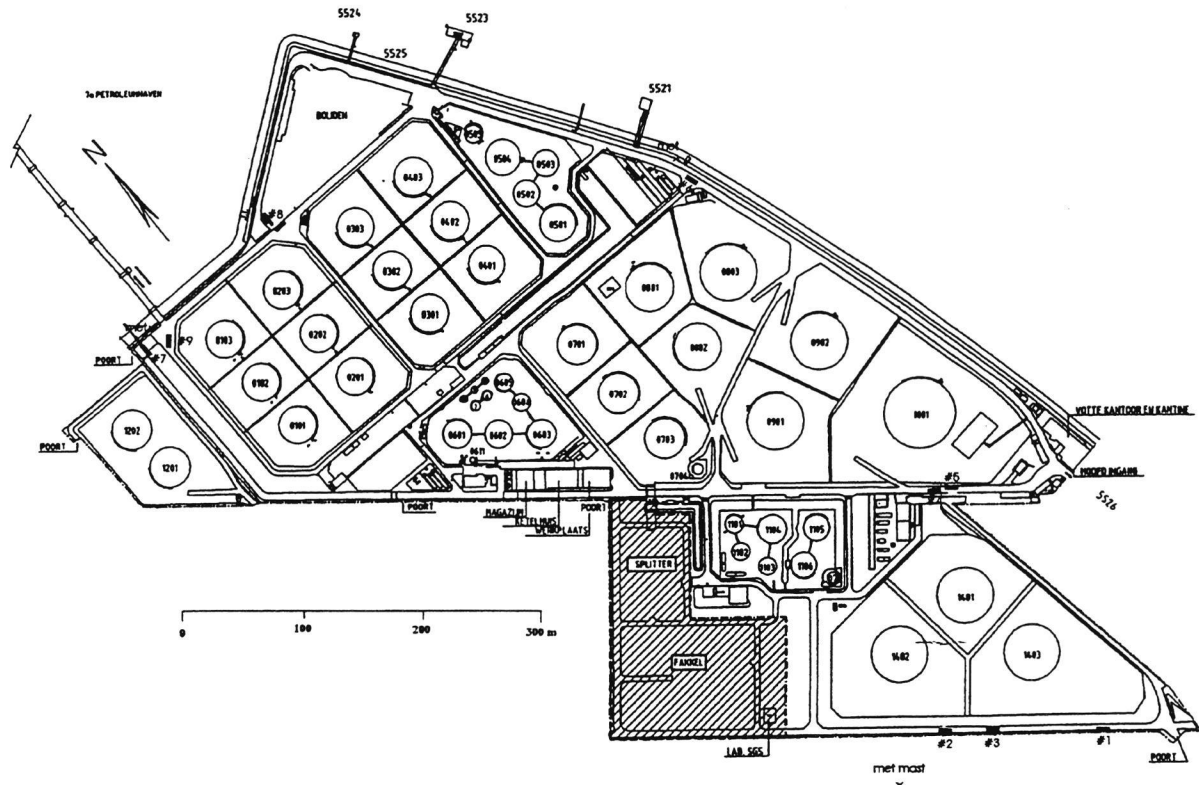
The remainder of the six day period of VOC measurements was spent checking and calibrating the DIAL system.

One day of the campaign (4/11/97) was used specifically for benzene measurements. DIAL measurements were made from various locations to locate and quantify any significant sources of benzene emissions.

### 3.3 Measurement Locations

Figure 3 shows the nine locations around the van Ommeren site that were used during the campaign. The majority of these locations were selected according to wind direction at the time of measurement in order to give a clear line of sight downwind of the entire site. Other locations were used to make measurement along lines-of-sight which bisected different areas of the site. This enabled the contribution of the different areas of the site to be assessed, and the main emission sources to be located.

Figure 4 Van Ommeren site-plan showing NPL DIAL measurement locations



A tenth location was used on the final two days of the campaign, when the wind was generally from the south. The DIAL facility was located on the far side of the Calland canal, approximately 120 metres to the northeast of tank 0505. This location was selected for two reasons. Firstly, the total site emissions could be measured using a line-of-sight back across the canal, and secondly, measurements could be made along the line of TNO monitors which were located in the same area during this period.

### 3.4 Measurement Resolution and Sensitivity

A single DIAL measurement determines the concentration distribution along a ~1 km line-of-sight, with a range resolution of ~10 metres. Each individual measurement along a line-of-sight takes approximately ten seconds. One important restriction of the technique is that measurements are not possible within the first 50 m of the line-of-sight, due to the configuration of the transmission and detection optics.

The two dimensional concentration distributions measured downwind of the source are built up from a series of single measurements made at a series of different vertical angles. The time taken to determine the two dimensional distribution depends upon the vertical extent of the emissions, and the step size between the

different vertical angles. For the measurements made during this campaign the duration of such a vertical scan was typically ten minutes.

The sensitivity of the DIAL measurements depends upon the meteorological conditions at the time of the measurement. However, the typical sensitivities (over a 100 metre pathlength) for the measurements described in this report are 20 ppb for VOCs and 10 ppb for benzene. It should be noted that, for DIAL measurements, the concentration sensitivity is inversely proportional to the pathlength.

## 4. Results

The results of the DIAL measurements made on each day of the campaign are described in sections 4.2.1 to 4.2.7 below. Each section (except 4.2.5) includes a table which summarise the measurements of the total site flux made on that day.

These tables contain the following information:

- a scan identification number
- the start and finish time of the scan
- the location of the DIAL facility for that measurement (locations 1 to 9 are shown on Figure 6, location 10 is on the far side of the canal)
- the line-of-sight along which the flux was measured. These are indicated with respect to true north.
- the measured value of VOC flux in units of kg per hour. The error on these individual measurements is approximately 20%.
- where appropriate, the number of the TNO measurement which was taking place simultaneously with the DIAL measurement.

Section 4.2.5 describes the benzene measurements made on the 4<sup>th</sup> November. This section includes a table which gives the peak concentrations observed rather than the mass fluxes.

### 4.1 DIAL Measurements on 31/10/97

The wind direction remained between north-north-easterly and north-easterly throughout the day, and the wind speed (at 15 m elevation) varied between 2 and 5 m/s. The total site fluxes are given in table 4.1.

Table 4.1 DIAL Flux Results on 31/10/97.

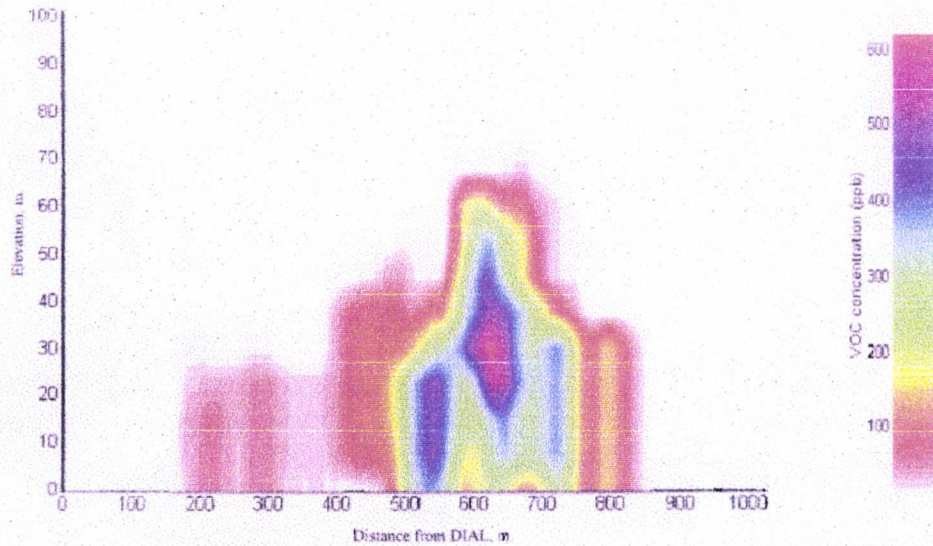
| Scan     | Time  |       | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) | TNO<br>Measurement |
|----------|-------|-------|----------|---------------------------------|---------------------|--------------------|
|          | Start | End   |          |                                 |                     |                    |
| OCT31-01 | 09:20 | 09:36 | 1        | 309°                            | 430                 |                    |
| OCT31-02 | 09:38 | 09:52 | 1        | 309°                            | 300                 |                    |
| OCT31-03 | 09:57 | 10:17 | 1        | 309°                            | 390                 |                    |
| OCT31-04 | 10:33 | 10:37 | 1        | 314°                            | 400                 |                    |
| OCT31-05 | 10:39 | 10:47 | 1        | 314°                            | 370                 |                    |
| OCT31-06 | 11:08 | 11:14 | 1        | 323°                            | 300                 |                    |
| OCT31-07 | 11:42 | 11:54 | 1        | 309°                            | 410                 |                    |
| OCT31-08 | 11:55 | 12:03 | 1        | 309°                            | 160                 |                    |
| OCT31-09 | 12:06 | 12:30 | 1        | 314°                            | 400                 |                    |
| OCT31-10 | 12:35 | 12:47 | 1        | 314°                            | 240                 |                    |
| OCT31-11 | 12:51 | 13:01 | 1        | 323°                            | 310                 |                    |
| OCT31-12 | 13:14 | 13:03 | 1        | 314°                            | 400                 |                    |
| OCT31-13 | 14:34 | 14:45 | 1        | 314°                            | 420                 | 1                  |
| OCT31-14 | 14:46 | 14:56 | 1        | 314°                            | 550                 | 1                  |
| OCT31-15 | 14:57 | 15:18 | 1        | 314°                            | 530                 | 1                  |
| OCT31-16 | 15:31 | 15:42 | 1        | 314°                            | 430                 | 1                  |
| OCT31-17 | 16:05 | 16:15 | 2        | 309°                            | 380                 | 2                  |
| OCT31-18 | 16:18 | 16:29 | 2        | 309°                            | 350                 | 2                  |
| OCT31-19 | 16:31 | 16:41 | 2        | 309°                            | 230                 | 2                  |
| OCT31-20 | 16:43 | 16:53 | 2        | 330°                            | 330                 | 2                  |
| OCT31-21 | 17:02 | 17:14 | 3        | 330°                            | 130                 |                    |
| OCT31-22 | 17:15 | 17:25 | 3        | 330°                            | 140                 | 3                  |
| OCT31-23 | 17:28 | 17:38 | 3        | 330°                            | 180                 | 3                  |
| OCT31-24 | 18:06 | 18:22 | 4        | 310°                            | 180                 | 3                  |
| OCT31-25 | 18:27 | 18:37 | 4        | 310°                            | 300                 |                    |
| OCT31-26 | 18:39 | 18:53 | 4        | 310°                            | 360                 |                    |
| OCT31-27 | 18:57 | 19:06 | 4        | 310°                            | 360                 |                    |
| OCT31-28 | 19:08 | 19:16 | 4        | 310°                            | 250                 |                    |
| OCT31-29 | 19:17 | 19:27 | 4        | 310°                            | 350                 |                    |

The DIAL facility was initially located at position 1, at the southern corner of the site. From this location the total site flux was measured using a line-of-sight parallel to the road along the southwest edge of the site. A series of flux measurements were made from three different locations along this road. A number of these were simultaneous with the three TNO measurements made during the afternoon.

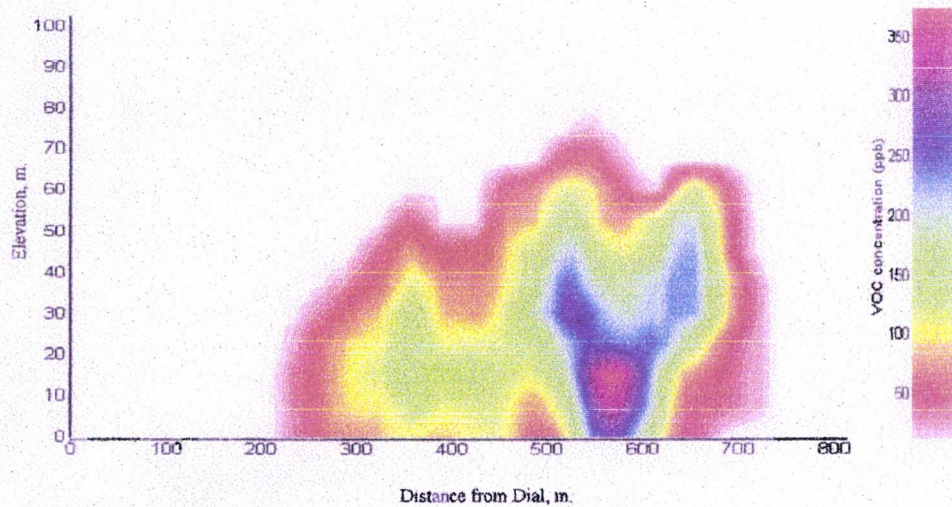
Figure \*\* shows the concentration distributions that was measured in scan OCT31-05, and this is typical of the distributions that were measured during this period. A diffuse VOC plume was observed between 200 m and 800 m from the DIAL facility associated with general emissions from the tankage. A more localised plume was observed between 500 m and 700 m, extending to elevations of up to 70 m and

with a peak concentration of ~600 ppb. This indicated the presence of a major VOC source within the site.

**Figure 5** VOC concentration distribution measured during scan OCT31-05 between 10:39 and 10:47



**Figure 6** VOC concentration distribution measured during scan NOV05-13 between 18:36 and 18:44



Later in the day the DIAL facility moved to location 4, to the southwest of tank 1001. Measurements were again made parallel to the road. The purpose of these measurements was to determine what proportion of the emissions were coming from southwestern area of the site (tanks 1101-1106 and 1401-1403). There was no significant difference between the flux values measured at the different locations. Therefore, it was concluded that the southwestern area was not contributing significantly to the total site emission, and all the flux values could be included in the table.

It is important to note that the variability in these (and later) flux measurements is significantly larger than the uncertainty in the individual measurements (~20%). The variations in the flux values therefore show the genuine variability of the source.

## 4.2 DIAL Measurements on 1/11/97

The wind direction remained approximately north-easterly throughout the day, and the wind speed (at 15 m elevation) varied between 1 and 2.5 m/s. The total site fluxes are given in table 4.2 below.

Table 4.2 DIAL Flux Results on 1/11/97.

| Scan     | Time  |       | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) |
|----------|-------|-------|----------|---------------------------------|---------------------|
|          | Start | End   |          |                                 |                     |
| NOV01-01 | 11:09 | 11:19 | 1        | 309°                            | 90                  |
| NOV01-02 | 11:23 | 11:35 | 1        | 309°                            | 100                 |
| NOV01-03 | 11:42 | 11:53 | 1        | 309°                            | 110                 |
| NOV01-04 | 11:56 | 12:12 | 1        | 309°                            | 140                 |
| NOV01-05 | 12:13 | 12:36 | 1        | 309°                            | 160                 |
| NOV01-06 | 12:37 | 12:47 | 1        | 309°                            | 150                 |
| NOV01-07 | 14:01 | 14:29 | 4        | 309°                            | 160                 |
| NOV01-08 | 14:31 | 14:49 | 4        | 309°                            | 170                 |
| NOV01-09 | 14:55 | 15:13 | 4        | 309°                            | 390                 |
| NOV01-10 | 15:15 | 15:32 | 4        | 309°                            | 240                 |

The total site emissions were monitored from location 1 between 11:00 and 13:00. The DIAL facility then moved to location 4 and repeated the measurements carried out on the first day. As on that occasion, no significant contribution was observed from the southwestern area of the site and the emissions were dominated by a localised VOC plume. The total fluxes measured were generally lower than those observed the previous day.

Following the flux measurements described above, a series of scans were made from locations 5 and 6. The purpose of these scans was try and locate the source of the localised plume. The scans from location 4 made parallel to the road (309° with respect to North) showed a localised plume centred at 450 metres from the DIAL facility with concentrations of up to 1.4 ppm. Scans made from location 5 along a slightly more northerly line of sight (314° w.r.t. North) showed a similar distribution, but with peak concentration of only 0.3 ppm. These measurements indicated that the major VOC source during these measurements lay just to the northeast of the road (running northwest through the site) between tanks 0601 and 0101. This area contains a large amount of pipework and switching gear, as well as the water

treatment area. Measurements from location 6 also confirmed this area as the major source.

### 4.3 DIAL Measurements on 2/11/97

The wind direction remained between south-south-westerly and southerly during the day, and the wind speed (at 15 m elevation) varied between 1.5 and 3 m/s. The total site fluxes are given in table 4.3 below.

Table 4.3 DIAL Flux Results on 2/11/97.

| Scan     | Time  |       | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) | TNO<br>Measurement |
|----------|-------|-------|----------|---------------------------------|---------------------|--------------------|
|          | Start | End   |          |                                 |                     |                    |
| NOV02-01 | 15:23 | 15:35 | 6        | 276°                            | 270                 |                    |
| NOV02-02 | 15:44 | 15:54 | 6        | 276°                            | 240                 |                    |
| NOV02-03 | 15:57 | 16:09 | 6        | 276°                            | 170                 |                    |

Heavy fog in the morning prevented any useful measurements being made. The fog cleared slightly in the afternoon. However, the light, variable wind coming generally from the south made it difficult to select a suitable location for total site flux measurements. A series of DIAL measurements were made from locations 6 and 7, but only a small sub-set of these were suitable to give flux results. It should be noted that, although emissions from the major source identified the previous day would be included in these measurements, any significant emissions from the area to the north of location 6 would not be included.

### 4.4 DIAL Measurements on 3/11/97

The wind was very light and variable during the day. The average direction was approximately north-easterly, and the wind speed (at 15 m elevation) varied between 0 and 1.5 m/s. The total site fluxes are given in table 4.4 below.



Table 4.4 DIAL Flux Results on 3/11/97.

| Scan     | Time  |       | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) | TNO<br>Measurement |
|----------|-------|-------|----------|---------------------------------|---------------------|--------------------|
|          | Start | End   |          |                                 |                     |                    |
| NOV03-01 | 09:44 | 09:52 | 3        | 314°                            | 60                  |                    |
| NOV03-02 | 14:05 | 14:09 | 3        | 309°                            | 140                 | 1                  |
| NOV03-03 | 14:32 | 14:41 | 3        | 309°                            | 70                  | 1                  |
| NOV03-04 | 14:42 | 14:50 | 3        | 309°                            | 50                  | 1                  |
| NOV03-05 | 15:44 | 15:55 | 3        | 309°                            | 180                 | 2                  |
| NOV03-06 | 15:56 | 16:01 | 3        | 309°                            | 60                  | 2                  |
| NOV03-07 | 16:07 | 16:12 | 3        | 309°                            | 220                 | 2                  |
| NOV03-08 | 16:27 | 16:37 | 3        | 309°                            | 40                  | 2                  |
| NOV03-09 | 16:39 | 16:49 | 3        | 309°                            | 130                 | 2                  |
| NOV03-10 | 16:51 | 17:12 | 3        | 309°                            | 110                 |                    |

The variable wind conditions mean that there is a much larger uncertainty in the flux measurements. On previous days the typical standard deviation of the wind direction was about 10°, which leads to an uncertainty of about 2% on the flux value. For the measurements made on the 3/11/97 the typical standard deviation in the wind direction was 60°, giving an uncertainty in the flux value of up to 50%. However, these results have been included so that they can be compared to the TNO measurements that were made on the same day.

#### 4.5 DIAL Measurements on 4/11/97

The wind direction remained between easterly and south-easterly throughout the day, and the wind speed (at 15 m elevation) varied between 1 and 4 m/s.

After the system had been configured for benzene measurements a series of scans were made at various locations around the site (6,7,8 and 9) to locate any significant benzene sources. Table 4.5 summarises the results of these measurements.

Table 4.5 Peak Benzene Concentrations Measured on 4/1/97.

| Scan     | Time  |       | Location | Line of Sight<br>(w.r.t North) | Benzene Conc.<br>(ppb) |
|----------|-------|-------|----------|--------------------------------|------------------------|
|          | Start | End   |          |                                |                        |
| NOV04-01 | 13:22 | 13:42 | 6        | 272°                           | 110                    |
| NOV04-02 | 13:45 | 13:56 | 6        | 276°                           | 180                    |
| NOV04-03 | 13:57 | 14:09 | 6        | 276°                           | 440                    |
| NOV04-04 | 14:13 | 14:24 | 6        | 276°                           | 210                    |
| NOV04-05 | 14:43 | 14:53 | 8        | 180°                           | <50                    |
| NOV04-06 | 14:54 | 15:05 | 8        | 180°                           | <50                    |
| NOV04-07 | 15:07 | 15:17 | 8        | 180°                           | <50                    |
| NOV04-08 | 15:18 | 15:28 | 8        | 180°                           | <50                    |
| NOV04-09 | 15:29 | 15:39 | 8        | 180°                           | <50                    |
| NOV04-10 | 16:12 | 16:26 | 9        | 180°                           | 100                    |
| NOV04-11 | 16:27 | 16:46 | 9        | 180°                           | 50                     |
| NOV04-12 | 16:57 | 17:03 | 9        | 180°                           | <50                    |
| NOV04-13 | 17:19 | 17:32 | 9        | 180°                           | <50                    |
| NOV04-14 | 17:33 | 17:36 | 9        | 180°                           | <50                    |
| NOV04-15 | 18:12 | 18:21 | 7        | 88°                            | <50                    |
| NOV04-16 | 18:22 | 18:31 | 7        | 88°                            | <50                    |
| NOV04-17 | 18:32 | 18:43 | 7        | 88°                            | <50                    |
| NOV04-18 | 18:46 | 19:11 | 7        | 88°                            | <50                    |

The concentrations given in this table correspond to the average benzene concentration over a 20 m pathlength. As indicated in the table, the benzene levels were often below the DIAL detection limit of 50 ppb (for this pathlength).

The measurements made from location 6 were made looking along the pipework between the northern and southern ends of the site. The local wind appeared to be blowing along this path, and the results were therefore not suitable for flux analysis. In addition, it was difficult to identify the location of the benzene source(s). However, these results did indicate the variability of the emissions.

The results from the other locations were also inconclusive as to the location of the source(s). However, no benzene was detected from location 8, and some was seen from location 9 which suggests that at least one source may have been located in the area between tanks 0101, 0201 and 0601.

#### 4.6 DIAL Measurements on 5/11/97

The wind direction started southerly and gradually shifted to south-south-easterly during the day. The wind speed (at 15 m elevation) varied between 3 and 5 m/s. The total site fluxes are given in table 4.6 below.

Table 4.6 DIAL Flux Results on 5/11/97.

| Scan     | Time  |        | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) | TNO<br>Measurement |
|----------|-------|--------|----------|---------------------------------|---------------------|--------------------|
|          | Start | Finish |          |                                 |                     |                    |
| NOV05-01 | 12:08 | 12:19  | 7        | 88°                             | 760                 | 2                  |
| NOV05-02 | 12:24 | 12:35  | 7        | 88°                             | 490                 | 2                  |
| NOV05-03 | 12:37 | 12:49  | 7        | 88°                             | 320                 | 2                  |
| NOV05-04 | 12:51 | 12:59  | 7        | 88°                             | 290                 | 2                  |
| NOV05-05 | 13:00 | 13:12  | 7        | 88°                             | 440                 | 2                  |
| NOV05-06 | 13:13 | 13:26  | 7        | 88°                             | 680                 | 2                  |
| NOV05-07 | 13:33 | 13:49  | 7        | 64°                             | 230                 | 3                  |
| NOV05-08 | 13:50 | 14:07  | 7        | 62°                             | 330                 | 3                  |
| NOV05-09 | 14:09 | 14:25  | 7        | 62°                             | 280                 | 3                  |
| NOV05-10 | 14:26 | 14:42  | 7        | 62°                             | 200                 | 3                  |
| NOV05-11 | 18:06 | 18:23  | 10       | 247°                            | 430                 | 6                  |
| NOV05-12 | 18:25 | 18:35  | 10       | 247°                            | 250                 | 6                  |
| NOV05-13 | 18:36 | 18:44  | 10       | 247°                            | 360                 |                    |

The meteorological conditions on this day were generally suitable for site flux measurements. Therefore, the DIAL was re-configured for VOC detection. Between 09:30 and 14:30 measurements were made from location 7 along the northern edge of the site. However, the wind conditions before 12:00 meant that there was a high probability of emissions from the main VOC source not being detected by the DIAL facility (as the DIAL system cannot measure within the first 50 m of the measurement line-of-sight). Therefore, the measurements made during this period were not suitable for comparison with the first TNO flux measurement.

The DIAL measurements between 12:00 and 14:30 were more suitable for site flux calculations, and a direct comparison can be made between these results and the second and third TNO measurements. However, there is still the possibility that not all of the emitted flux was detected in every one of these scans.

The period between 15:00 and 16:00 was spent moving the DIAL facility to location 10 on the far side of the Calland canal. The fourth TNO measurement took place during this period.

Once at location 10, DIAL scans were made along the same measurement line as was being monitored by the TNO samplers. No VOC concentrations above the DIAL detection limit (~20 ppb over 100 m pathlength) were observed within the one kilometre measurement range. The combination of the wind direction at the time of these measurements (SSE), the location of the major emission source (see section 4.3.2) gives an estimated position of the main emission plume at a distance of ~2.5 km from the DIAL facility along this line-of-sight (326° with respect to North). The fifth TNO measurement took place during this period.

A new measurement line-of-sight was selected looking across the canal at an angle of 247° w.r.t. North. Figure 8 shows an example of one of the concentration distributions that was measured along the new line of sight (scan NOV05-13). This shows a diffuse plume between 300 and 700 metres from the DIAL facility (approximately the entire width of the northern end of the site). The peak concentration of 350 ppb was observed at a distance of 550 metres, as would be expected with a major emission source located near the road, between tanks 0101 and 0601. This data was ideal for emission flux calculations, and the results can be compared the sixth and final TNO measurement made on this day.

#### 4.7 DIAL Measurements on 6/11/97

The wind direction remained between southerly and south-south-westerly throughout the day, and the wind speed (at 15 m elevation) varied between 3 and 5 m/s. The total site fluxes are given in table 4.7 below.

Table 4.7 DIAL Flux Results on 06/11/97.

| Scan     | Time  |        | Location | Line of Sight<br>(w.r.t. North) | VOC Flux<br>(kg/hr) | TNO<br>Measurement |
|----------|-------|--------|----------|---------------------------------|---------------------|--------------------|
|          | Start | Finish |          |                                 |                     |                    |
| NOV06-01 | 10:18 | 10:40  | 10       | 326°                            | 300                 | 1                  |
| NOV06-02 | 10:41 | 10:59  | 10       | 326°                            | 110                 | 1                  |
| NOV06-03 | 11:07 | 11:21  | 10       | 326°                            | 160                 | 1                  |
| NOV06-04 | 11:22 | 11:34  | 10       | 326°                            | 240                 | 1                  |
| NOV06-05 | 11:36 | 12:05  | 10       | 326°                            | 140                 | 2                  |
| NOV06-06 | 12:25 | 12:45  | 10       | 247°                            | 180                 | 2                  |
| NOV06-07 | 13:09 | 13:27  | 10       | 247°                            | 110                 | 3                  |
| NOV06-08 | 13:29 | 13:43  | 10       | 247°                            | 330                 | 3                  |
| NOV06-09 | 13:45 | 13:59  | 10       | 247°                            | 180                 | 3                  |
| NOV06-10 | 14:00 | 14:13  | 10       | 247°                            | 190                 |                    |
| NOV06-11 | 14:15 | 14:25  | 10       | 247°                            | 300                 | 4                  |
| NOV06-12 | 14:26 | 14:51  | 10       | 247°                            | 180                 | 4                  |
| NOV06-13 | 14:52 | 15:03  | 10       | 247°                            | 190                 | 4                  |
| NOV06-14 | 15:04 | 15:23  | 10       | 247°                            | 190                 | 4                  |

All DIAL measurements on the final day of the campaign were made from location 10. Measurements were initially made along the line as the TNO samplers. The wind direction during this period (SSW) meant that the emissions from the site were within the detection range of the DIAL system. Flux calculations were performed using this data, although there is a possibility that some of the emissions were still beyond the DIAL detection range.

Between 12:30 and 15:30 measurements were performed along a line-of-sight across the canal and, as on the previous day, good flux data was acquired. These measurements were made simultaneously with three of the five TNO measurements made on this day.

During the final TNO measurement period, 15:30 to 16:30, DIAL measurements were again made along the same line as the TNO samplers. As on the 5<sup>th</sup> November, no concentrations above the detection limit were observed within the 1 km range.

## Appendix 4 Description of the conventional method

### Contents

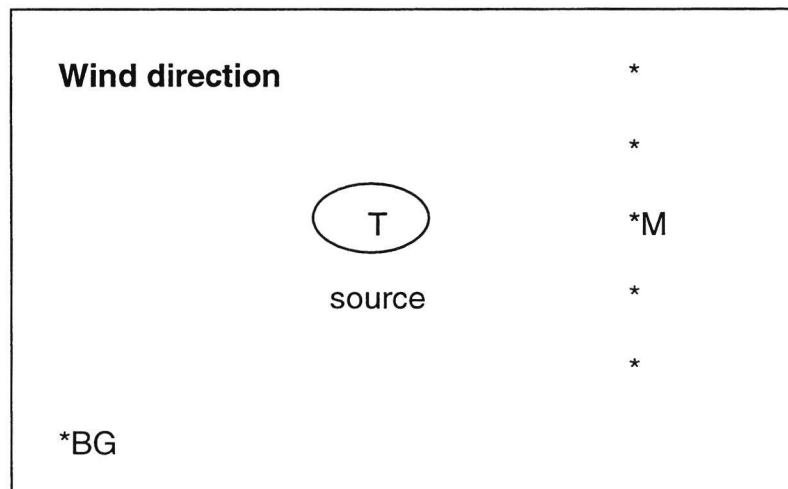
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## 1. General

TNO is frequently asked to provide information about the emissions of various compounds from diffuse sources. Therefore a method has been developed to estimate emission levels, using inverse modelling.

The method that is used by TNO consists of upwind and downwind concentration measurements, which are used to calculate the emission by using Gaussian plume dispersion models. Usually a tracer gas is released and measured, from which the actual dispersion parameters are calculated. This method enables more accurate results to be obtained. This method has been used in the past for different sources, e.g. sprayed fields and orchards, and various industrial sources. It should be noted that the method was developed to determine the emissions from relatively small sources, and that the van Ommeren tank storage is a larger site than those to which the method has previously been applied. .

The TNO measurements are usually carried out by measuring the concentration of the compound of interest downwind simultaneously at 4 –6–selected sites. This is often done in combination with the release and measurement of a tracer gas (SF<sub>6</sub>). Schematically the measurements are carried out as is shown in the figure below:



- T = tracer gas release point
- \* = sampling point (both for tracer and for hydrocarbons)
- \* BG = sampling point background concentration
- M = meteorological measurements (wind speed and wind direction)

When there are no major disturbances in the wind conditions a Gaussian plume profile is measured over the sampling points. The source emission can be back-calculated with short term plume modelling. This is done in three steps:

- 1) The dispersion parameters are determined such that the tracer gas concentrations fit best to the measured concentrations (the wind speed and wind direction are measured independently);
- 2) The same dispersion parameters, wind speed and wind direction are then used to describe the dispersion of the compound of interest;
- 3) The emission (expressed in kg/hour) is used to scale the calculated concentration to the measured concentrations.

The location of the tracer gas release is selected so that the plume centre is expected to bisect the centre of the sampling line.

## **2. On site application**

### **2.1 Location of the measurements**

The wind direction and the local surroundings determine the location where the measurements can be carried out. When the measurements are carried out relatively far from the site the model calculations become easier because the size and shape of the source become less important. On the other hand, the concentrations become lower at larger distances from the source. This may result in problems with background concentrations. Usually the measurements are carried out at about 100 metres from the source. In this specific case a greater distance was required because of the area and height of the source.

When these restrictions were considered, the north-east side of the source (on the other side of the canal) was identified as the best place to carry out the measurements. At this location the emission of the site as a whole can be determined. This location is approximately 800 metres away from the centre of the van Ommeren site.

During the first days of the measurement the wind came from an easterly direction. Under these conditions the only option was to carry out the measurements at the western side of the site, where only a small part of the emission of the whole tank storage park could be measured. Carrying out the measurements further away from the source was not possible because of neighbouring installations

Five measurement points were set out downwind from the site at 80 - 100 meters increments. Upwind background measurements were also carried out.

### **2.2 Sampling**

The air samples were held in aluminium coated sample bags for the C<sub>2</sub> - C<sub>5</sub> measurements and for the tracer gas measurements. Tenax tubes were used for the meas-



urement of higher hydrocarbons. All hydrocarbons were measured individually. The individual results were combined to give the total VOC levels for comparison with the DIAL system which measures the total VOC emissions.

Samples were taken at all locations for each of the measurement periods. However, not all samples have been analysed because of the cost involved. All tracer gas samples were analysed and after evaluation of the tracer gas measurements selected hydrocarbon samples were analysed. Usually 2 or 3 hydrocarbon samples were analysed (both for C<sub>2</sub> - C<sub>5</sub> and for higher hydrocarbons) per hourly measurement.

### **2.3 Time averaging of the measurements**

All measurements were carried out with an averaging time of one hour. After one hour the samples were changed for the next series of measurements. Background measurements were carried out, with an averaging time equal to the complete time of all downwind measurements during one day.

Other averaging times are also possible, although any changes in wind speed or wind direction may bias the measurements. In practise, averaging times between half an hour and several hours can be used, with one hour being a favourable optimum. A number of air concentration guidelines are also directed to hourly averaged measurements.

### **2.4 Additional measurements**

Because of the size of the source all tanks were equipped with passive hydrocarbon samplers (measuring C<sub>6</sub> and higher), in order to see which tanks gave the highest emissions. These samplers were installed on the first day of the measurement period and were removed on the final day of the campaign (averaging time equalled about one week). This information was then used in the Gaussian Plume model calculations to assess the emissions due to specific tanks (the individual tanks were treated as point sources in the model calculations).

This was done by measuring the total hydrocarbon content of the sampler (expressed in ng/badge). For some of the tanks high hydrocarbon concentrations were measured, while there was only a slight elevated level for the other tanks. Only the tanks with high hydrocarbon concentrations were included in the model calculations (9 out of 29 tanks were taken up in the calculations). The relative emission of the tanks was also taken from these measurements.

## 2.5 Background measurements

In order to anticipate problems with high background concentrations due to sources situated in the local area around the site, four measurement points were installed upwind of the site. These points were set in a square of about 200 metres length. The possible difference in the background concentration (caused by emissions from Paktank) could then be extrapolated to the location where the measurements were performed.

## 3. Results

### 3.1 Background concentrations

During the measurements on Friday and Monday the wind was Easterly. For this reason the background measurements were carried out at one sampling point on the South side of the tank storage, where the sampling point was not downwind from the site. All measured concentrations were corrected for the background concentration. The background concentration equalled about  $110 \mu\text{g}/\text{m}^3$ .

The background measurements on Wednesday and Thursday were carried out at four sampling points. A high background concentration was expected (and measured) caused by emissions from the neighbouring Paktank site. The wind direction was used to establish the location of the emission and the Gaussian plume model was used to calculate the background concentration at the downwind sampling points. Background concentrations (for total hydrocarbon concentration) at the sampling points were estimated to be  $170 \mu\text{g}/\text{m}^3$  on Wednesday and  $240 \mu\text{g}/\text{m}^3$  on Thursday.

### 3.2 Results of the passive measurements at the different tanks

High hydrocarbon concentrations were measured from nine out of the 29 tanks studied. The table below lists the tank numbers together with the relative emissions from each tank. A tank was included in this list when the hydrocarbon content of the badge was higher than  $200 \mu\text{g}/\text{badge}$ . No concentrations were calculated from these measurements because the results were only used for the model calculations to assess the contribution to the total emission from specific tanks. In some cases the results may have been biased by neighbouring emission sources or the specific location of the measurements on the tank. But because the results are only used relatively the end outcome will not differ because of this.

*Table 3.1 Relative tank-emissions.*

| <b>Tank number</b> | <b>Relative emission</b> |
|--------------------|--------------------------|
| 1402               | 2.8                      |
| 0802               | 1.0                      |
| 0703               | 1.5                      |
| 0504               | 1.7                      |
| 0401               | 1.1                      |
| 0403               | 1.7                      |
| 0303               | 2.6                      |
| 0201               | 2.5                      |