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National Physical Laboratory

A Determination of the Emissions of Volatile Organic Compounds from Oil Refinery Storage Tanks

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P T Woods, B W Jolliffe, R A Robinson, N R Swann, T Gardiner and A Andrews
Division of Quantum Metrology
National Physical Laboratory
Teddington, Middlesex TW11 5LU

and

P H Downes and S Day
Shell UK Ltd
Shell Mex House
Strand, London WC2 0DX

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National Physical Laboratory
Teddington, Middlesex TW11 0LW

Approved on behalf of the Chief Executive, NPL,
by Dr J R Gott, Head, Division of Quantum Metrology

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by

Division of Quantum Metrology
National Physical Laboratory
Queens Road, Teddington, TW11 0LW, UK

and

Shell UK Ltd
Shell Mex House
Strand, London, WC2R 0DX

1. BACKGROUND

Ozone is formed in the atmosphere by reactions of volatile organic compounds (VOCs) with nitrogen oxides when sunlight is present. Ozone, when present at high concentrations in the atmosphere near ground-level, causes ecological damage and can have detrimental effects on human health [1, 2]. There is thus a clear requirement to ameliorate these effects, but as ozone is a secondary pollutant this is not straightforward. However, there is now considerable scientific evidence to support the modelling predictions that reductions in the concentrations of VOCs in the atmosphere will result in reductions in the concentrations of atmospheric ozone. As a result, international negotiations have recently been completed under the aegis of the United Nations Economic Commission for Europe's Convention on Transboundary Air Pollution [3]. Within this Convention, in November 1991, 20 countries including the UK signed a new Protocol which is designed to limit the emissions to the atmosphere of volatile organic compounds. Under this Protocol, the UK has agreed to secure a reduction of at least 30% in its annual emissions of VOCs to the atmosphere by the year 2000, compared with 1988 levels. In addition to this Protocol, EC legislation is also being introduced which requires reductions in the emissions to the atmosphere of VOCs associated for example, with the storage of oil industry products, including gasoline [4].

In order to formulate an effective strategy for conforming to these international legislative initiatives, it is necessary:

- to quantify as accurately as possible the current levels of emission of VOCs;
- to investigate the effectiveness of future methods of control and abatement.

The work described in this Report forms part of a larger programme in which Warren Spring Laboratory (WSL), supported by the UK Department of the Environment, has been commissioned to establish an improved UK inventory of VOC emissions. It gives the results of an exercise which has the aim of improving the accuracy of the emission inventory of VOCs from one industrial sector.

Two industrial sectors are believed to make significant contributions to the total emissions of non-methane VOCs to air in the UK, in addition to those produced by automobiles and the solvent industry. These are the oil refinery and petrochemical industries. For the purpose of this report the oil refinery industry is defined as those industrial sites where crude oil is used as the feedstock for various industrial processes to produce, for example, motor vehicle gasoline, kerosine, diesel fuel, fuel oil etc and feedstock to the petrochemical industry. The petrochemical industry is defined as that which takes in some of the products of the oil refinery industry, and processes them into other chemical compounds such as plastics etc.

There are a range of potential sources of emissions of VOCs to the atmosphere in these industries. The largest of these are considered to be:

(a) Fugitive emissions which occur from processing plant, such as blending and distillation equipment, mainly from the large number of valves, flanges, joints etc that are present.

(b) Filling and standing emissions which occur from storage tanks used to contain the liquid feedstocks and the intermediate and finished products. These tanks contain liquid hydrocarbons with widely differing volatilities ranging from bitumen and fuel oil, to naphtha and gasoline.

(c) Fugitive emissions which arise from incomplete combustion of light hydrocarbons by industrial flares. Flares are used to incinerate VOCs and other gaseous species and are designed to convert VOCs into water vapour and carbon dioxide with high efficiency.

(d) Emissions which arise from waste-water treatment plants. In these, liquid organic compounds and water, previously intermixed during the various processing operations, are separated using air flotation and other methods. Gaseous hydrocarbons are emitted fugitively during this process.

(e) Emissions which arise from the loading of hydrocarbon products into containers which enable them to be transported by road, rail and sea.

Of the above, it has been estimated that the most significant sources of gaseous VOC emissions are (a) and (b). Industrial flares may also be a contributing source. The efficiency with which they destroy non-methane VOCs is generally estimated to be greater than 98%, although individual estimates for combustion efficiency vary from 75% to greater than 99%. However, the frequency of industrial flaring varies considerably and their use is generally decreasing and now usually only occurs during industrial plant malfunctions. Nevertheless, it may be necessary in future to establish more accurately their contribution to the UK VOC emission inventory.

Estimates of the emissions to atmosphere from storage tanks and from processing plant are prepared and reported by the industries concerned. The European oil industry has for some time estimated the emissions from storage tanks using methodologies prescribed by the Conservation of Clear Air and Water in Europe (CONCAWE), the oil companies' European organisation for environmental and health protection [5]. These methodologies incorporate calculations for storage tank emissions published by the American Petroleum Institute (API) (see Section 4). The gaseous emissions produced by processing plant in the oil and petrochemical industries are generally estimated using statistical analysis procedures, known as Synthetic Organic Compound Manufacturing Industry (SOCMI) factors, [6]. These are derived for various industrial plants by carrying out detailed counts of equipment including valves, flanges, vents etc and then applying representative emission factors for each class of these sources. However, there has been some recognition in the oil and petrochemical industries that these calculation methods could provide inaccurate estimates of the actual emissions.

Recently, other methods have become available for determining the rate of emissions (ie the fluxes), of a range of gaseous species, including methane and other VOCs, which are emitted fugitively by industrial sites [8]. These are remote, open-path optical techniques which can be employed for direct measurements of the emitted fluxes of the gases. Currently, the most versatile of these techniques is known as differential-absorption lidar (DIAL). This technique makes it practical to investigate and/or improve on the accuracy of the emission estimates made by the traditional API, SOCMI and other empirical methods. A summary of the operating principles of the DIAL technique is given in Section 3.2, and the methodology for using the technique to measure the fluxes of gaseous pollutants emitted by industrial sites is outlined in Section 3.3.

This Report discusses a measurement study carried out at an oil refinery, which used the DIAL technique. This had the objective of measuring directly and specifically the emissions of non-methane VOCs from a number of storage tanks and a flare. The results of these measurements are presented. In addition, a series of calculations, based on the API procedures (see Section 4), were carried out. These provided estimates of the emissions from the same storage tanks during the same time periods, and these are also presented. The two sets of results are compared, in order to establish the relationship between losses estimated by the API methodology and those determined by the DIAL technique. Some of the advantages and limitations of these two methods for determining emissions from storage tanks containing volatile hydrocarbons are also discussed (Sections 7 and 8).

2. OBJECTIVES OF THE MEASUREMENT EXERCISE AT SHELL STANLOW MANUFACTURING COMPLEX

The joint project between the National Physical Laboratory and Shell UK had the following objectives:

(i) To determine the fluxes of volatile organic compounds emitted from selected storage tanks using the NPL DIAL facility;

(ii) To identify, where practical, the main sources of these emissions;

(iii) To calculate the emissions of volatile organic compounds to atmosphere from the same storage tanks using the procedures specified by the API.

(iv) To carry out detailed comparisons of the DIAL results with those produced using the API procedures, in order to provide information on the accuracy of the UK emission inventory for this industrial sector.

(v) To use DIAL measurements as a first attempt to quantify the efficiency of industrial flaring, as this source may represent a significant uncertainty in the total VOC emissions for the industries in which they are employed.

3. REMOTE TECHNIQUES FOR DIRECT MEASUREMENTS OF INDUSTRIAL EMISSIONS

3.1 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 [7]. These techniques operate on spectroscopic principles using wavelength tunable sources. They rely on the fact that each gaseous species in the atmosphere has a characteristic absorption spectrum, and that the wavelength of the source can be chosen so that it coincides with one feature of this spectrum. Then, tuning the source wavelength on and off the spectral absorption feature and measuring the absorption that occurs, allows the concentration of the selected species to be determined. The performance of these remote techniques have been extended continually, 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.

3.2 THE DIFFERENTIAL-ABSORPTION LIDAR TECHNIQUE

One of these remote monitoring facilities uses a principle similar to optical radar, known as differential-absorption lidar (DIAL). In this technique, tunable laser radiation is 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. It is collected by a telescope close to the source, and measured on a detection system. 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 transmitted 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. The NPL DIAL techniques operates using these principles in the infrared and ultraviolet spectral regions. This enables a wide range of gases including CO, HCl, N_2O, CH_4, C_2H_4, C_2H_6, higher molecular weight alkanes and alkenes, and aromatics such as toluene and benzene, to be monitored specifically and sensitively [8]. Table 1 gives examples of the range of species that are potentially detectable with the NPL DIAL and other remote sensing techniques.

A two-dimensional scanning system directs the transmitted laser beam in different directions 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 1. Figure 2 shows in more detail the scanning mirror, the receiving telescope and the detection system of this mobile laboratory

3.3 METHOD FOR MEASURING GAS FLUX USING THE DIAL TECHNIQUE

As noted above, the DIAL technique measures directly the concentrations of the selected gas as a function of range along a selected direction up to the maximum range. By scanning the direction in which the transmitted laser beam and the receiving telescope are 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 then scanned in a plane downwind of an industrial plant, in a manner similar to that shown in Figure 3, the total amount of the selected gas(es) passing through the plane can be measured. The methodology for this is discussed in more detail below. 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 measurements.

Data on the atmospheric wind speed and direction are also required to calculate the emitted fluxes. An array of wind sensors, as indicated in Figure 4, is deployed wherever possible during the measurements. These include:

- a set of anemometers which may be mounted on tripods at elevations up to 4 m above the ground. These are used to check the wind field in a horizontal plane;

- anemometers mounted on a telescopic mast which can be raised up by to 15 metres in elevation;

- anemometers which can be mounted on a tethered balloon, capable of measurements from near ground level up to an elevation of about 1 km.

A simple model is also available which calculates the variation of wind speed with height, as a function of various parameters (such as the roughness of the terrain). This is used to supplement the meteorological measurements and, where appropriate, these model results are combined with the measurements to improve the accuracy of the estimates of the wind field pattern.

The emitted flux is then determined using a computer-based data analysis algorithm. This algorithm carries out the following 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 emitted flux.

The wind field over the complete concentration profile must be determined from a limited set of measurements either by a linear or non-linear interpolation of the anemometer results, weighted by the distances that the anemometers are from the selected point in the profile. In addition, where appropriate, the variations of the anemometer measurements of wind speed with height, are combined with the associated meteorological model noted above, to extrapolate the wind speed to greater altitudes. However, if this extrapolation increases the emitted flux by more than 15%, it is not applied since an unrealistically large value of the flux could be produced. The highest anemometer measurement is then used as a best estimate to represent the wind speed at greater altitudes.

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 is then combined with the measured gas concentration profile and integrated to produce the emitted flux.

For the measurement exercise at Shell Stanlow, the wind speed and direction were generally monitored at elevations of 1-2 m and 3-5 m above ground level, with a third measuring system at about 15 m above ground level. This procedure enabled an accurate estimate of the variations of wind speed with altitude to be determined up to heights above the storage tank elevations. All of these anemometers were carefully calibrated by NPL and compared before the measurement exercise. The instruments were set up as close as possible to the DIAL line of sight, ie not necessarily close to the emission sources. These measured wind speeds were used directly to determine the emission fluxes measured by DIAL, and as input data to the API calculations. As noted above, combinations of the anemometer results were generally used, as appropriate, for the DIAL elevation flux determinations. The API calculations used only the wind measurements at 15 m obtained on the DIAL vehicle, as these were considered the best estimate for the API calculations during the measurement periods.

3.4 VALIDATION OF DIAL MEASUREMENTS

The accuracy of the DIAL technique depends critically on the wavelengths selected for a given measurement application. These wavelengths must be chosen:

- to avoid interferences due to gaseous atmospheric species which may potentially have overlapping spectra;

- to avoid spectral interferences from other gaseous pollutants which may be present.

Before any field measurement exercise is carried out, a list of possible species emitted from the selected site is studied and spectral regions unique to the target molecules are chosen for the measurements. An in-house spectroscopic facility at NPL enables target wavelengths for a large number of gaseous species to be selected from their absorption coefficients, which are available on a comprehensive database. The gas mixtures used to produce this database are generally prepared gravimetrically at NPL. For this measurement exercise, DIAL wavelengths were selected:

- to monitor the total concentrations (by mass) of a wide range of gaseous aliphatic hydrocarbons irrespective, in general, of whether their relative concentrations vary in the atmosphere under study;

- to avoid spectral interferences due to atmospheric water vapour, methane, carbon dioxide etc. (Hence these DIAL measurements were insensitive to any methane which may have been emitted from the areas under study).

These wavelengths were monitored on-line using diagnostic facilities. Some of the diagnostic facilities built into the NPL DIAL facility to ensure the validity of the field measurements are noted below:

i) The energies of the transmitted radiations are monitored on-line throughout the measurements. This information is used to normalise the resulting atmospheric backscatter signals, thereby allowing effects of variations in the backscattered signals caused by fluctuations in the output laser pulse energies to be removed.

ii) The wavelengths of the transmitted DIAL radiation are monitored on-line throughout the measurements using a calibrated wavemeter and a set of calibration gas cells. These cells are filled with known mixtures of the gases being monitored, and their concentrations are traceable to NPL primary gas standards. These allow the accuracy of the atmospheric measurements to be checked by monitoring the amount of absorption of the DIAL radiation after transmission through the gas cells.

iii) Similar gas cells, containing gas mixtures with a range of known concentrations, are inserted manually into the return beam in the receiving telescope, immediately prior to the detection system, to confirm the linearity and accuracy of the complete detection system.

In addition to these calibration checks, which are performed during all field measurements, a number of specific field exercises have been carried out to validate the results obtained with the NPL DIAL system. Examples 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_2 - C_8. The results obtained for the total concentrations of VOCs measured by the point samplers and those measured by the infrared DIAL technique agreed within ± 15%. The concentrations of atmospheric toluene measured by the ultraviolet DIAL system agreed with those obtained by the point samplers to within ± 20%.

ii) The ultraviolet DIAL facility 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 ± 12%.

iii) A series of field trials have been completed in collaboration with British Gas plc where controlled methane emissions were measured. These utilised an instrumented facility which enables known fluxes of methane to be emitted from a one metre diameter stack. Measurements were made downwind of the source using the infrared DIAL facility. These were supplemented by an array of meteorological sensors to determine the wind field. The DIAL flux measurements agreed with the emitted fluxes to within ± 15%.

A national facility is now under development, which will utilise long-path optical gas cells and nationally-traceable gas mixtures with accurately-known concentrations. This will enable different remote long-path and range-resolved measurement techniques to be calibrated and their performance characteristics validated, as they become available.

4. PROCEDURES FOR CALCULATING THE EMISSIONS FROM HYDROCARBON STORAGE TANKS

A number of recommended international procedures are available for calculating the emissions from storage tanks containing hydrocarbons. These procedures, which have been produced primarily by the API are outlined below.

4.1 FIXED-ROOF TANKS

In 1952, the API sponsored an international Symposium on Evaporation Loss identified the need to develop a procedure for estimating the evaporative losses from fixed roof tanks which would be accepted by the oil industry. An extensive study was made of data on evaporative losses data from crude and gasoline storage tanks, and the first Bulletin 2518 was published in 1962 [9]. During the mid 1970s, the energy crisis and an increasing concern for the environment caused the API to review the data available. A further test programme was carried out and computer models were developed that simulated the losses that occur when no liquid VOC movements take place (ie the 'standing' losses). This resulted in a second edition of API Bulletin 2518 which was published in 1991 [10].

The method calculates the evaporative loss of VOCs on an annual basis. It takes into account the dimensions of the tank, the number of tank turnovers per annum, the vapour pressure of the product, and the range of ambient air temperatures.

4.2 EXTERNAL FLOATING-ROOF TANKS

In 1957, the API initiated a programme to collect data available from the petroleum industry on evaporative losses from external floating-roof storage tanks. These results were published in API 2517 Bulletin in 1962 [11]. As with the work on fixed-roof tanks, a review and further research were initiated in 1976. The results were published in 1980 as the second edition of API 2517 [12]. In 1984, as a result of other related work, the API started a test programme which investigated the effect of different tank fittings. This work resulted in the third edition of API 2517, which was issued in 1989 [13].

Annual emissions are calculated with this procedure using the physical properties of the bulk product and its temperature, and the atmospheric pressure and the average annual ambient wind speed. The calculations have been developed to take account of the storage tank dimensions and fittings which connect the stored product and the atmosphere. From these, and from the annual turnover of the tank, a total loss may be calculated.

4.3 INTERNAL FLOATING-ROOF TANKS

The first edition of API 2519, which provided information on evaporative losses from fixed-roof tanks using internal floating covers, was published by the API in 1962 [14]. The second edition published in 1976 [15] presented a calculation method for estimating this evaporative loss. As with the API 2517 and 2518, this report was reviewed and a further experimental test programme undertaken during the 1980's. The results of this work were incorporated in to the third edition of API 2519 in 1983 [16].

5. WORK PROGRAMME AND RESULTS FROM SHELL STANLOW OIL REFINERY

5.1 INTRODUCTION

The Shell Stanlow Manufacturing Complex comprises both an oil refinery and a petrochemicals complex. Although a bitumen and lubricating-oil complex were in existence on this site prior to 1940, the main process area and the associated storage tankage have progressively been developed since the 1950's.

In order to meet the objective of comparing the measurements of VOCs and the calculated tank losses in the time available, it was agreed to focus attention on storage tanks containing intermediate and finished product. However, over the years that the Shell Stanlow complex has been developed, industry standards have changed. Lighter products are generally now stored in floating roof rather than coned-roof tanks. However, due to the age of the refinery, some storage tank areas contain both coned and floating-roof tanks. In these cases, floating internal roofs have been fitted to some of the coned-roof tanks in these areas, in order to reduce emissions.

5.2 PREPARATORY WORK

The Stanlow site was visited on 13th December 1991 in order to identify probable emission sources and to establish suitable locations for monitoring these emissions with the DIAL facility. Two areas of the hydrocarbon storage tank farm were selected for study. These are indicated in Figure 5. Suitable locations were defined for the meteorological measurements required to determine the emitted fluxes. Suitable places were also identified where the refinery flare could be monitored. The location of this flare is also shown in Figure 5.

The NPL DIAL facility was driven to the refinery on February 23rd 1992 and deployed on site during the period February 24th to March 5th 1992.

5.3 METHODOLOGY FOR STORAGE TANK STUDIES

The concentration profiles of VOCs were measured in the two areas of the storage tankage noted above. These are shown in more detail in Figures 6 and 7. The contents of the tanks in these areas are listed in Table 2. The VOC concentration profiles measured using the DIAL facility were taken typically over a twenty minute period downwind of the selected source and these scans were repeated at least twice in order to average out short-term fluctuations in the emitted concentrations.

DIAL measurements were made intermittently of the concentration profiles upwind of the source under study in order to determine the fluxes arising from upwind sources. Generally, these were repeated when significant changes in wind direction occurred. In addition, the upwind measurements were checked regularly by monitoring the concentration profiles in selected lines-of-sight of the DIAL system, where it had been established that there was no significant contribution from the source under study.

During some of the DIAL scan measurements in this exercise, significant changes in wind speed or direction occurred. The results of such measurements could potentially be in error and are thus not included in this Report.

As discussed in Section 3.3, the atmospheric temperature and humidity, and the wind speed and direction were also monitored at representative locations during all the measurements using calibrated instruments. These allowed the pattern of the wind field in the measurement plane to be determined.

The measured data was analysed by NPL in order to derive the emitted fluxes during each scan, and averaged to produce approximate hourly mean values for the emitted VOC fluxes.

In parallel, Shell UK calculated the evaporative losses for each tank over each DIAL scan period using the appropriate API calculation procedure.

Discussions then took place between Shell and NPL personnel, and detailed comparisons have been made between the results obtained by the two methods on the fluxes emitted by the selected storage tanks.

5.4 RESULTS OF STORAGE TANK STUDIES

5.4.1 General

The emissions from a total of 56 storage tanks were investigated during the measurement period. These comprised fixed-roof tanks, ventilated fixed-roof tanks with internal floating roofs and external floating-roof tanks. Some of these external floating-roof tanks have single (ie only primary) seals whilst others were also fitted with double (ie primary and secondary) seals.

Most of tanks studied contained motor gasoline, intermediate components or other finished high-volatility products. However, some of the DIAL scans included tanks containing products such as kerosine and gas oils from which significant VOC emissions would not normally be expected. In addition, in the second area (Figure 7) there are six coned-roof tanks with internal floating roofs. When these were installed a decision was made to fit air ducts onto the tanks to avoid explosive mixtures in the roof space. This type of storage is not covered in the API methodology. For these cases, it was considered more appropriate to use the API calculation method for external floating roof tanks, rather than that for internal-roof tanks which are not exposed to the wind and are protected by pressure-vacuum valves.

An added complication was that the motor gasoline blender and a small pumphouse were in the vicinity of this second area of tankage (Figure 7). This blender contributed to the measured fluxes.

As noted previously, it was agreed that the wind speed to be used for all the API calculations was that measured by the calibrated anemometer on the 15 metre mast on the mobile DIAL facility.

A specific scan number and a letter indicating the measurement location have been assigned to all the DIAL measurements in order to aid in the presentation and interpretation of the results. These scan numbers, and the letters related to the measurement locations are not necessarily arranged in chronological sequence, since the measurements at any one time were selected to take account of the wind directions occurring at that time.

It should also be noted that the DIAL technique provides range-resolved measurements directly in the atmosphere. This, in some cases, enabled the fluxes emitted from different sets of tanks to be determined from the same measurement scan. When results were obtained in this way, they are labelled as n, m or f in the tables of results, corresponding to the near, middle and far-field measurements of a particular numbered DIAL scan.

A summary of all the NPL and API results is given in Table 3. These are discussed in more detail below.

5.4.2 Storage Tank Area I

The first area studied, shown in Figure 6, contained seventeen tanks. As listed in Table 2, six of these contained finished product motor gasoline in floating roof tanks, two of which had dual (ie primary and secondary) seals. The remaining eleven coned-roof tanks contained kerosine and gas oil components. DIAL measurements were made from two locations - A and B.

Figure 8 shows the results of the measurements on five gasoline and three kerosine tanks. The API calculations predict that the emissions from the gasoline tanks would have been in the range 70-98% of the measured total, depending on what form of tankage activity took place around the time of the scan. The DIAL measured values for the total emissions were in the range 44-100 kg/hr, with an average result of 76 kg/hr. The average NPL/API ratio was 2.0.

Figure 9 reports the results obtained in the same area, excluding the gasoline tanks. The average flux measured by NPL in this case was 12 kg/hr (compared to 76 kg/hr obtained for both the gasoline and kerosine tanks.) The average ratio of the NPL to API results was 2.6. However, due to the relatively low emissions from these tanks, any small contributions from other adjacent sources (eg fugitive emissions from valves, pipe-tracks or drainage ditches) would significantly enhance the DIAL results and thus increase this ratio.

In this area it was also possible to study the emissions from an individual floating-roof tank fitted with dual seals (tank number 4231, Figure 6). As shown in Figure 10, the measured value obtained for this was 12 kg/hr, which is a factor of 5.0 greater than the API value.

This high ratio might be explained by several factors. Firstly, although the tank was stationary, two days earlier product VOC had been withdrawn, and it is therefore possible that the some emissions were as a result of the wetted walls. Secondly, this measurement could have been influenced by upwind concentrations which may have included fugitive emissions from, for example, refinery drains. However, the limited upwind measurements which were taken with the DIAL facility during this time showed that, if any such upwind emissions were present, they must have been local to the area of the storage tank.

A further complication may have arisen in these single tank DIAL measurements. This arises because recirculation patterns and eddies in the wind field occur immediately downwind of a large object such as a storage tank. Limited measurements carried out in wind tunnels, and the results obtained with dispersion models, have shown that the contributions of such recirculation eddies are significant at downwind distances which are within a range of two diameters of an object with the shape of a tank, and are significantly less outside of these ranges. The single-tank DIAL measurements discussed above were obtained at downwind distances of about 120 metres. This should be sufficient to reduce significantly any recirculation pattern which occurs. In addition, the DIAL results are derived from time-averaged measurements and this will reduce the effects of small-scale eddies. However, the magnitude of these eddies and distance downwind at which they occur will, in practice, be dependent on the exact dimensions of the storage tank, the presence of any upwind obstructions, the roughness of the surrounding terrain and the meteolological conditions. The effects of these are difficult to evaluate accurately with simple dispersion models, and wind-tunnel experiments may be the only practical way of estimating their contributions. The single-tank DIAL measurements carried out during this exercise may therefore be less accurate than most of the other measurements.

5.4.3 Storage Tank Area II

The second area measured contained 39 tanks, the majority of which contained motor gasoline blending components, naphtha, and recovered hydrocarbon residues (slops). In addition, it can be seen from Figure 7 that the refinery's motor-gasoline blender was located in this area and this proved to be a significant source of VOC emissions, when operating. The results of the DIAL measurements were therefore corrected for this source. However, due to the presence of this blending area in close proximity to the tanks being studied, it was not always possible to delineate accurately the emissions of the blender from those of the storage tanks. In addition, the blender contribution varied significantly with time. In some DIAL scans the wind direction was such that only some of the emissions from the gasoline blender contributed to total measured VOCs. In other cases, the emissions produced by the blender were all entrained in the measurement plane. From Table 3 it can be seen that the contribution of the blender to the DIAL measurements ranged from 30 to 185 kg/hr. Where the blender emissions were present in the scan, its contribution to the total emissions varied from between 31% and 48% of the VOCs measured in that scan. In scans 23-36, which were all taken from the same DIAL location, the blender emissions varied between 185 and 70 kg/hr. It was not possible to explain these variations. However, it has been suggested that maintainance work, which entailed opening or draining equipment in the blender area could have occurred during the measurement periods.

The results of all the DIAL measurements carried out on these tanks, corrected for blender emissions, together with the API calculations for these same tanks, are given in Figures 11 to 14.

Figure 11 shows the results obtained for a batch of coned-roof tanks under conditions where there were no movements of the VOC liquids within them. In these cases, the average NPL/API ratio was 1.1 - ie the DIAL measurements agreed with the API calculations in this particular situation. However, it should be noted that this type of tank has a small number of components to maintain and there were no VOC movements to the complicate the calculation. In addition, the API calculations of the emissions from this type of tank are less dependent on assumptions about, for example, the quality of the tank seals and fittings, the properties of the stored liquid, and the prevailing meteorological conditions. It is thus perhaps not surprising that the two procedures agree under these circumstances.

Figure 12 shows the measurements made from position E which includes additional tankage to that measured from position D. The additional tankage includes both coned-roof and floating-roof tanks where liquid movements were taking place, as well as a contribution from the motor gasoline blender. After correction for the blender, the NPL/API ratio obtained by measurements from position D averaged 4.4, whilst for position E the ratio averaged 2.1. This gives an overall average of 3.1.

Figure 13 shows further results obtained from position E. The ratio of the NPL and API results obtained for this was 2.4, after corrections were applied for the blender emissions. This is of the same order as other reported results, although the wind velocity at time of the measurements was at the lower end of the acceptable range.

The emissions in the tankage area shown in Figure 14 were significantly influenced by the emissions produced by the motor-gasoline blender, as can be seen from Table 3. As noted previously, this contribution varied significantly between the scans. In these measurements, if the VOCs measured downwind of the blender are all ascribed to that source, the ratio of the DIAL and API results for scan 23 is reduced from 4.0 to 2.7 and that for scan 24 from 4.9 to 4.3.

There were also tanks with internal floating roofs in this area. As noted in Section 5.4.1, these are fitted with air scoops around the roof to prevent explosive mixtures from forming, and thus the wind can pass freely across the vapour space in the tank in much the same way as it passes over an external floating roof. For these tanks it was decided that the API floating-roof procedure was more applicable. The average ratio of the DIAL and API results using the floating-roof procedure was 3.4, which is higher than many others. However, in view of the possibly unrepresentative nature of these tanks, this result should be treated with caution.

5.4.4 Summary of Results of the Storage Tank Study

Figure 15 summarises all the data sets taken. It shows the comparisons of the VOC fluxes determined from the DIAL measurements with those calculated by the API procedures. They are displayed in terms of increasing DIAL measured values. The labelling on the horizontal axis represents the number of the data set (or scan number), and the results are therefore not arranged in time sequence. The NPL DIAL measurements are generally higher than the API calculations. Figure 16 shows the frequency distribution of this ratio of DIAL to API results, in terms of the occurrence of the ratio. Figure 17 shows the distribution of this ratio of DIAL and API results, plotted as a function of the emitted flux determined by the DIAL method.

A number of conclusions may be drawn from the results summarised in Figures 15 to 17.

(i) The ratios between the DIAL measured results and the API calculations for all the storage tankage studied range from 0.8 to 5.8.

(ii) 20 of the 32 measurements have ratios in the range 1.5 to 3.0.

(iii) 7 of the 12 sets of data where the ratio lies outside the range 1.5 to 3.0 are those corresponding to the lowest measured emissions ($\leq$ 22 kg/hr). Of the remaining five, two had some uncertainty associated with entrained emissions from the motor gasoline blender.

(iv) For the tankage in Area II, two of the largest ratios observed between the DIAL and API results occurred when the absolute contribution to the measured flux from the motor gasoline blender was at its maximum. It is thus possible that the contributions from the motor gasoline blending area were not completely corrected for.

(v) In Area I, where the blender clearly made no contribution, the ratio was lower, with an average value of 2.1. In these cases, the storage of the lighter products was entirely in floating roof tanks, which mainly had single seals.

(vi) It was not possible to differentiate sufficiently between the fixed-roof and floating roof tanks emissions to allow an evaluation of the relative accuracies of the different API procedures to be derived, (with the exception of the set of measurements (Figure 11) carried out on coned-roof tanks where there were no movements of the tank contents). This was due partly to the fact that the storage tanks in Area II were of mixed types, and also because of the complication which arose from the gasoline blender in this area.

(vii) The weighted mean value for the ratio of the DIAL to API results, averaged over all the measurements taken during this exercise, is 2.7.

(viii) It is estimated from the DIAL measurements that the emissions of VOCs to atmosphere from the motor-gasoline blending area at the Stanlow Manufacturing Complex ranged from 70 to 190 kg hr^{-1} during the exercise.

(ix) The emissions of VOCs to atmosphere, from all the storage tanks studied at the Stanlow Complex, as measured by the DIAL facility, ranged from 180 to 280 kg hr^{-1}.

5.5 STANLOW FLARE STUDIES

A number of attempts were made to measure the fluxes of unburnt hydrocarbons emitted by the main flare at Stanlow oil refinery. In total, flare measurements were carried out on seven days in order to try and quantify the emissions of non-methane VOCs. However, for nearly all the time of this measurement exercise only a pilot flame or a very small flare were present. In all these cases the fluxes of unburnt non-methane hydrocarbons were at or below the detection threshold of the DIAL technique, as it was configured for this exercise.

On one specific occasion, a controlled test was carried out for a short period on the refinery flare. During this period a measured amount of gas, similar in constitution to that generally used as refinery fuel gas, was injected into this flare whilst DIAL measurements were carried out simultaneously. The flux of emitted hydrocarbons observed under these circumstances was around the detection limit of the DIAL technique as it was configured during this exercise.

The constituents of this gas were analysed subsequently by Shell UK using gas chromatography. Table 4 shows the results of the analysis, and the value for the total gas flux injected into the flare. From this and from a knowledge of the detection sensitivity of the DIAL facility during this exercise, a lower limit can be obtained for the combustion efficiency of the flare for non-methane hydrocarbons on this occasion. This lower limit was calculated to be 99.3%.

It is clear from the above discussion that it is generally not very cost effective to carry out measurements of the efficiency of industrial flares at an industrial site such as an oil refinery, since it is then a matter of chance whether the flare is used operationally during the exercise. Instead, it would be more efficient to use the DIAL facility to determine the combustion efficiency of VOCs in industrial flares in a well-designed experiment where controlled gas releases can be produced, rather than in industrial sites where conditions are difficult to control.

6 ADVANTAGES AND POTENTIAL LIMITATIONS OF THE LOSS ESTIMATION PROCEDURES SPECIFIED BY THE AMERICAN PETROLEUM INSTITUTE

As discussed in Section 4, the internationally-recognised procedures specified by the API for calculating the emissions of volatile organic compounds from different types of hydrocarbon storage tanks, have been prepared and revised following considerable research work. As a result, these API procedures have a number of advantages over many other methods. Some of these are outlined below. However, it is also possible that incorrect results may be obtained when applying these procedures. Some of the limitations are intrinsic to the API procedures, whilst others are associated with the way the procedures were applied during the measurement exercise reported here. These two types of limitations are also noted below.

6.1 ADVANTAGES OF THE API PROCEDURES

As noted above, research work has been carried out to investigate the emission losses associated with different types of storage tank containing volatile organic compounds. The resulting procedures stemmed partially from experimental work on different types of tanks under controlled operating conditions in enclosed housings. Consequently, their advantages are:

(i) The API calculations provide low-cost procedures for calculating the emissions over extended periods. It would be difficult to carry out direct measurements at reasonable cost over such long periods, except on a very selective basis.

(ii) The API provide different procedures for each type of storage tank, and certain allowances can be made, for example, for the number of tank fittings and the quality of their seals. It is thus possible to produce an inventory for the entire tankage at an industrial site taking into account the tank numbers and the types of fittings etc. It would thus be practical, in principle, to estimate, in a cost-effective way, the complete emissions from the storage tankage in an industrial sector. However, this has yet to be carried out at a national level and the potential limitations in the procedures could cast doubt on the accuracy of such an estimate.

(iii) The API procedures have widespread recognition and therefore their use brings about consistent results, even if the calculated losses are under-estimated. In addition, any subsequent updating will be widely applied by the industries concerned.

(iv) These procedures allow for different tank fittings and seals, and it is therefore possible to quantify, within the limits of uncertainty of the calculations, the effects of modifications, and therefore to project the most cost-effective improvements.

6.2 POTENTIAL LIMITATIONS OF THE API PROCEDURES

6.2.1 Intrinsic Limitations

Examples of the limitations which could potentially be present when the API procedures are applied in practice to different types of tanks, even when the calculations are used to predict long-term emissions, are outlined below.

(i) The API procedure for monitoring floating-roof tanks uses the temperature of the stored liquid as an input parameter. Any variations in this temperature, which is usually assumed to be that of the bulk liquid, will significantly affect the vapour pressure of any gas which may be present in any head-space above the liquid or at the interface between the liquid and the atmosphere. If solar insolation is present, the temperature near the liquid surface may be significantly greater than the bulk liquid. This will therefore increase the emission rate of the volatile species from the liquid. During the night the surface temperature may cool to below that of the bulk temperature, and this will ameliorate the effects of solar radiation. However, as the vapour pressure is not a linear function of temperature, any daytime temperature rise may not be cancelled out completely. Some measurements [17] have been made of the increase in temperature between that of the bulk liquid and that for the liquid surface when the tank is exposed to direct solar radiation. These showed that this temperature difference could be in excess of 15°C, and this could clearly give rise to increased emissions.

(ii) The API procedures use a single wind speed as an input parameter to the calculations. This wind speed parameter is obtained from the averaged readings of an amenometer located in the atmosphere some distance from all obstructions, since it is assumed in the API procedures that this represents the best approximation to the average wind speed present in the enclosed housings used in the original experimental tests which contributed to the formulation of the procedures. However, the actual emissions from the storage tanks will be determined by the wind field present in the open atmosphere at the large number of locations where the VOCs come into contact with the air, and this will be very complex.

A further difficulty occurs with external floating-roof tanks if the average wind speed determined over an extended period is applied in the API calculations to estimate the emissions over that period, since the emissions are not linear as a function of wind speed.

(iii) Losses from floating roof tanks are believed to be related to the height of the roof. This parameter is not employed in the API calculations. Instead, an assumption is made that any effect is averaged out as the roof height varies over a long period of time. This assumption may not be justified.

(iv) As a storage tank is emptied, a film of liquid hydrocarbons remains on the tank walls. This subsequently evaporates during the following hours or days, the exact rate of which depends on the properties of the liquid, the condition and topography of the tank, and the meteorological conditions. This effect may not be corrected for accurately in the API calculations.

6.2.2 Limitations Specific to this Measurement Exercise

There are a number of specific shortcomings in the API calculations as they have been applied to the measurement exercise discussed in this Report, in addition to the above limitations which may apply more generally. These specific limitations are associated with the fact that the API procedures are usually intended to be used for extended time periods of up to about a year. Thus, if they are used to estimate the emissions over short periods, errors are likely to occur. Typically, in this exercise each of the DIAL measurements were made over a period of about 20 minutes. Accurate information on the movements and the temperatures of the liquid in the storage tanks, and on the meteorological conditions, is therefore required if the API calculations are to be valid over these short periods. During the normal operations of a refinery such detailed data is not retained. Areas where this could present a problem when comparing DIAL measured and short-term API calculated values of the emissions, are as follows:

(i) A complete evaluation of the tests was not undertaken until some time after the measurements, at which time the two-minute-averaged computer data on movements in the tanks was unavailable, and only the six-hourly data was retained on computer files. It was therefore necessary to assume constant filling/emptying rates during these six hourly periods, which was not necessarily the case.

(ii) The API calculations used during this exercise make use of the bulk temperatures of the liquid hydrocarbon in the tanks. However, unlike the tank level data, only values of the daily average temperatures were retained and employed, and this could, in principle, lead to errors, particularly as all the measurements were made during daytime. Nevertheless, as the trials were conducted during the period February to March, when the intensity of solar radiation is too low to raise the surface temperature of the liquid in the tanks significantly, this error in unlikely to be large.

iii) Some of the physical properties of the tank contents (eg the saturated vapour pressures of the liquids) are used as input data to the API calculations. In certain cases, particularly in the case of the oil-refinery intermediate products, these are not routinely sampled and the vapour pressures used in the calculations could therefore have been inaccurate. In order to avoid this source of error, it would have been necessary to undertake additional laboratory tests. These were not usually carried out during the periods of the DIAL measurements.

(iv) The API emission calculations allow the status of the seals of the tank to be designated as either good or average. There is currently no category which covers poor seals.

(v) It is possible that operational procedures could have some impact on the emissions of VOCs to atmosphere (eg the covers over tubes which are used to sample the tank contents might not have been shut properly.) No comprehensive checks were made on the days of the tests, and although subsequent checks showed no undue problems, this factor cannot be ruled out.

(vi) For the case of external floating-roof tanks, it is likely that wind induced evaporative losses will be a function of the distance that the floating roof is below the top of the storage tank walls. As noted above, API procedure 2517 states that this is not considered significant over a period of a year for operational tanks. However, for the short time periods of this exercise, this may have affected the accuracy of the calculated values.

(vii) The air movements generated by the wind around the fixtures and fittings of the storage tank are one of the dominant factors in determining the evaporative losses. Therefore it would be desirable to determine accurately the wind speeds around all these fittings. However, this is clearly impossible as the actual wind patterns in storage tank areas are complex. Instead, the API calculations, as they are generally applied, use annual average wind speeds for the site. However in this exercise, use was made of the wind speeds measured by the calibrated anemometer located on the DIAL facility at an elevation of 15 m. This was considered a better approximation than anemometer measurements carried out more remotely. Nevertheless, this will necessarily only be an approximation for the wind speeds at all the points where VOCs are in contact with the ambient atmosphere.

(viii) As a tank's contents are emptied the floating roof moves downwards. The exposed tank walls may then remain "wetted" as liquid hydrocarbon clings to their surface. The amount of liquid which remains attached to the storage tank wall under these circumstances will depend on a number of factors including the viscosity of the liquid in the tank and the roughness of the tank walls. This liquid hydrocarbon film will subsequently evaporate, but the evaporation rate will also depend on a number of factors including, for example, the constituents of the liquid and the atmospheric conditions. In some cases in this exercise, storage tanks were not moving at the time of the DIAL measurement, but had been moving previously. Typically, the loss from a "wetted wall" could amount to about 5 kg/hr. This value has been estimated from the clingage factor given in the API bulletin, and the surface area of a typical tank wall.

(ix) The API procedure for internal floating roof tanks states that there is no statistically-significant change in the amount of evaporative loss as the air flow varies. Thus for this type of tank the wind velocity and ambient temperature changes are not considered as significant parameters in the calculation methods. However, during this exercise the evaporative emissions from a group of internal floating-roof tanks were measured, and values for the emissions were obtained that appeared to be proportional to the wind velocity. These emissions also varied considerably in magnitude, whilst the API procedure 2519 gave values which were constant. This could be explained by the fact that the tanks measured had internal floating roofs which were fitted with air scoops in order to prevent explosive mixtures from being formed. Thus the wind passes freely across the vapour space in the tank in much the same way as it passes over an external floating roof. For these tanks, as stated in Section 5.2, use was made of API procedure 2517 as well as API 2519. The results calculated using API 2517 were in better agreement with the DIAL measurements, although differences still exist. The physical conditions of an internal floating-roof tank and its rim seals cannot be accurately defined without internal inspection. Such internal inspections only take place infrequently (generally when the tank is empty), and there is some possibility that degradation may have occurred. No allowance has been made for this in the calculations.

7. ADVANTAGES AND POTENTIAL LIMITATIONS OF THE DIAL TECHNIQUE FOR INDUSTRIAL FLUX MEASUREMENTS

It is useful to review, in a similar manner to that done for the API procedures above, some of the advantages and potential limitations of the multiwavelength DIAL technique when used to determine the fluxes of VOCs or other species emitted by industrial sites, in order to establish their contributions to overall annual emission inventories.

7.1 ADVANTAGES OF THE DIAL TECHNIQUE

The DIAL technique, when supported by appropriate meteorological measurements, has a number of advantages over other measurement methods and estimation procedures for the accurate determination of the emissions of VOCs:

(i) It is capable of making direct measurements of the complete concentration profiles of the emitted VOCs in the atmosphere, irrespective of the size and shape of the emitted plumes. Since it is a direct measurement method there is no need to make some of the, possibly inaccurate, assumptions that are implicit in estimation procedures such as those prescribed by the API and by SOCMI. Other measurement methods, such as point samplers and integrated-path monitors, need to make theoretical assumptions about the concentration profiles of the emissions in the atmosphere, which are generally derived from atmospheric dispersion models. These may also be inaccurate, particularly in the complex topography of an industrial plant.

(ii) Both the API procedures and the DIAL technique require accurate information on wind speed if the derived fluxes are to be valid. However, the wind data required is different for the two methods. The DIAL technique requires accurate wind velocity data in the plane in which the DIAL measurements are made, downwind of the industrial site where the wind field will be more uniform than within the area of the tankage. In practice, it is relatively straightforward to determine this. In contrast, although the API procedures use only a single wind speed as an input parameter, the emissions will be determined by the complex wind field which is actually present in the storage tank area at the large number of locations where the VOCs come into contact with the atmosphere.

(iii) The DIAL technique requires no information on the temperature of the liquid in the storage tank in order to produce an emitted flux. Therefore it is unnecessary to know the temperature of the bulk liquid or its surface (see Section 6). However, data on the temperature of the liquid is required if the measured DIAL fluxes are to be extrapolated to provide annual emissions.

(iv) The DIAL technique requires no information on the properties of the liquid in the storage tank (their species composition, vapour pressure etc) in order to determine the emitted flux. Such information may be difficult to acquire with adequate accuracy, for example, in the case of intermediate products of the refinery processing operations. However, this information will be important if the measured DIAL fluxes are to be extrapolated to provide annual emissions.

7.2 POTENTIAL LIMITATIONS OF THE DIAL TECHNIQUE

The results obtained with the DIAL technique, as with all sophisticated instrumentation, should be treated with care, as they may suffer from hidden inaccuracies. These fall into two categories - those which are intrinsic to the method, and those which could occur if the measurement procedure is not applied correctly.

7.2.1 Intrinsic Limitations of the Technique

(i) The multiwavelength, ultraviolet/infrared DIAL facility is a high-cost unit which currently needs to be operated by skilled technical personnel. It is therefore not practical to utilise the technique for continuous, year-long, measurements of the emissions from a specific industrial site, process plant or storage area. The emissions obtained must be based on measurement exercises of limited duration, and it is therefore necessary to take considerable care when scaling the results to make long-term predictions of emissions, such as required for an inventory. The extrapolation process needs to take account of the representativeness of the operations occurring during the measurement period, the properties of the stored liquids and the variability of the meteorological conditions. For example, for the case of industrial process plant which operates continuously, this scaling up procedure may only need to take account of any, possibly small, effects of changing ambient temperatures on the emissions. For the case of storage tank emissions other factors, such as variations in wind velocity and solar insolation, should also be taken into account. Nevertheless, it is practical to allow for these factors, and the NPL DIAL facility has been used in a previous measurement exercise in combination with API procedures, [17] to produce a reliable estimate of the annual emissions of a complete refinery.

(ii) There are inherent approximations in the assumption that the pattern of the wind field across the measurement plane (which encompasses the complete concentration profile of gases emitted from the area under study) can be represented by the results obtained from a limited number of anemometers. In principle, the largest errors in the calculated wind field will occur when the industrial area has a large irregular topographic structure. However, the DIAL measurement plane is ideally selected to be sufficiently downwind of the site so that irregularities induced in the wind field by these structures are substantially averaged out. In addition, the measurement plane in which the DIAL measurements are made is generally selected to be perpendicular to the prevailing wind direction and thus small topographically-induced changes in wind direction within this plane will have negligible effects on the derived fluxes.

In practice the limitation due to finite sampling of the wind field is circumvented by selecting the measurement plane carefully to minimise the spatial variability of this wind field. The validity of the measured flux is then investigated, when possible, both by using measurement planes which are at different distances downwind of the source, and by monitoring the source from different directions. By these means it is possible to reduce wind field errors to a level where they constitute a small component of the overall error budget for the measurements.

(iii) Fluxes are obtained using the DIAL technique by directing the laser beam sequentially in a 'fan' of different lines-of-sight (Figure 3) to encompass the emitted plume. The measurement scan over these different lines-of-sight, takes a short but finite time period to complete. If during this scan period, atmospheric turbulence causes the emitted plume to move significantly across these lines-of-sight, an incorrect value for the concentration profile will be obtained. The flux value derived will be higher or lower than the true result depending on whether high concentrations are blown into or out of the lines-of-sight of the DIAL measurements. This atmospheric turbulence effect thus translates into a statistical (random) uncertainty in the measurement process. The magnitude of this uncertainty is greater for flux measurements on a single point source, and is less significant for an area where emissions arise from a number of smaller sources. The magnitude of the errors which could arise from this effect has been investigated experimentally for the case of a point source with known emissions (see eg Section 3.4). In the case of fugitive sources covering a larger area, the magnitude of the statistical uncertainty has been estimated by carrying out repeated measurements in different circumstances, where it is believed the source is emitting at a nearly constant rate.

In practice, the uncertainty due to this effect is reduced in a given measurement exercise by carrying out repeated measurements on the selected area, and by making measurements, as far as possible, under meteorological conditions for which the effects of plume movements due to atmospheric turbulence are reasonably small.

(iv) The aromatics, particularly benzene, toluene and xylene, are not detected in the infrared with the same sensitivity as other hydrocarbon species, and they are therefore monitored in the ultraviolet. Currently, it is only possible to employ the DIAL technique to determine the fluxes of one aromatic at any given time. Thus DIAL measurements may under-estimate the total amount of aromatics emitted. During the Stanlow exercise the DIAL facility was tuned to monitor toluene, since this is usually the aromatic that is present with the largest concentrations. Another aromatic which is often present at relatively high concentrations is benzene, but this was not measured. However, benzene is extracted at Stanlow before the liquid products measured in this exercise were stored. There is thus no underestimate in these measurements due to the fact that benzene was not monitored specifically.

7.2.2 Potential Errors in the DIAL Technique

The intrinsic limitations of the DIAL technique for determining fluxes are predominantly related to the representativeness of the results when only a restricted time series of measurements are made. In addition, there are a large number of areas where incorrect results could potentially occur if insufficient expertise is applied during the measurement procedure. It is believed that the results produced in this Report do not contain any significant errors due to this cause. Nethertheless, some of the potential problem areas are presented below to provide a more complete description of where errors in DIAL measurements can occur.

(i) Incorrect spectroscopic data could be used. Spectroscopic data is used to compare the amount of absorption which occurs at the DIAL wavelengths due to the gaseous species in the atmosphere under study, with the absorption produced by a known concentration of the same gas. Thus, if this data (which is produced beforehand in the laboratory) is incorrect, or is incorrectly applied, the DIAL results will be in error. The spectroscopic data required for this exercise was produced at NPL by the use of a sensitive high-resolution fourier-transform spectrometer, coupled to a long-path gas cell. Known concentration gas mixtures, prepared by the UK Primary Gas Standards Laboratory, are injected into this gas cell to produce accurate spectral data of all the gaseous pollutants which are likely to be present in significant concentrations in industrial atmospheres.

(ii) A number of other problems can occur when applying spectroscopic data. For example, incorrect assumptions can be made about the different gaseous species that are present in the industrial atmosphere. Then if a gas is overlooked which has spectral absorption features which interfere with the gas(es) being measured, the flux measurements may be incorrect. This problem is overcome by NPL by the following procedures:

    (a) whole air samples are taken simultaneously with the DIAL measurements. These are subsequently analysed by gas chromatography and infrared spectroscopy. The results are then used with the spectral data-base, to check that no gaseous species are present which would interfere spectrally and thereby reduce the accuracy of the results.

    (b) The DIAL facility is used to carry out wavelength scans in the atmosphere over the spectral region of interest. This records the spectral 'fingerprint' of the atmospheric species actually present and compares it with the spectrum of the species assumed present.

(iii) If the combined optical and electronic detection system, which is used to detect the atmospherically-backscattered radiation at the infrared and ultraviolet wavelengths, does not have a linear response to changes in received optical signals, incorrect results will be obtained. It is necessary that the linearities of these systems are evaluated over the wide range of signal intensities which are encountered in practice, and corrections made for any nonlinearities. This correction procedure is itself not straightforward to apply, but has been implemented for the measurements reported here.

(iv) The optical characteristics of the infrared and ultraviolet sources in the DIAL system will affect the accuracy of the results, particularly if these vary between measurements or within a measurement scan. Examples of this include the wavelength stability and the spectral bandwidths of the transmitted radiation. A range of on-line diagnostic facilities are needed to evaluate these characteristics and the results obtained from these are used, when necessary, to apply corrections to the flux measurements. These procedures were followed, where applicable, in this study.

(v) Data processing algorithms are employed, as outlined in Section 3.3, which assimilate the concentration measurements along each line-of-sight of the DIAL system and the meteorological data, to produce the emitted fluxes. It is relatively straightforward to derive fluxes from the DIAL measurements. However, the algorithms are complex and expertise is needed to ensure that the flux values produced are valid. This is particularly an issue when the measured concentration profiles are complex and contain features at different spatial positions. The validity of the DIAL measurements and the processing algorithms can be demonstrated using field measurements similar to those outlined in Section 3.4, and these validation activities are ongoing at NPL.

8. SUMMARY AND CONCLUSIONS

An international Protocol has recently been agreed under the aegis of the United Nations Economic Commission for Europe's Convention on Long-range Transboundary Air Pollution. This is designed to secure reductions in the emissions of volatile organic compounds to atmosphere, at a national level, by at least 30% by the year 2000, compared to 1988 levels.

As part of the UK research programme required to underpin this Protocol, a measurement exercise has been carried out at Shell Stanlow Manufacturing Complex which has the aim of improving the accuracy of the UK inventory of the emissions of volatile organic compounds for the oil refining and petrochemical industries. The results of this exercise will also be relevant to new EC regulations on storage tank emissions from the downstream petroleum industry. The exercise involved measurements of the fluxes of VOCs emitted from a range of storage tanks containing different products using a recently developed tunable infrared and ultraviolet differential-absorption lidar facility. The VOC emissions from these storage tanks were also calculated using internationally-recognised procedures prescribed by the American Petroleum Institute.

The results of the two methods were compared in detail and some of their advantages and potential limitations are given. The emissions measured by the DIAL technique were found generally to be two to three times those calculated by the API procedures. The total VOC emissions measured by the DIAL facility, from the storage tankage studied and the refinery's motor gasoline blender were 250-470 kg hr^{-1}. This is not inconsistent with the results of a recent study which estimated refinery losses based on the mass balance of an 'average' UK refinery [18] and which also suggested that established calulation procedures could lead to underestimates of fugitive VOC emissions.

These results indicate that the emissions to atmosphere of non-methane volatile organic compounds from different types of storage tanks used in the oil refining and petrochemical industries could be underestimated when the API procedures are used.

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10. REFERENCES

1. Ozone in the United Kingdom, UK Photochemical Oxidants Review Group Interim Report, Department of the Environment, February 1987.

2. Ozone in the United Kingdom 1992, Third Report of the UK Photoxidants Review Group - to be published 1993.

3. United Nations Economic Commision for Europe Convention on Transboundary Air Pollution, November 1991.

4. Draft EC Directive - Control of Volatile Organic Compound Emissions Resulting from the Storage and Distribution of Gasoline (Stages 1 and 2).

5. CONCAWE Report 87/52: Cost Effectiveness of Hydrocarbon Emission Controls in Refineries from Crude Receipt to Product Despatch.

6. EPA/600/7-85/022a: Model for Evaluation of Refinery and Synfuels VOC (Volatile Organic Compounds) Emission Data.

7. P T Woods, Remote Sensing Techniques for Gas Detection, Air Pollution and Fugitive Loss Monitoring: Conference on Optical Remote Sensing Applications to Enviromental and Industrial Safety Problems, Air and Waste Management Association, Special Publication 81, 3-29, 1992.

8. P T Woods, R H Partridge, M J T Milton and A J Davenport, Gas Standards and Monitoring Techniques for Measurements of Vehicle and Industrial Emissions, Workplace Exposure and Air Quality. Bulletin de L'Organisation Internationale de Métrologie Legalé, 131, 11-25, 1993.

9. API Bulletin 2518: Evaporation Loss from Fixed-Roof Tanks, 1962.

10. API Bulletin 2518 Second Edition: Evaporative Losse from Fixed-Roof Tanks, October 1991.

11. API Bulletin 2517: Evaporation Loss from External Floating-Roof Tanks, 1962.

12. API Publication 2517 Second Edition: Evaporation Loss from External Floating-Roof Tanks, 1980.

13. API Publication 2517 Third Edition: Evaporative Loss from External Floating-Roof Tanks, February 1989.

14. API Bulletin 2519: Evaporation Loss from Internal-Floating Roof Tanks, 1962.

15. API Publication Second Editions 2519: Evaporation Loss from Internal-Floating Roof Tanks, 1976.

16. API Publication Third Edition 2519: Evaporation Loss from Interanl-Floating Roof Tanks, 1983.

17. Fugitive Emission Survey at BP Refinery, Gothenburg, Sweden, 1989: Report available from Swedish Ministry of the Environment 1989, and Gothenburg Local Environmental Authority.

18. E R Robinson, VOC Emissions from Oil Refineries: Proceedings of the 1993 European Conference on Estimation Measurement and Reduction of VOC Emissions in the Petroleum Industry, London, June 1993.

LIST OF TABLES

TABLE 1

Examples of Detection Sensitivities Attainable with NPL Remote Monitoring Facilities

Tunable diode-laser system		Ultraviolet/visible DIAL system		Infrared DIAL system	
CO	0.5 ppb	NO	5 ppb	CH_4	30 ppb
CH_4	1 ppb	NO_2	10 ppb	C_2H_2	40 ppb
NH_3	5 ppb	SO_2	10 ppb	C_2H_4	40 ppb
C_2H_4	5 ppb			C_2H_6	20 ppb
C_2H_6	1 ppb	O_3	5 ppb	Higher Alkanes Alkenes Alkynes	25 ppb
C_2H_2	2 ppb	Hg	0.5 ppb		
		Benzene	5 ppb	H_2S	2 ppm
H_2S	1 ppm	Toluene	8 ppb	OCS	50 ppb
N_2O	0.2 ppb	Xylenes	20 ppb	HCl	50 ppb
NO_2	20 ppb			N_2O	50 ppb
COS	0.5 ppb				
HCl	1 ppb				
HCHO	1 ppb				
HNO_3	1 ppb				

TABLE 2

List of Tanks and Tank Contents in DIAL Measurement Areas

Tank Contents in Area I	
Tank Number	**Contents**
T4211	Gas Oil
T4212	Gas Oil
T4213	Gas Oil
T4215	Gas Oil
T4216	Gas Oil
T4217	Gas Oil
T4218	Gas Oil
T4223	Kerosine
T4224	Kerosine
T4225	Kerosine
T4226	Motor Gasoline
T4227	Motor Gasoline
T4228	Motor Gasoline
T4229	Motor Gasoline
T4230	Motor Gasoline
T4231	Motor Gasoline

Tank Contents in Area II	
Tank Number	**Contents**
T4000	Naphtha
T4001	Naphtha
T4002	Naphtha
T4003	Naphtha
T4004	Motor Gasoline
T4005	Motor Gasoline
T4062	Motor Gasoline
T4063	Motor Gasoline
T4064	Gas Oil
T4065	Motor Gasoline
T4066	Naphtha
T4067	Gas Oil
T4068	Gas Oil
T4069	Slops
T4070	Slops
T4071	Gas Oil
T4072	Slops
T4073	Slops
T4090	Water
T4091	Motor Gasoline
T4092	Water
T4093	Naphtha
T4094	Motor Gasoline
T4095	Motor Gasoline
T4096	Motor Gasoline
T4097	Motor Gasoline
T4109	Empty
T4123	Naphtha
T4124	Naphtha
T4125	Naphtha
T4126	Naphtha
T4127	Naphtha
T4128	Motor Gasoline
T4129	Naphtha
T4130	Naphtha
T4138	Empty
T4139	Motor Gasoline
T4144	Motor Gasoline
T4180	Motor Gasoline

TABLE 3

Summary of NPL and API Results in Kilograms per Hour

25/2/92	Scan Number		(1)	(2)	(3)	(4)
Position A						
Times:						
14.08-14.18(1)	API		31	35	34	25
14.20-14.32(2)	API		84	76	66	44
14.43-14.54(3)	NPL/API		2.7	2.2	2.0	1.8
15.46-16.01(4)	Average NPL/API	2.1				

26/2/92	Scan Number		(5)	(6)	(7)	(8)
Position C						
Times:						
14.58-15.08(5)	API		23	18	17	10
15.10-15.25(6)	NPL		22	19	16	18
15.35-15.45(7)	NPL/API		0.9	1.0	1.0	1.7
15.59-16.09(8)	Average NPL/API	1.2				

26/2/92	Scan Number		(9)	(10)
Position E				
Times:				
16.23-16.51(9)	API		37	33
16.54-17.06(10)	NPL		79	88
	NPL/API		2.2	2.7
	Average NPL/API	2.4		

27/2/92	Scan Number		(11n)	(12n)	(13n)
Position A					
Times:					
11.54-11.59(11n)	API		52	52	51
12.02-12.22(12n)	NPL		91	83	100
13.48-14.08(13n)	NPL/API		1.8	1.6	2.0
	Average NPL/API	1.8			

TABLE 3
(Continued)

27/2/92	Scan Number		(11f)	(12f)	(13f)
Position A					
Times:					
11.54-11.59(11f)	API		5	5	4
12.02-12.11(12f)	API		12	15	9
13.48-14.08(13f)	NPL/API		2.3	3.1	2.3
	Average NPL/API	2.6			

27/2/92	Scan Number		(14)	(15)
Position A				
Times:				
15.43-15.58(14)	API		2	2
16.05-16.14(15)	NPL		14	10
	NPL/API		5.8	4.2
	Average NPL/API	5.0		

27/2/92	Scan Number		(16)
Position B			
Times:			
17.40-17.50(16)	API		24
	NPL		60
	NPL/API		2.5
	Average NPL/API	2.5	

2/3/92	Scan Number		(17)	(18)
Position D				
Times:				
14.15-14.29(17)	API		14	10
14.35-15.03(18)	NPL		99	80
	NPL Blender		45	30
	NPL Tanks		54	50
	NPL/API		3.8	5.1
	Average NPL/API	4.4		

TABLE 3
(Continued)

2/3/92	Scan Number		(19)	(20)	(21)
Position E					
Times:					
16.22-16.32(19)	API		24	21	22
16.43-16.53(20)	NPL		76	113	79
17.57-18.05(21)	NPL Blender		30	35	35
	NPL Tanks		46	78	44
	NPL/API		1.9	2.5	2.0
	Average NPL/API	2.1			

3/3/92	Scan Number		(22n+m)
Position E			
Times:			
10.31-11.50(22n+m)	API		109
	NPL		220
	NPL Blender		75
	NPL Tanks		145
	NPL/API		1.3
	Average NPL/API	1.3	

3/3/92	Scan Number		(22f)
Position E			
Times:			
10.31-11.50(22f)	API		10
	NPL		8
	NPL/API		0.8
	Average NPL/API	0.8	

TABLE 3
(Continued)

5/3/92	Scan Number		(23)
Position E			
Times:			
10.29-10-50(23)	API		47
	NPL		386
	NPL Blender		185
	NPL Background		11
	NPL Tanks		190
	NPL/API		4.0
	Average NPL/API	4.0	

5/3/92	Scan Number		(24)	(25)	(26)
Position D					
Times:					
15.17-15.28(24)	API		34	43	43
15.29-15.37(25)	NPL		268	194	200
15.38-15.46(26)	NPL Blender		90	85	70
	NPL Background		11	11	11
	NPL Tanks		167	98	119
	NPL/API		4.9	2.3	2.8
	Average NPL/API	3.3			

5/3/92	Scan Number		(27)	(28)
Position E				
Times:				
16.09-16.20(27)	API		23	24
16.23-16.35(28)	NPL		111	88
	NPL Blender		49	33
	NPL Tanks		62	55
	NPL/API		2.7	2.3
	Average NPL/API	2.5		

TABLE 3
(Continued)

5/3/92	Scan Number		(29)
Position F Times: 17.37-17/44(29)	API		4
	NPL (measurements more uncertain)		31
	Average NPL/API	7.7	

LIST OF FIGURES

Figure 1


ATMOSPHERIC MONITORING UNIT
DEPARTMENT OF TRADE AND INDUSTRY
NATIONAL PHYSICAL LABORATORY
LONG VEHICLE
LONG VEHICLE
C460 DGS

Figure 2

Arrangement for Flux Measurement Using DIAL

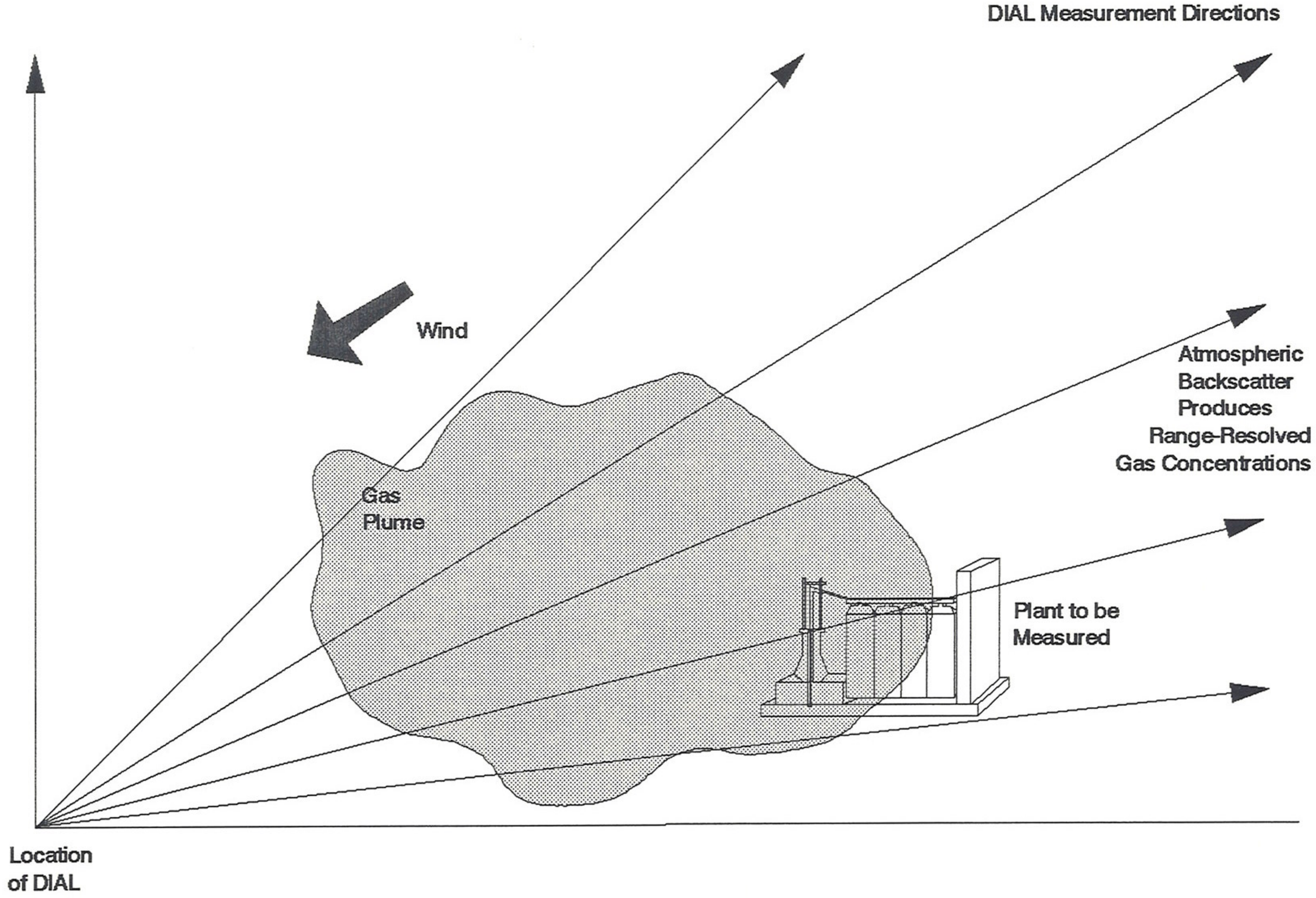

Figure 3

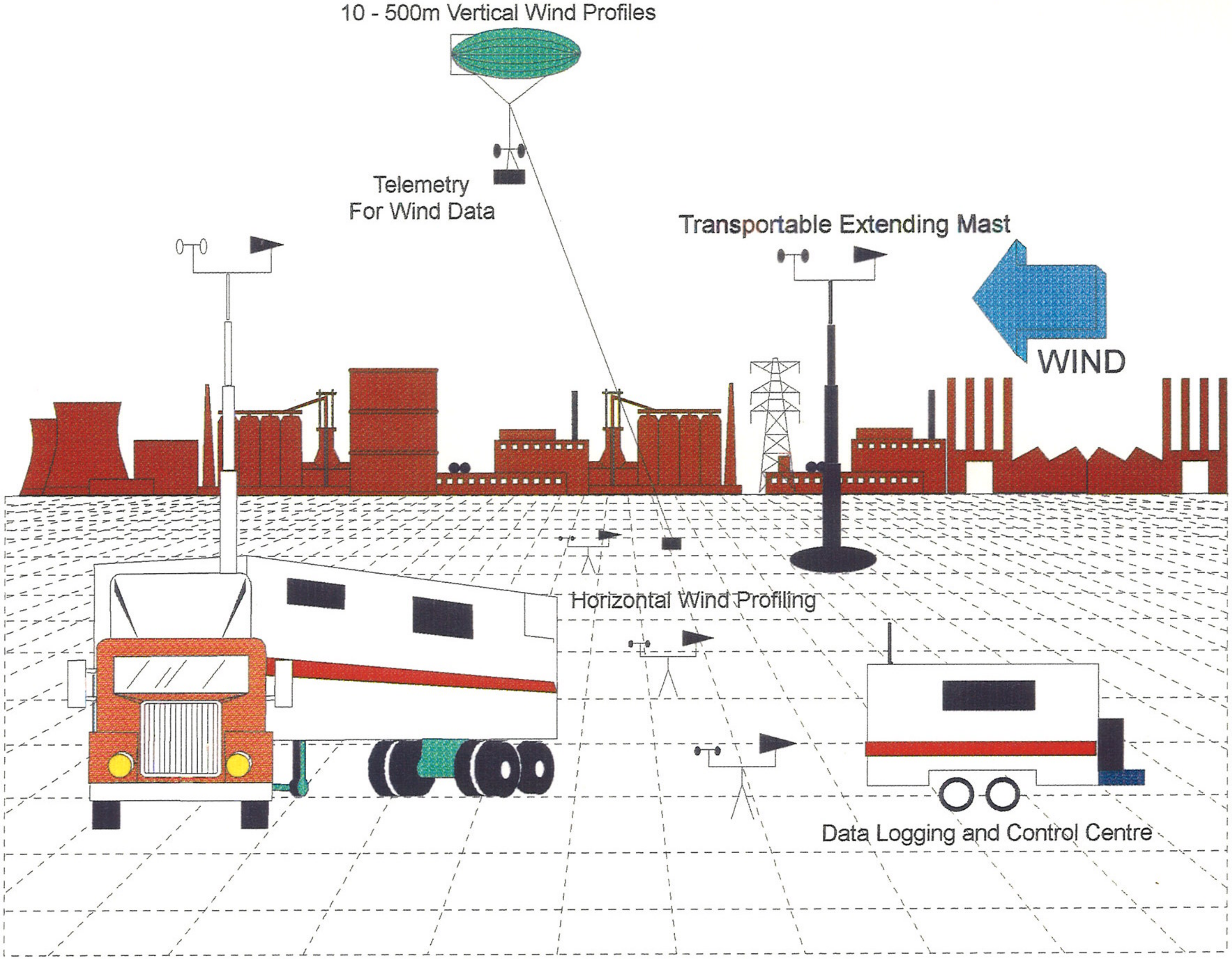
10 - 500m Vertical Wind Profiles
Telemetry
For Wind Data
Transportable Extending Mast
WIND
Horizontal Wind Profiling
Data Logging and Control Centre

Figure 4

Stanlow Site Layout

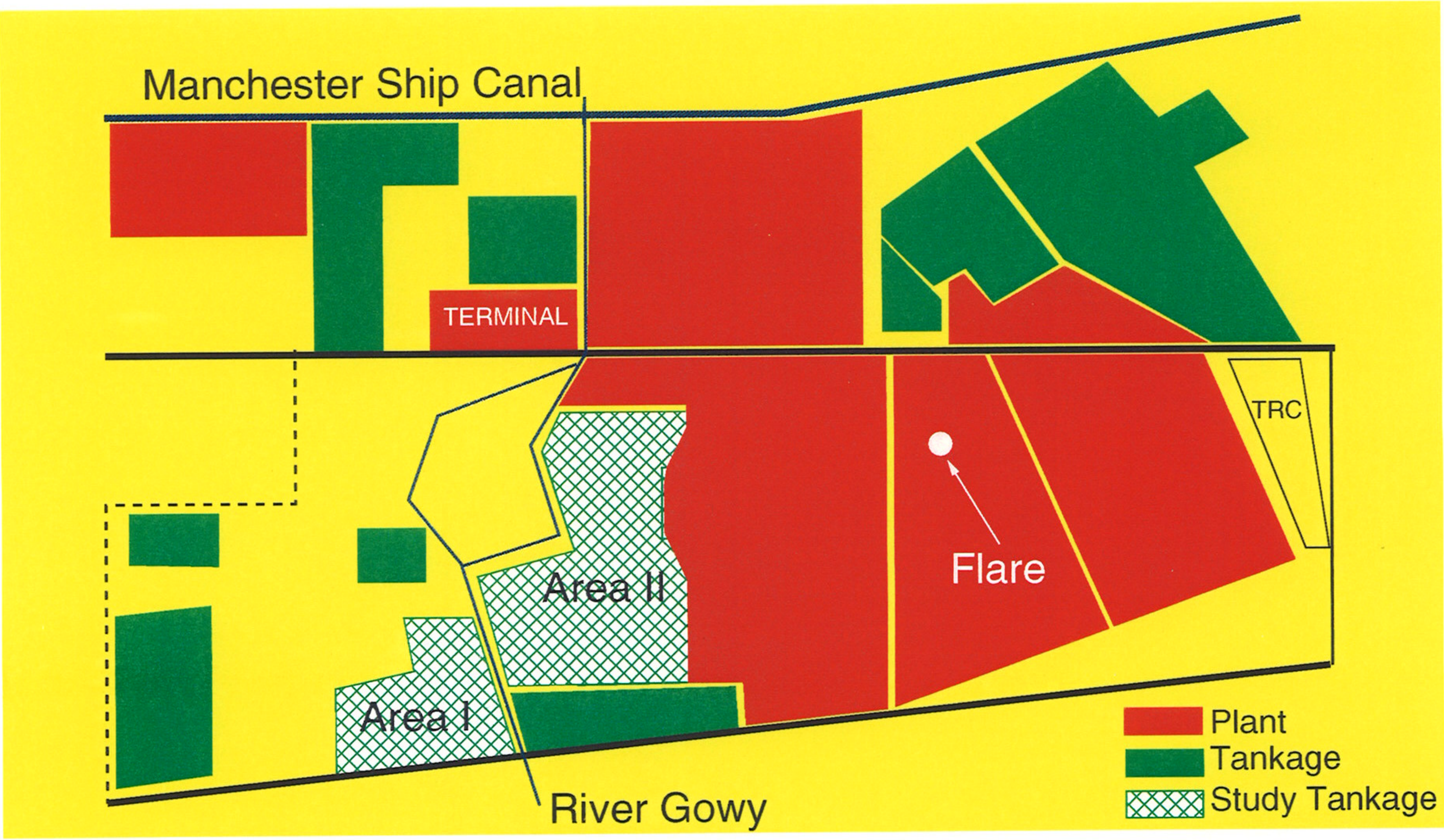

Figure 5

DIAL Locations A and B

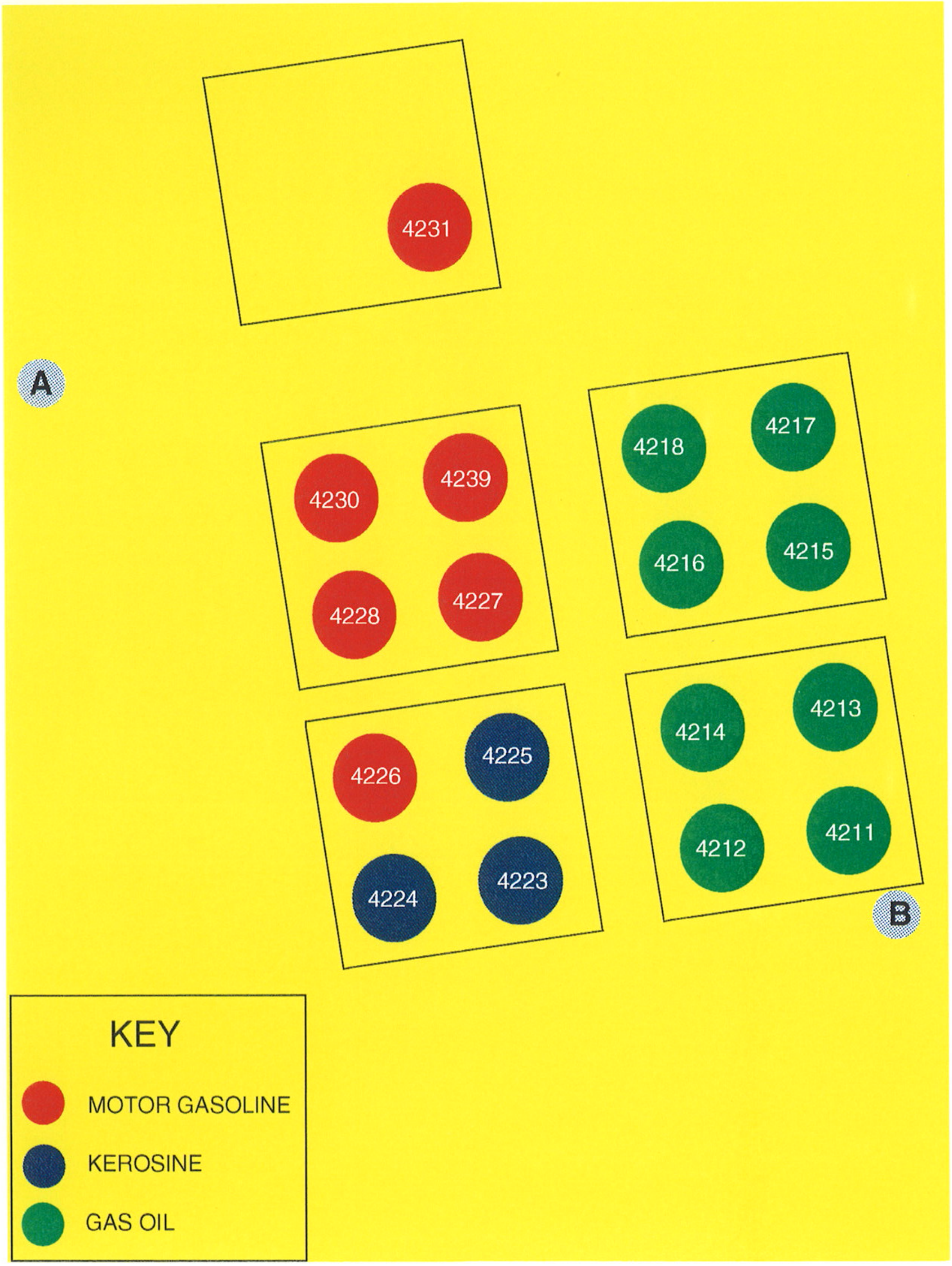

Figure 6

DIAL Locations C-H

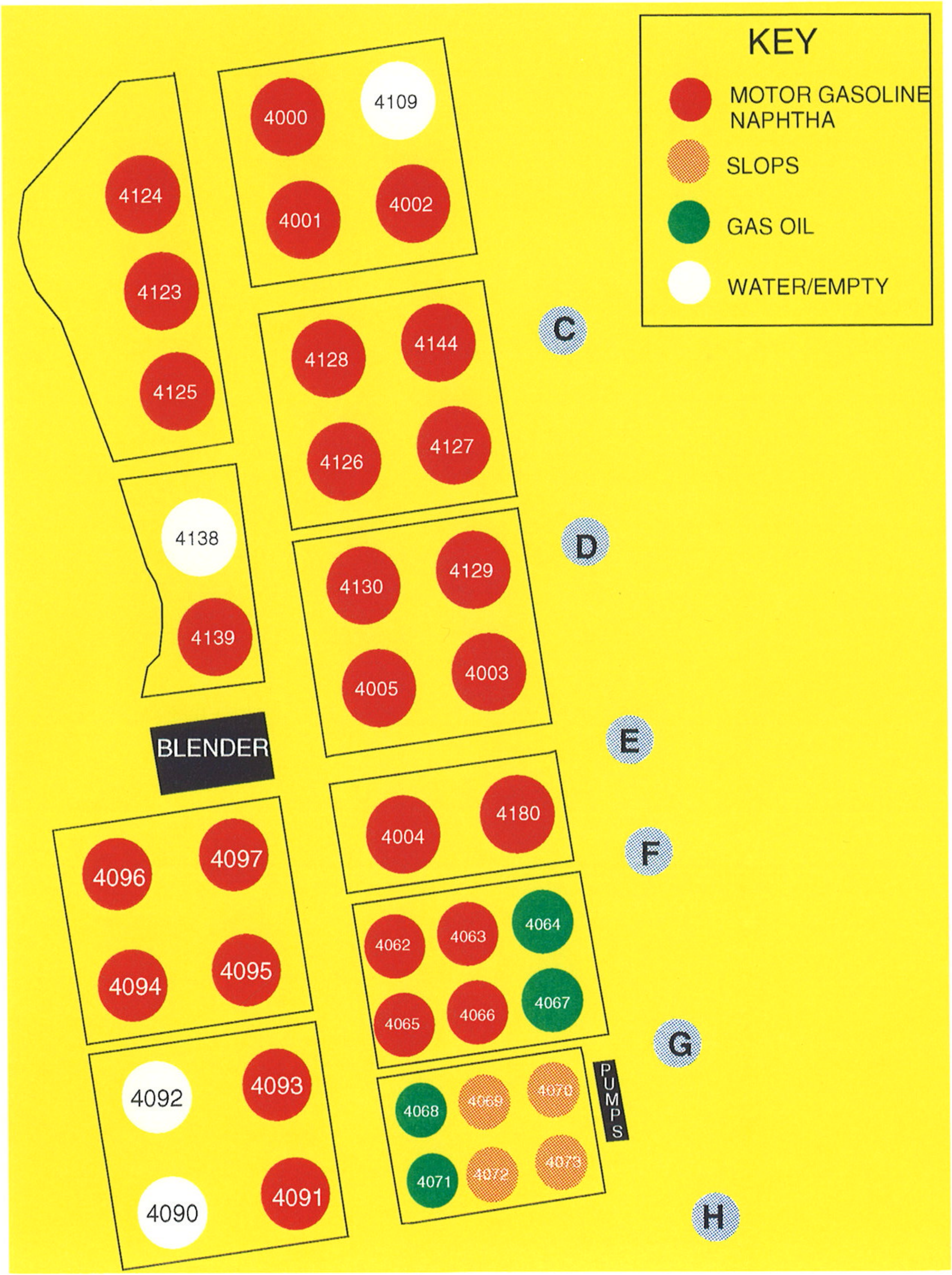

Figure 7

Summary of Sources & Results Area I (1)

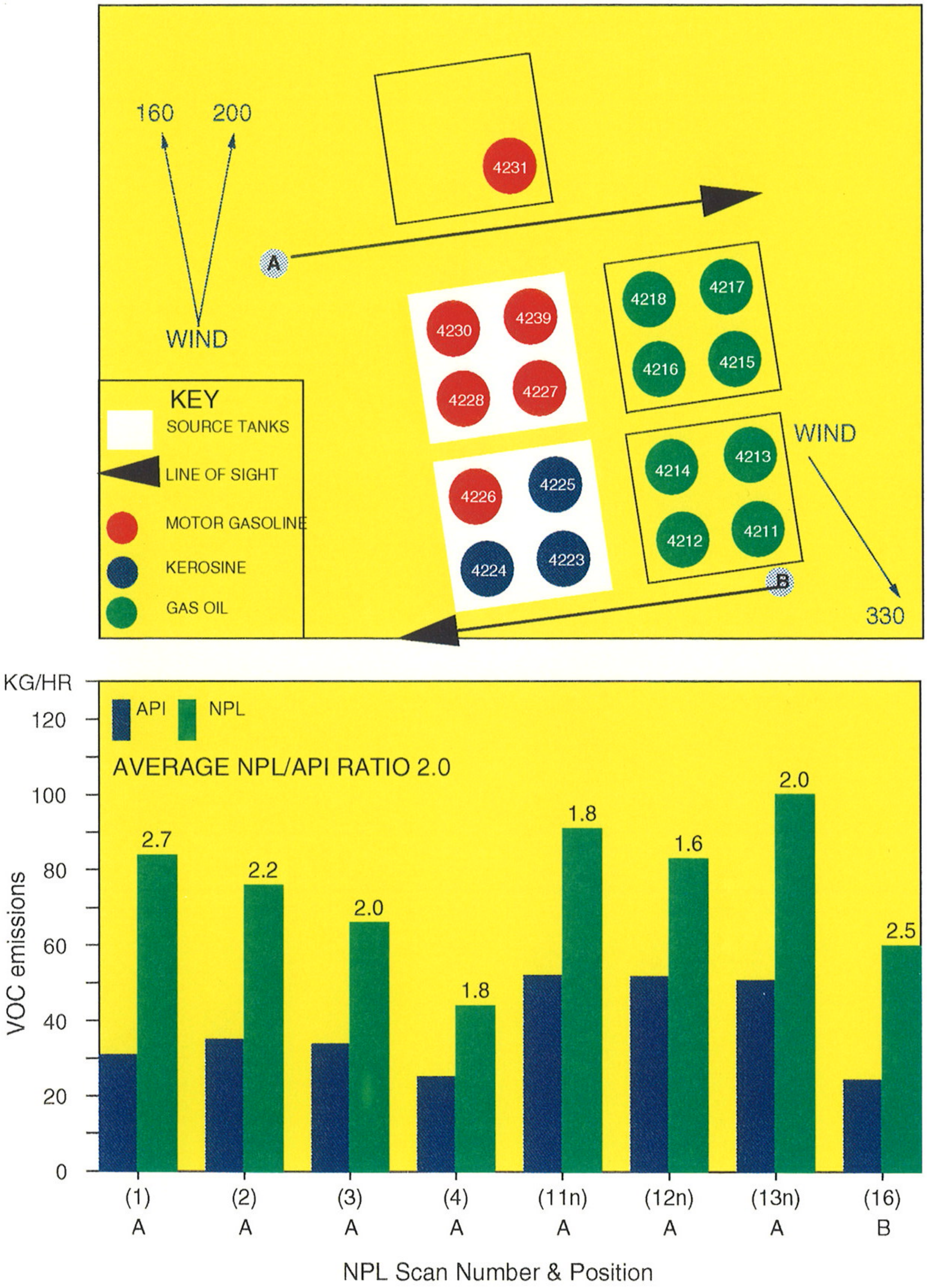

Figure 8

Summary of Sources & Results Area I (2)

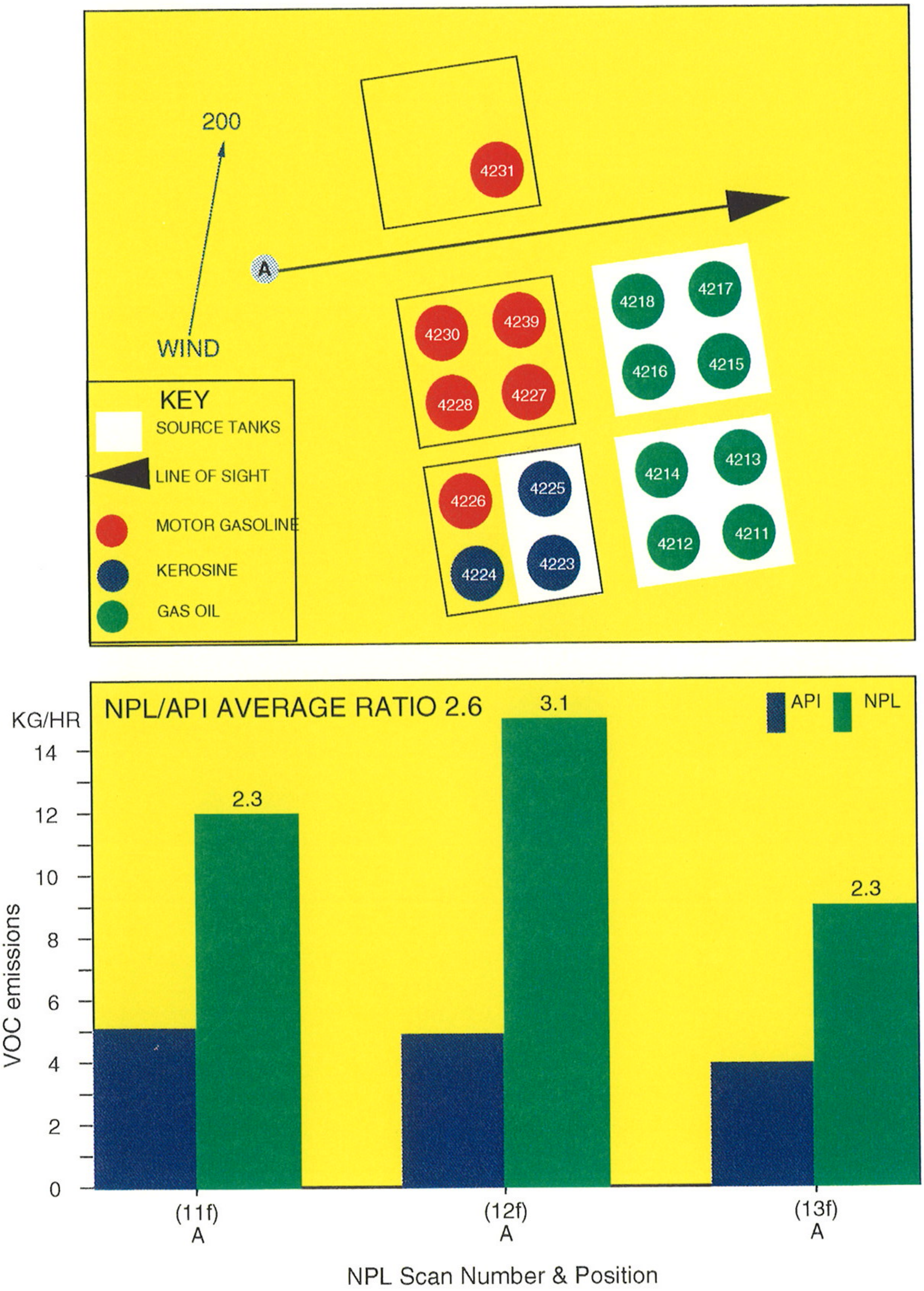

Figure 9

Summary of Single Tank Measurement

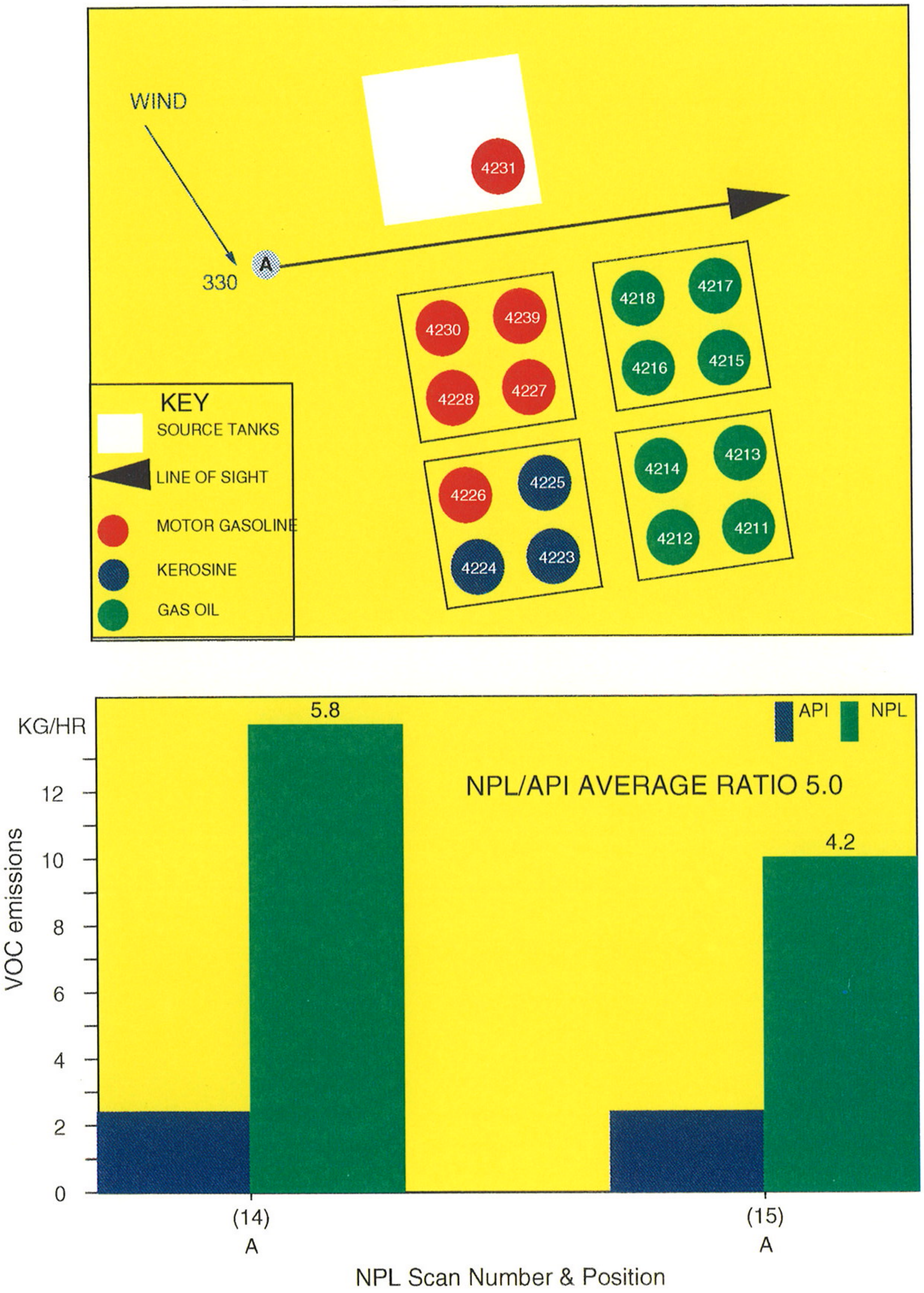

Figure 10

Summary of Sources & Results Area II (1)

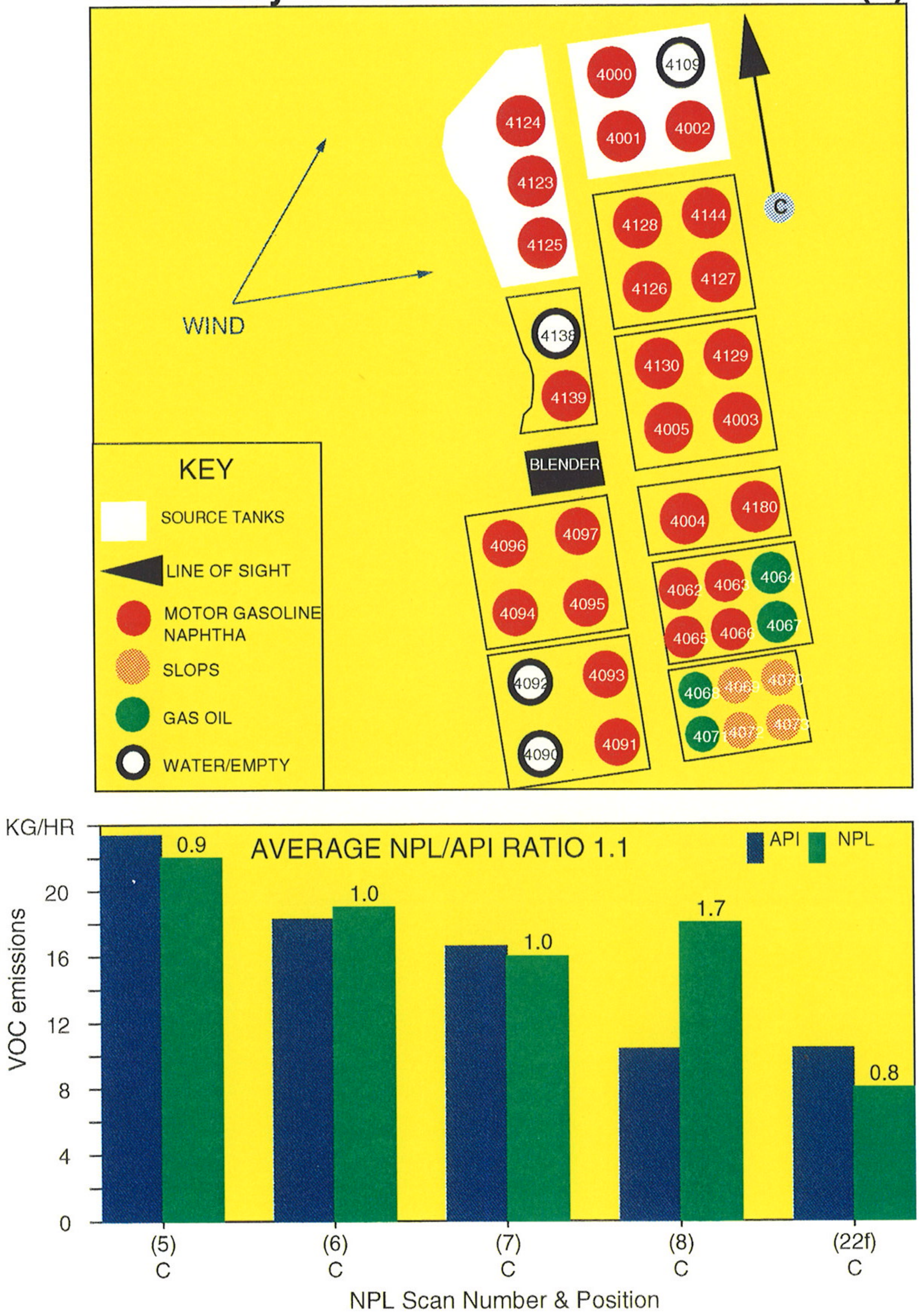

Figure 11

Summary of Sources & Results Area II (2)

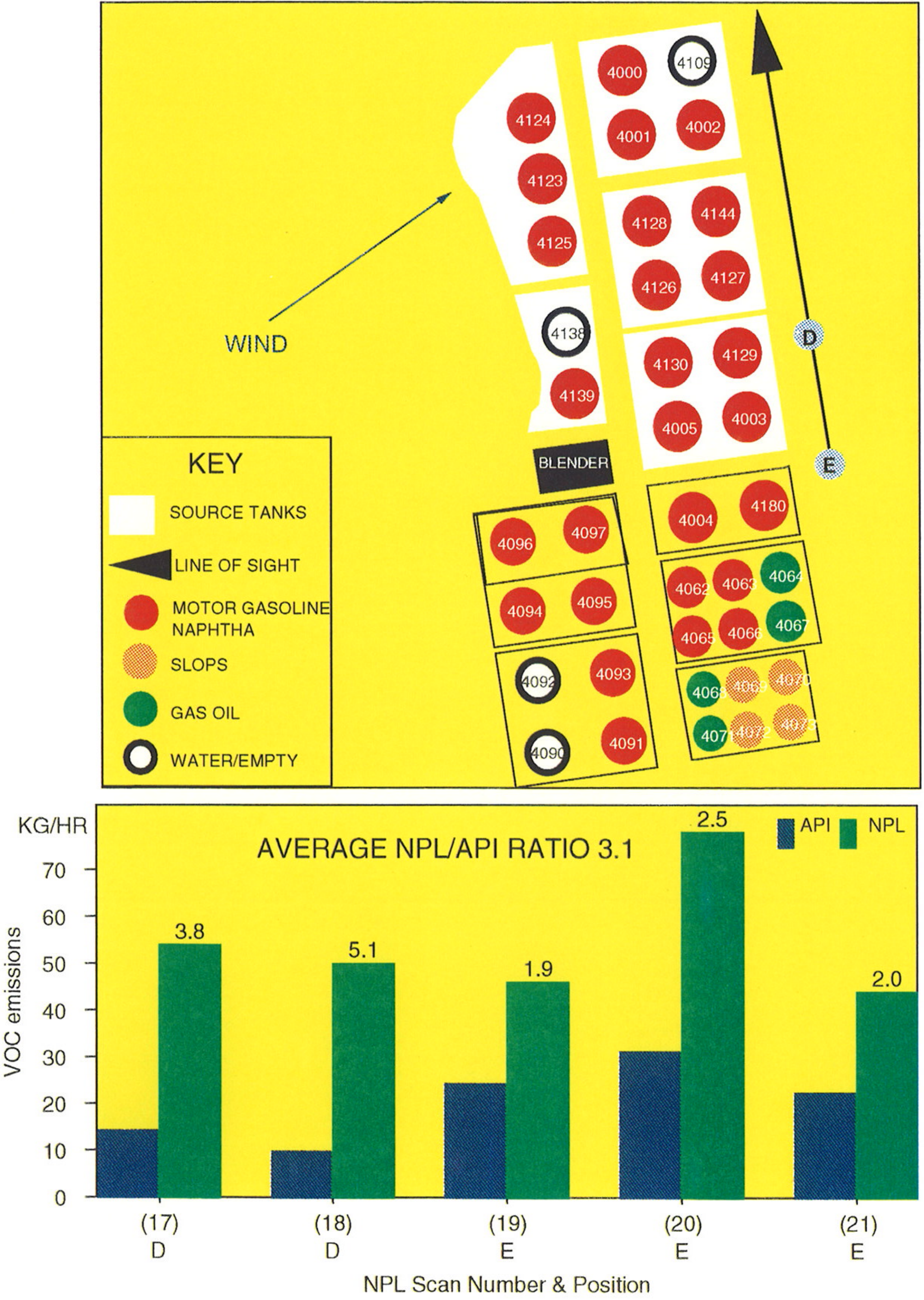

Figure 12

Summary of Sources & Results Area II (3)

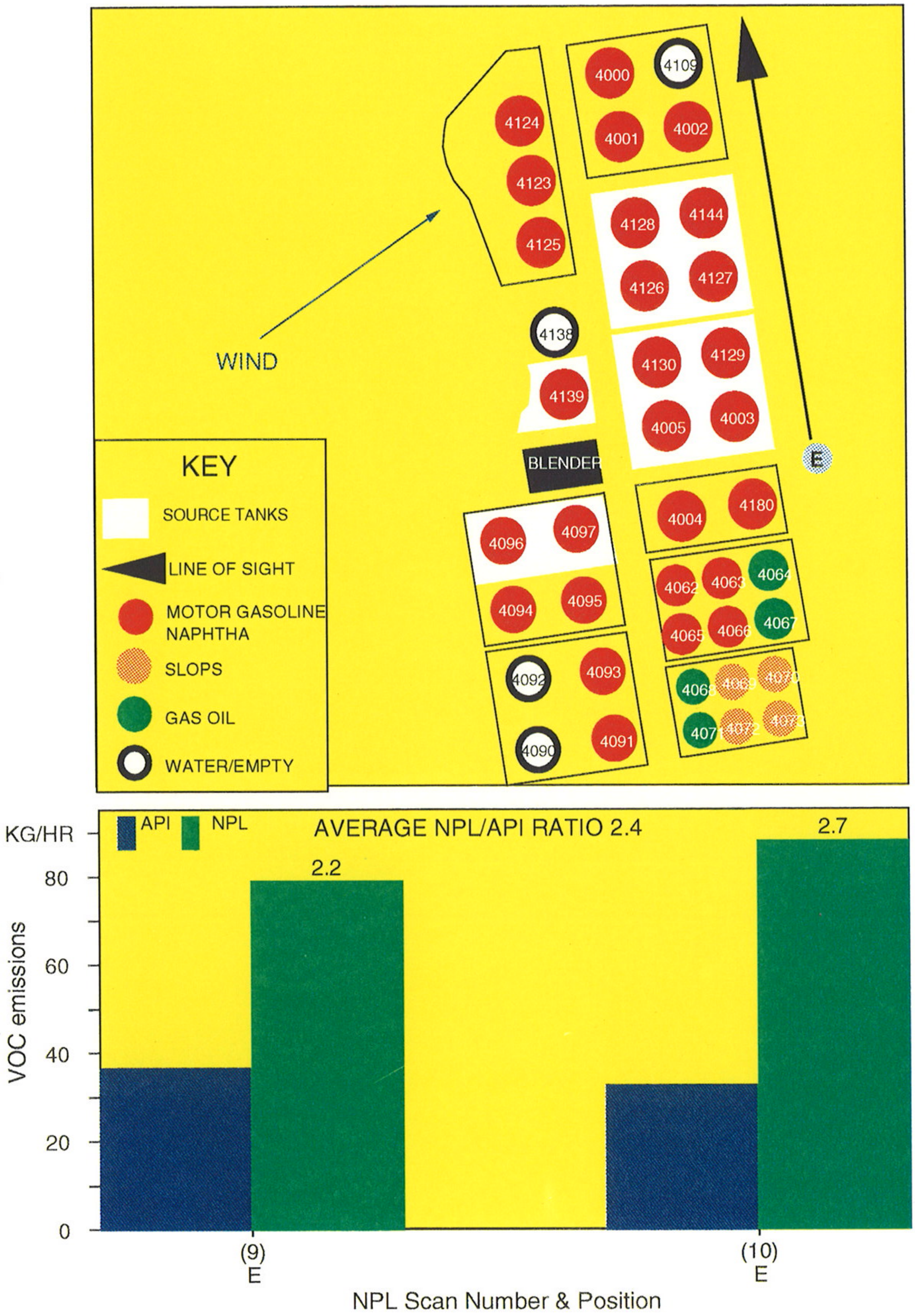

Figure 13

Summary of Sources & Results Area II (4)

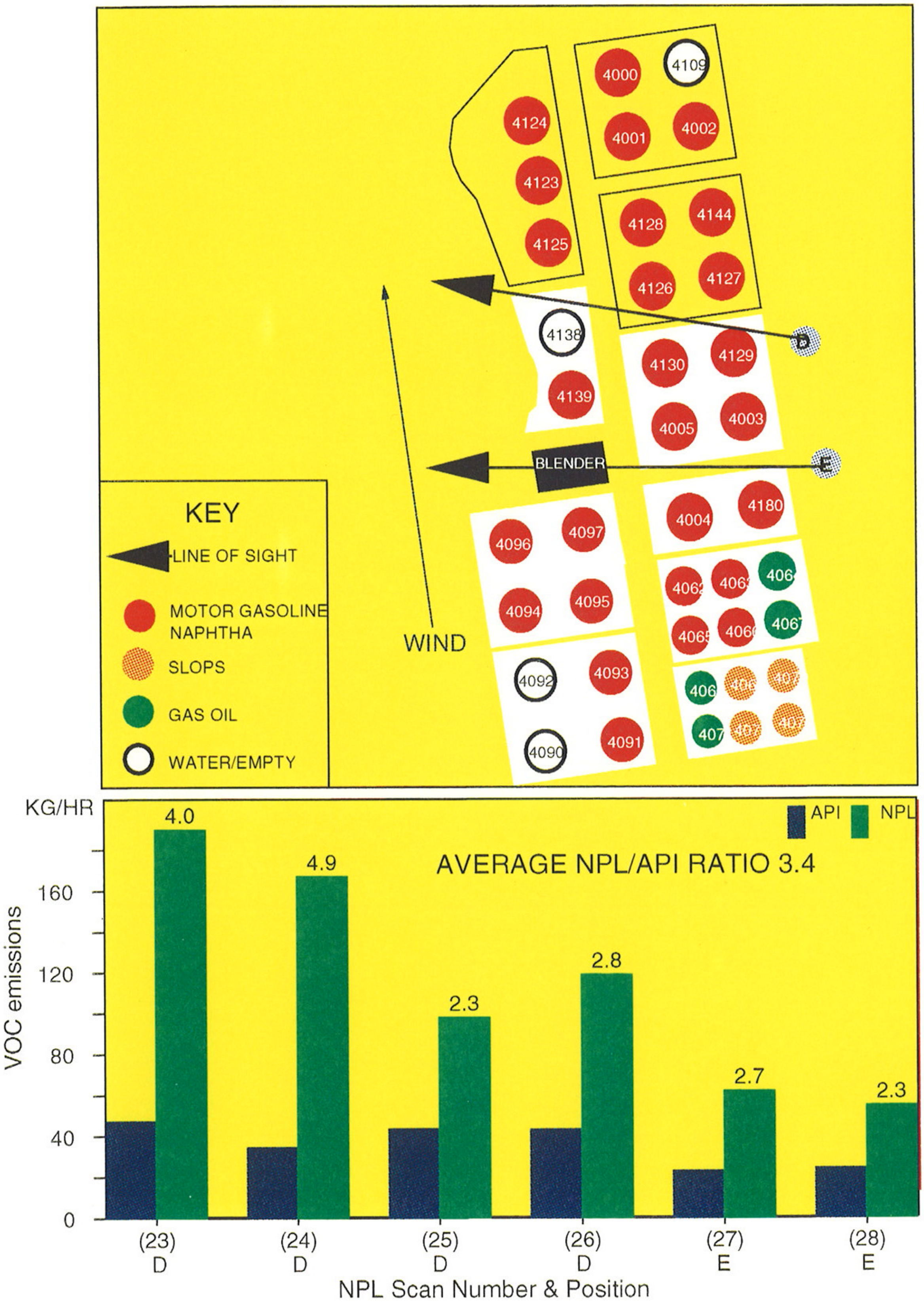

Figure 14

Summary of Results

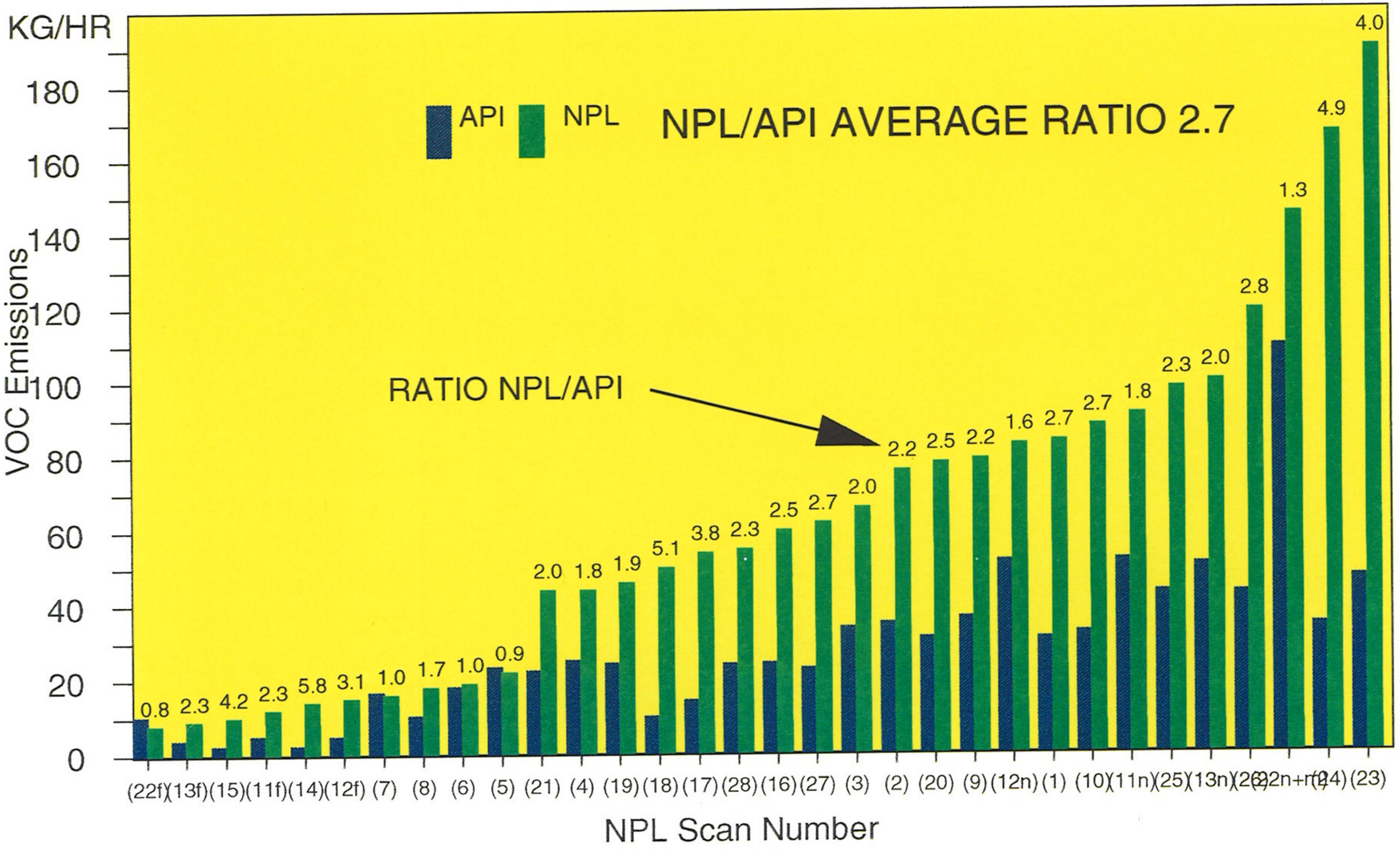

Figure 15

Distribution of NPL/API Factors

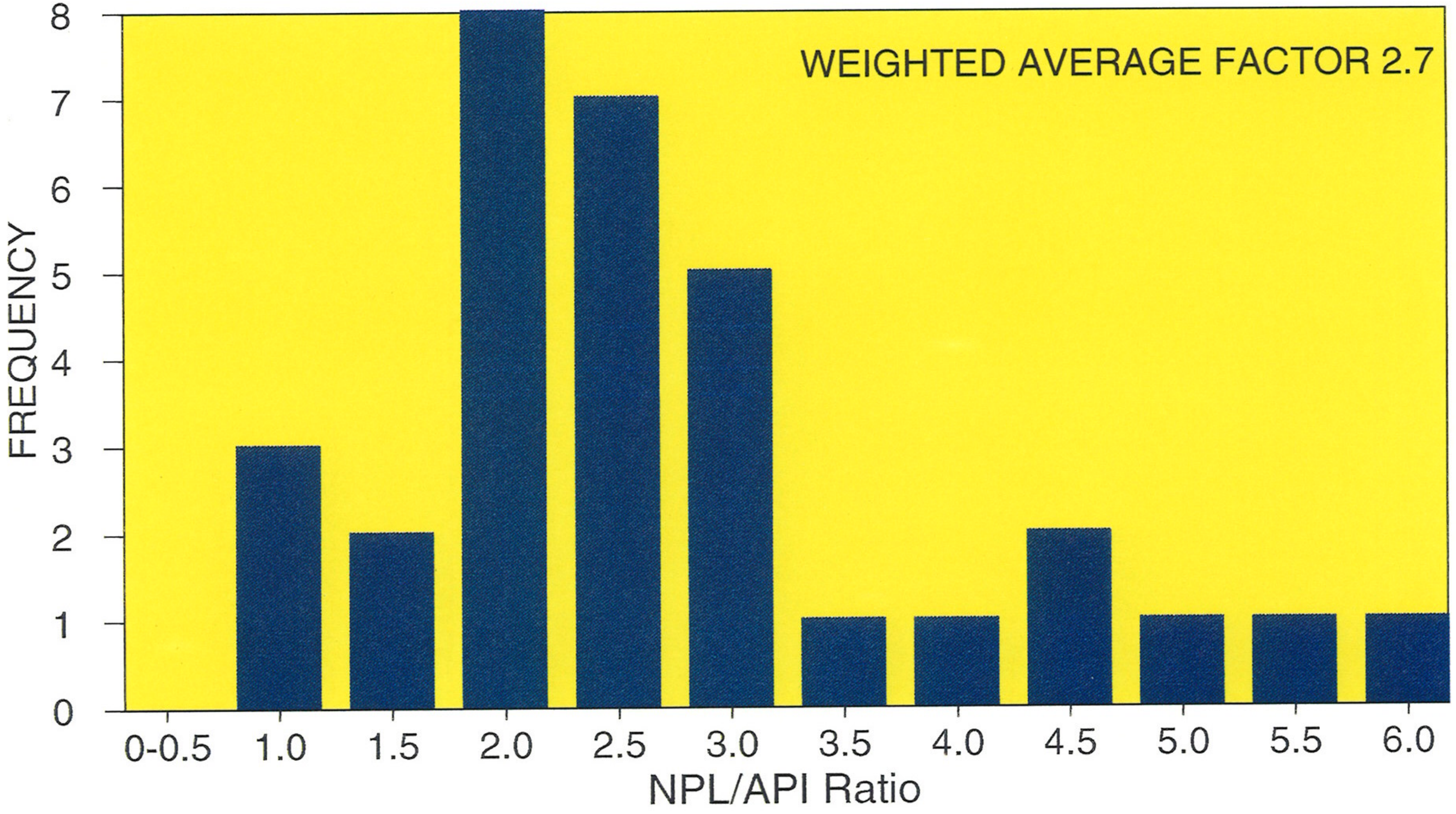

Figure 16

Figure 17: Comparison of NPL/API Ratio with NPL Measured Emissions