NPL Report QM108

National Physical Laboratory

Measurements at a Chemical Works to improve the UK Emission Inventory of Volatile Organic Compounds for the Petrochemical Industry

by

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ISSN 1361-4045

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MEASUREMENTS AT A CHEMICAL WORKS TO IMPROVE THE UK EMISSION INVENTORY OF VOLATILE ORGANIC COMPOUNDS FOR THE PETROCHEMICAL INDUSTRY

EXECUTIVE SUMMARY

1. Background

This Report forms part of a larger programme of research which has been commissioned by the Department of the Environment to establish an accurate inventory of the emissions of volatile organic compounds to atmosphere in the United Kingdom. The Report presents the results of a collaborative measurement exercise carried out by scientists from the National Physical Laboratory (NPL) and from the Shell Research Ltd, at the Shell Carrington Manufacturing Complex.

The emissions of volatile organic compounds to atmosphere from the oil and petrochemical industries have traditionally been estimated using industry-standard procedures which are based on methods prescribed by the United States of America Environmental Protection Agency and the Synthetic Organic Compounds Manufacturing Industry, an association of industrial companies manufacturing organic chemicals in the USA. However, although they are used throughout the industries concerned, there is some recognition within these industries that these procedures may not always provide valid estimates of the actual emissions from a particular petrochemical process.

Recently other methods have become available for determining the emissions of gaseous species which are emitted fugitively by industrial sites. These are remote, open-path optical techniques which can be employed for direct measurements of gaseous emissions. One of these, a differential-absorption lidar (DIAL) facility, has been developed by the National Physical Laboratory (NPL). The infrared DIAL technique is the most appropriate method for making direct measurements in the atmosphere downwind of complex industrial plant, since this produces emissions to atmosphere from a large number of small sources at different elevations and locations within a large, relatively inaccessible area. This DIAL facility was used during the measurement exercise at the Shell Carrington Works in order to obtain more accurate results than currently available in the UK Emission Inventory of Volatile Organic Compounds, and to compare the measured results with those predicted by the industry estimation procedures.

2. Objectives of the Project

The objectives of this collaborative NPL and Shell project were:

i) To measure the fluxes of VOCs emitted to atmosphere from the polyethylene plant under normal operating conditions, using the NPL DIAL facility.

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

iii) To measure the fluxes of VOCs from the polystyrene plant and the associated pentane storage tanks on site and to quantify, as far as practical, the total losses of pentane vapour which occurred to atmosphere during this process. These included losses which took place during the delivery by road tankers of liquid pentane to the storage tanks.

iv) To analyse the measured results in order to provide the fluxes of VOCs emitted by the industrial processes, and thereby assess their potential contributions to the UK emission inventory.

v) To carry out further measurements on one of the polyethylene process plants, in order to provide the required data for calculating VOC emissions using the industry-standard procedures.

vi) To compare the fluxes measured by the DIAL facility with those determined using the industry estimation procedures, in order to assess the accuracy of these procedures, and to facilitate the application of the measured results to other UK sites with similar characteristics.

vii) To measure, as far as practical, methane and non-methane VOC emissions from an industrial flare at the Carrington Works which arise from incomplete combustion by the flare of the gaseous feedstock.

3. Results of the DIAL measurements

Measurements were carried out at the Carrington site using the NPL DIAL facility during a ten-day period. Table S1 summarises the results obtained for the average emissions from each area of the plant, and the range of results obtained. These are derived from the daily means of the VOC emissions measured by the DIAL facility.

Table S1: Summary of VOC Emissions Measured by the DIAL Facility

Source	Target Species	Emission Flux (kg/hr)	Range (kg/hr)	Emission Flux Equivalent (t/a)	Range Equivalent (t/a)	Measured emissions as percentage of throughput
Polyethylene Plant and Storage Warehouse	Ethylene	60	55-63	478	438-502	0.26
Polystyrene Plant and Storage Warehouse	Pentane (mainly)	18	17-20	147	138-156	4.8 (of total pentane)
Storage Tankage filling from Road Tanker	Pentane (mainly)	7.3 kg per load	-	-	-	0.04* 0.04**
Flare	Methane/ propylene	not determined	-	-	-	≤ 2

* Based on 1993 figures for the total pentane delivered during the year
** Based on 3 deliveries/week

The above Table also shows the annualised emissions, which would occur from the complete plant monitored during this project. These are based on the assumption that the hourly values for the hydrocarbon emissions can be scaled linearly to annual values (with a 91% plant utilisation rate which was considered realistic by Shell Carrington personnel). An estimate has also been made, where possible, of the measured loss as a percentage of throughput of the operation.

The following conclusions may be drawn from the measured results:

a) The best estimate of the total ethylene emissions from the complete polyethylene plant is 60 kg/hr. This is equivalent to an annual emission rate of 478 tonnes per year. There were two processing units within the plant which contributed to this.

b) When the results of daily averages are taken into account, the measured total emissions were in the range 55-63 kg/hr, which is equivalent to 438-502 tonnes per year.

c) The results include the fugitive emissions from the two process plant and the emissions from vents to atmosphere on the plants and on the associated product storage bunkers.

d) The total losses of ethylene from the whole of the polyethylene plant, including storage bunkers, are equivalent to 0.26% by mass of total ethylene throughput.

e) The losses of ethylene emitted fugitively from the new polyethylene plant alone were equivalent to 0.18% of its' throughput. The losses from the older polyethylene plant were equivalent to 0.36% of throughput. These exclude the emissions from the polyethylene storage bunkers, which correspond to 0.02% of throughput.

f) The majority of the emissions emanated from high-level sources, which included the vent stacks. There were, however, significant emissions from the old plant at lower levels than these vents.

g) The average value for the emissions (mainly pentane) around the polystyrene plant and the principal storage warehouse were 18 kg/hr. This is the equivalent of 147 tonnes per year. However, this annualised figure may be inaccurate due to the fact that this is a batch, rather than a continuous, preparation process for polystyrene. Most of the emissions were from the vent stacks at high elevations.

h) The losses of VOCs (mainly pentane) to atmosphere during filling of storage tanks from a road tanker were measured to be 7.3 kg during transfers of 17 tonnes. This represents a loss of 0.04%.

i) Very low concentrations of hydrocarbons were observed in the industrial plant flare. The flare combustion efficiency for these hydrocarbons was estimated to be $\geq$ 98% during the period of the tests.

4. Results of Industry Estimation Procedures

Four industry-standard procedures have been published by the United States Environmental Protection Agency (EPA) and Synthetic Organic Compound Manufacturing Industry (SOCMI). These require an inventory to be made of all the potentially leaking components within a given petrochemical process plant. Three of these procedures then require measurements to be made of the concentrations of gaseous VOCs around these potentially leaking components using simple *in-situ* instruments. EPA/SOCMI-prescribed formulae are then used to translate these measured concentrations into emissions (by mass) of VOCs from all the components of the plant.

A set of measurements were made, using two types of *in-situ* instruments, of the concentrations of VOCs around the valve and flange components of one of the two processing units (LDPE-3) of the Shell Carrington Complex. These have performance characteristics within EPA specifications (Foxboro OVA model 108 and Thermo Electron model HVM 680). The results of these measurements were used with the EPA/SOCMI procedures to produce estimates of the VOC emissions to atmosphere from the measured valves and flanges in this unit. The results obtained are shown in Table S2. Two different sets of results are presented, obtained using the two types of instrument. Calculations were also performed to define the overall uncertainties in these estimates. These are shown in Table S2, expressed as lower and upper emission limits (95% confidence level).

Table S2: Emissions from Measurement Valves and Flanges of LDPE-3 Plant Estimated by API/SOCMI Procedures

	Estimation Procedure (tonnes/year)					
Instruments used	Leak/ no leak	Stratified	Correlation	Lower emission limit (95% confidence)	Upper limit (95% confidence)	Average emission factor
OVA	14	12	14	2.5	50	23
HVM	2.6	4.3	6.3			

The results shown in Table S2 have also been scaled up to produce an estimate of the total fugitive emissions from this process plant, including the emissions from those components which were not sampled because they were inaccessible to the *in-situ* measurements. These results are shown in Table S3. The overall uncertainties in these emission estimates were also calculated. These are shown in Table S3, expressed as 95% lower and upper confidence limits.

Table S3: Estimated Total Annual Emissions from the LDPE-3 Plant

	Estimation Procedure (tonnes/year)					
Instruments used	Leak/ no leak	Stratified	Correlation	Lower limit (95% confidence)	Upper limit (95% confidence)	Average emission factor
OVA	36	27	36	6.4	124	56
HVM	9.1	9.1	18			

The following conclusions may be drawn:

a) The VOC emissions determined by the industry procedures from the valves and flanges measured within the LDPE-3 plant (73% and 11% respectively of the totals) are in the range 1.5-2.9 kg/hr, with a best estimate derived from the OVA measurements of 1.6 kg/hr. This is equivalent to an annual emission rate of between 12 t/a and 23 t/a, with a best estimate of 13 t/a (assuming 91% plant utilisation).

b) The uncertainties in the emission estimates have been calculated statistically in this Report to provide upper and lower limit values for the emissions (95% confidence level). These correspond in the case of the measured valves and flanges to the range 0.32-6.3 kg/hr. This is equivalent to the range 2.5 t/a to 50 t/a.

c) The total fugitive emissions from the LDPE-3 process plant, obtained by scaling up the above results, are in the range 3.4-7.1 kg/hr, with a best estimate of 4.6 kg.hr. This is equivalent to an annual emission rate of between 27 t/a and 56 t/a, with a best estimate of 36 t/a.

d) The uncertainties in the emission estimates of the total fugitive emissions have been determined by scaling up the statistically-calculated lower and upper limits of the measured emissions from this plant. These covered the range 0.8-15.5 kg/hr. This is equivalent to the range 6.4 t/a to 124 t/a.

e) The *in-situ* VOC measurements, which were employed as inputs to the EPA/SOCMI procedures were carried out with one instrument (OVA model 108). Similar measurements made with a different instrument (Thermo Electron model MVM6 80) generally produced results which were about 2 to 5 times lower in concentration value. However, both types of instrument conform to the specifications given by the United States Environmental Protection Agency.

f) The uncertainty estimates arise partly from the original EPA/SOCMI estimation procedures, and partly from the procedure adopted during this measurement exercise. The EPA/SOCMI emission factors and other parameters are derived for each type of component from a few hundred measurements. This could give rise to uncertainties of at least a factor of three. Further uncertainties were introduced in this measurement exercise because it was not possible to sample all the components of the process plant. These latter uncertainties were estimated to be about a further factor of five. It is important that the uncertainties in the emission rates that arise from these and other factors should be assessed thoroughly by all users of the EPA/SOCMI methodology.

5. Comparisons of the Results obtained using the Dial Technique and the Industry Procedures

Comparisons may be made between the measured emissions from the LDPE-3 polyethylene processing plant determined by the DIAL facility, and those obtained using the industry procedures for the same plant. The total fugitive emissions measured by the DIAL techniques (Table S1) included those produced by valves and flanges on the plant and those produced by high-level vents which were inaccessible to *in-situ* measurements. The industry procedures provided estimates of the emissions from the measured valves and flanges (Table S2) and by extrapolation, the emissions from the complete LDPE-3 plant (Table S3). The following comparisons may be made:

(i) The estimate obtained by the DIAL technique of the emissions from the valves and flanges measured for the EPA/SOCMI procedures on the plant is in the range 13-35 tonnes per year, with a best estimate of 25 tonnes per year. The EPA/SOCMI procedures, based on the *in-situ* measurements of valves and flanges, gave emissions of about 13 t/a. The DIAL measured emissions were therefore about 1.9 times higher than those determined using the industry procedures for this plant.

(ii) The DIAL results are within the range of uncertainty calculated for the industry procedures (2.5-50 t/a).

(iii) The total emissions from the LDPE-3 plant measured by the DIAL technique (excluding the degassing bunker vents) was 27 kg/hr (212 t/a). The result obtained by extrapolating the industry valve and flange emission estimates to the complete process plant was 4.2 kg/hr (33 t/a). The DIAL measured emissions are therefore about 6 times higher than those obtained using this procedure.

(iv) The DIAL measured results for the complete LDPE-3 plant are a factor of 1.7 higher than the upper confidence limit (124 t/a) calculated from the industry procedures.

(v) From the results presented here, it is likely that these industry estimation procedures could produce systematically low emission estimates when used in the United Kingdom for these industrial applications.

6. Contribution to the UK VOC Emission Inventory

The total UK production of all types of polyethylene is currently 460 ktonnes per year, with about 40% being the low density type manufactured by the Shell Carrington Complex. The

VOC emissions to atmosphere, measured by the DIAL technique, from both the Shell processing plant and the storage facilities, correspond to 0.26% of the ethylene throughput. Using this factor, an estimate can be made of the total VOC emissions to atmosphere from all UK polyethylene processing plant. This corresponds to 1200 tonnes per year.

The DIAL and whole-air sample measurements, and the other loss estimation methods (including mass balance and vent emission measurements) carried out at the Shell Carrington Complex, indicated that similar emissions occured for the polypropylene processing plant, as a percentage of throughput. If this is the case elsewhere in the UK, an estimate can be made of the contribution from polypropylene processing to the UK VOC Emission Inventory. The annual UK production of polypropylene is 420 ktonnes per year. The estimated VOC losses from this correspond to about 500-1000 t/a.

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1 BACKGROUND

The work described in this Report forms part of a larger programme in which the UK's Warren Spring Laboratory, (now integrated into the National Environmental Technology Centre), was commissioned by the Department of the Environment to establish an improved UK inventory of VOC emissions.

Photochemical pollution, particularly ozone, is formed in the atmosphere near ground level by reactions of volatile organic compounds (VOCs) with nitrogen oxides in the presence of solar radiation. Atmospheric ozone, when present at high concentrations 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 of ozone. However, as ozone is a secondary pollutant, this is not straightforward. Nonetheless, there is now considerable scientific evidence to support the predictions made by atmospheric models, 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, twenty countries signed a Protocol which is designed to limit the emissions to atmosphere of volatile organic compounds. Under this Protocol, the UK has agreed to bring about 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 emissions of VOCs;
- to investigate the effectiveness of methods of control and abatement.

Two industrial sectors are believed to make the most significant contributions to the total emissions of non-methane VOCs to air in the UK, in addition to those produced by automobiles and the solvents industry. These are the oil refinery and petrochemical industries. For the purpose of this Report, the oil refinery industry is defined as covering those industrial sites where crude oil is used as the feedstock for various processes to produce, for example, gasoline, kerosine, diesel fuel, fuel oil etc. It also provides a variety of feedstocks to the petrochemical industry. The petrochemical industry is defined as covering all the different types of industrial plant which take the products of the oil refinery industry, to manufacture other chemical compounds such as plastics etc. One part of the petrochemical industrial sector is the subject of this Report.

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

(a) Fugitive emissions which occur from processing plant, used to blend VOCs or to react different VOCs to produce different products, mainly from the very large number of valves, flanges, joints etc that are present. These may be emitted directly to atmosphere, or collected from the individual sources and then released to atmosphere through vents which are usually located at high elevations.

(b) Filling and standing emissions which occur from storage tanks and other storage media used to contain the liquid feedstocks and the intermediate and finished products. These contain hydrocarbons with widely differing volatilities ranging, for example, from bitumen, fuel oil and gasoline, to low molecular-weight alkanes, alkenes and alkynes, and liquid natural gas.

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

(d) Emissions which arise from waste-water treatment plants, where these are present. In these, liquid organic compounds and water, previously intermixed during the various processing operations, are separated using a range of methods. Gaseous hydrocarbons are emitted fugitively both during their transport to the treatment plant, and during this separation process.

(e) Emissions which arise from the unloading of raw materials at oil refineries and petrochemical plant, and from the loading of hydrocarbon products into containers to 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), (b) and (e). However, 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 of combustion efficiency vary from 75% to greater than 99%. However, the frequency of industrial flaring varies considerably from site to site, and their use is generally decreasing and now usually only occurs during industrial plant malfunctions. Nevertheless, it may be necessary to establish more accurately their contribution to the UK VOC emission inventory in future.

Estimates of the emissions to atmosphere from processing plant and from storage tanks are prepared and reported by the industries concerned. The gaseous emissions produced by processing plant in the oil and petrochemical industries are generally estimated using statistical analysis procedures, based on factors prescribed in the United States of America by the Synthetic Organic Compound Manufacturing Industry (SOCMI) and the Environmental Protection Agency [5]. These are derived for various industrial plants by carrying out detailed counts of equipment including valves, flanges, joints etc and then applying representative emission factors for each class of these sources. The methodologies for estimating storage tank emissions are published by the American Petroleum Institute (API). The European oil industry has for some time estimated the emissions produced by processing plant and 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 [6]. These draw on the methodologies noted above, which were produced in the USA. However, there has been some recognition in the industries concerned that these methods may not always provide accurate estimates of the actual emissions. In addition, it is possible to apply these procedures in different ways and this can lead to different emission estimates. This is particularly true of those used to calculate fugitive emissions from processing plant.

Recently, other methods have become available for determining the rates of emissions (ie the fluxes), of a range of gaseous species, including methane and other VOCs, which are emitted fugitively by industrial sites [7]. 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 for determining fugitively-emitted fluxes 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, EPA and other empirical methods. A summary of the operating principles of the DIAL technique is given in Section 4.2. The methodology for using the technique to measure the fluxes of gaseous pollutants emitted by industrial sites is outlined in Section 4.3.

This Report describes a measurement exercise carried out at a petrochemical site, using a DIAL facility developed by the National Physical Laboratory. This exercise had the objective of measuring directly the emissions of specific non-methane VOCs from petrochemical processing plant, storage tanks and a flare. The results of these measurements are presented.

A summary of the appropriate EPA/SOCMI VOC loss-estimation procedures, which are applied to petrochemical processes, are outlined in Section 5. A complementary set of measurements were carried out to provide data for use as input parameters to the emission calculations performed using these EPA/SOCMI procedures. The results of these measurements and the total emissions derived using the EPA/SOCMI calculation procedures are also presented.

The results obtained from the DIAL measurements are compared with those determined using the EPA/SOCMI procedures. Some of the limitations and advantages of the DIAL and EPA/SOCMI procedures are also outlined.

The contribution that the emissions from this petrochemical process make to the total UK Emission Inventory of volatile organic compounds is also presented. Estimates are also made of the contributions of similar industrial processes.

2 OBJECTIVES OF THE MEASUREMENT EXERCISE AT SHELL CARRINGTON MANUFACTURING COMPLEX

The NPL DIAL facility was used in a measurement exercise to accomplish the following objectives:

2.1 To determine directly the fluxes of VOCs emitted to atmosphere from the polyethylene plant under normal operating conditions.

2.2 To identify, where practical, the main sources of these emissions.

2.3 To monitor the emissions from the polystyrene plant and the associated pentane storage tanks on site and to quantify, as far as practical, the total losses of pentane vapour which occurred to atmosphere from this process. These included losses taking place during the delivery of pentane to these tanks by road tankers.

2.4 To analyse the measured results in order to provide the fluxes of VOCs emitted by these industrial processes, and thereby assess their potential contribution to the UK emission inventory.

2.5 To carry out a further set of measurements on the polyethylene processing plant and use these measurements to calculate the estimated VOC emissions by industry-standard procedures.

2.6 To compare the fluxes measured by the DIAL technique with these independent estimates produced by the industry concerned, in order to assess the accuracy of the industry procedures, and to facilitate the application of the measured results to other

UK sites with similar characteristics.

2.7 To measure, as far as practical, methane and/or non-methane VOC emissions from a flare, which may be present due to incomplete combustion by the flare of the olefin feedstock.

2.8 To collaborate with the National Environmental Technology Centre, and the Department of the Environment, in order to provide additional technical expertise, with the aim of improving the accuracy of the UK VOC emission inventory relating to the chemical, petrochemical and oil refinery industrial sectors.

3 THE SHELL CARRINGTON MANUFACTURING COMPLEX

3.1 OVERVIEW

This Section provides an explanation of the operation of the Shell Carrington polyethylene processing plant, in order to provide an understanding of where process emissions could occur.

The low-density polyethylene production plant comprises two separate process plants, having a combined production capacity of about 170,000 tonnes per year. The older of the two process plant, called LDPE-2, has a nominal capacity of 65,000 tonnes per year, whilst the capacity of the newer plant, LDPE-3, is about 107,000 tonnes per year.

Both plants convert ethylene to polyethylene by using a high-pressure process in a tubular reactor. This process entails the following principal steps:-

- Compression of the ethylene gas, from 1 to 3000 bar;
- Polymerisation, at 2000 - 3000 bar and 180 - 330°C;
- Recycling of unreacted ethylene, both at high pressure (250 bar) and low pressure (0.6-3 bar above atmospheric pressure);
- Extrusion and pelletisation of the polyethylene;
- De-gassing of the granulated polymer produced.

An outline of the chemistry of this polyethylene production process, covering the process steps noted above, is given below, together with a discussion of possible process emissions to atmosphere which might occur from each stage.

3.2 PROCESS CHEMISTRY

The high-pressure polymerisation of ethylene is a very rapid, free-radical addition reaction that releases considerable heat. The reaction is started by the generation of free radicals derived from the controlled addition of traces of oxygen into the reactor feed. The polymer chains produced have a wide range of molecular weights and include variable amounts of short and long-chain branches that have important effects on the physical properties of the finished products. Both the molecular weight and the degree of chain branching of the product are strongly influenced by the controlled addition of small amounts of a "reaction moderator". Product properties are also varied by the incorporation of up to 5% of a co-monomer.

Deviations in high-pressure process conditions can potentially lead to the occurrence of an extremely rapid and highly exothermic decomposition reaction, forming carbon, hydrogen and methane. This reaction would contaminate the product and could also damage process equipment. Thus, it is necessary to control process conditions very closely and to provide a rapidly acting automated shut-down system, to prevent these detrimental reaction.

3.3 COMPRESSION OF GASEOUS FEEDSTOCK

Each plant is equipped with two large compressors.

(i) A five-stage primary compressor, which takes a gas stream comprising low-pressure recycled unreacted ethylene at about 0.3 - 2 bar above atmospheric pressure, the feedstock ethylene at about 18 bar, and the required amounts of reaction initiator and moderator, and boosts this combined gas stream to about 250 bar.

(ii) The output from this is mixed with the main flow of recycled ethylene which is at about 250 bar. It is then pressurised up to 3000 bar by a two-stage hyper-compressor of specialised design.

Pressure-relief valves are fitted to each stage of both compressors. Most of these are vented to the Works flare. The two exceptions are those which are located on the fifth stage of the primary compressor and on the first stage of the hyper-compressor. These relief valves vent directly to atmosphere because the temperature of the de-pressurised gas is below the minimum design temperature of the flare system. In addition, on the LDPE-2 plant, there is also a vent to atmosphere from the crankcase of the primary compressor that could release ethylene to air in the event of leakage of the seals of the piston rod or cylinder. The outlets of these vents are located at heights of 25 m in both plants.

The hyper-compressors are multiple-head machines. Each compression head incorporates a cylindrical plunger that reciprocates through a series of up to six mechanical seals. Each mechanical seal is located in an annular disc that is clamped against its neighbours via lapped-metal surfaces, which should prevent any radial flow of gas. On the LDPE-2 plant, these discs are surrounded by gas at compressor discharge conditions, whilst on LDPE-3 they are surrounded by cooling oil. There is thus a possibility for gas to leak to the crankcase of the primary compressor of the LDPE-2 plant. On both machines, cooling oil is circulated around the crankcase end of the moving piston, where it is retained between oil lip-seals. Any high-pressure gas that leaks axially past the mechanical seals is intended to be returned either to the low pressure gas recycle system or into a bleed-gas recovery system. However, some penetrates the lip-seals into the cooling oil. On the LDPE-3 plant, there is an additional possibility of gas entering the cooling oil by leaking radially between the discs that hold the mechanical plunger seals. The hyper-compressor cooling-oil vessels on both plants, and the crankcase of the primary compressor on the LDPE-2 plant all vent to atmosphere. All compressor, cooling and emergency vents are located at a height of 25 m, except for the vent from the LDPE-2 hyper-compressor cooling-oil vessel, which is at 13 m.

3.4 POLYMERISATION AND GAS RECYCLING

High-pressure ethylene from the hyper-compressor enters a tubular high-pressure reactor, where it is heated in order to initiate the reaction, and subsequently cooled to remove the heat of polymerisation. Despite this cooling, the temperature of the reacting mass increases up to about 330°C, so that the polymer is formed as a melt mixed in with super-critical ethylene. This high presure reactor is contained in an enclosed cell at high elevations on both plants. At the end of the reactor vessel, the pressure is reduced to around 300 bar so that the molten polymer separates from the bulk of the unreacted monomer. This monomer is then returned to the hyper-compressor via a series of coolers in which residual low molecular-weight waxes are separated and removed. The separated polymer is further reduced in pressure, leading to an additional separation of ethylene, which is cooled and returned to the primary compressor for low-pressure recycling. The molten polymer passes to an extruder.

The high pressure systems are protected from overpressures and decomposition reactions by an emergency vent system, backed up by bursting discs. If the automated reactor shut-down system is triggered, appropriate sections of the system are isolated and vented via a polymer separation vessel and a vent stack to atmosphere at a height of 33 m on the LDPE-2 plant, or at 41 m on LDPE-3. The high-pressure and low-pressure recycle systems are also protected by relief valves. These are directed to the flare system, unless significant polymer is present in the gas stream, or the temperature of the gas is outside the flare design limits. Where these situations occur, the gases are directed to atmosphere through vents at a height of 25 m.

3.5 EXTRUSION AND DEGASSING

Polyethylene obtained from the polymerisation reactor is processed in an extruder, where further removal of the dissolved ethylene occurs. It is then converted into small, lens-shaped granules in an underwater pelletiser. These granules still contain dissolved ethylene (about 700 mg of ethylene per kg of polyethylene on the LDPE-2 plant, and 300 - 900 mg/kg on LDPE-3.) This is removed by holding the polymer in air-purged de-gassing silos for about 15 hours. The purge air, which can contain around 200 mg of ethylene per cubic metre of air, is vented to atmosphere at a height of 5 m at a point located south of the de-gassing silos. After de-gassing, the polyethylene granules are transferred either into bulk finished-product containers or packed for storage.

3.6 INDIVIDUAL PROCESS EMISSION ESTIMATES

Staff at Shell Carrington have estimated the emissions from the de-gassing silo vents to be around 20 kg/hr. This is regarded as a reasonably-reliable estimate which is based on the plant throughput, and intermittently-measured concentrations of ethylene in the polymer entering the silos.

The vent emissions from the compressor cooling oil vessels have been estimated to be approximately 10 kg/hr for the LDPE-2 plant and 20 kg/hr for LDPE-3. The LDPE-2 vent emissions were estimated from a few intermittent measurements within the vent stacks. However, the LPDE-3 plant estimate is more indirect as it has been derived solely by scaling the LDPE-2 plant estimate using the relative throughputs of the two plants.

The total vent emissions are principally a combination of the compressor oil and degassing silo emissions, which are estimated from the above discussions to be 50 kg/hr. The uncertainties in this result have not been quantified. However, they are estimated to be large (ie greater than a factor of ten).

The equivalent annual emission rate may then be calculated from this estimate. If a plant utilisation of 100% is assumed, the annual emission rate is 440 tonnes per year. However, a more realistic plant utilisation figure provided by Shell personnel was 91%. This translates into an annual emission rate for VOCs from the <u>vents</u> <u>only</u> of the two polyethylene plants of 400 tonnes per year. This has a large uncertainty due to the fact that few direct measurements have been made of the losses from each of the sources.

3.7 ESTIMATION OF ETHYLENE EMISSIONS BY MATERIALS BALANCE FROM THE PLANT

An estimate of the emissions of ethylene and other species to atmosphere has also been made by mass balance. This entailed comparing the overall quantity of materials entering the process (excluding air and water), with the quantity of product obtained. The differences obtained between the total material inputs and the product outputs are typically about 2.5 - 3%. The quantity of emissions to air were then estimated by subtracting the known amounts of solid and liquid wastes produced, and the estimated losses of gases to the site flare. However, the metering of the gaseous ethylene input to the plant is subject to an uncertainty of about ± 1.2%, and the measurement of the flows to the plant flare are subject to uncertainties of about ± 30%. Consequently, this method of estimating emissions to air is subject to significant uncertainties. This is illustrated by the example in Table 1, which shows the possible range of fugitive ethylene losses determined by this procedure that might occur during the production of 170,000 tonnes of polyethylene per year. It can be seen that this has an uncertainty of about a factor of ten.

3.8 ESTIMATION OF EMISSIONS USING DOWNWIND POINT-SAMPLE MEASUREMENTS

A further technique has been used by Shell, in addition to mass balance, to estimate the total emissions of VOCs to atmosphere from the Carrington Manufacturing Complex. This technique utilises atmospheric point-samplers which are placed in a linear array downwind of the plant to measure the ground level concentrations of a number of VOCs (including ethylene and propylene, see Section 7.6.1). These downwind concentration measurements are then combined with an atmospheric dispersion model to obtain an estimate of the mass loss of VOCs from the plant [8, 9].

Table 2 summarises the estimated total emissions of certain gases to atmosphere from the Shell Carrington Manufacturing Complex, which have estimated using this procedure. It can be seen that these fugitive emission estimates are subject to considerable uncertainty, in a similar way to the emission estimates obtained by mass balance (Section 3.7).

An improved technique for determining the total emissions to atmosphere from the plant (ie the combined fugitive and vent emissions) is therefore required if they are to be quantified with the accuracy required for the UK Emission Inventory.

4 REMOTE TECHNIQUES FOR DIRECT MEASUREMENTS OF INDUSTRIAL EMISSIONS

4.1 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 [10]. 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 optical (generally infrared or ultraviolet) absorption spectrum, and that the wavelength of the source can be chosen so that it coincides with one feature of this spectrum. Then, if the source wavelength if tuned on and off the spectral absorption feature and the absorption that occurs is measured, the concentration of the selected species can be determined. The performance of these remote techniques at NPL has been extended continually, particularly in terms of the number of gaseous species that are detectable, their detection sensitivities, and the measurement range. In addition, field trials have been carried out regularly to demonstrate the extending capabilities of these measurement techniques.

4.2 THE DIFFERENTIAL-ABSORPTION LIDAR TECHNIQUE

One of these remote monitoring facilities uses a principle similar to optical radar, known as differential-absorption lidar (DIAL) [7]. 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, alkenes and alkynes, other volatile organics, and aromatics such as toluene and benzene, to be monitored specifically and sensitively [7, 10]. Table 3 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. More details of the scanning mirror, the receiving telescope and the detection system of this mobile laboratory are shown in Figure 2.

4.3 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 any selected direction up to a maximum range. This maximum range is dependent on a number of different parameters, including the atmospheric conditions and the detection sensitivity required for the specific gas measurement, but is typically 1-2 km. 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 locations (ie the integral of the gas concentration along the line-of-sight direction and the pathlength in the atmosphere) in any measurement direction can also be determined. Then, if the direction in which the laser beam and the telescope are pointed is 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 this plane can be measured. The methodology for doing this is discussed in more detail below. If similar measurements are carried out upwind in addition, the total flux of gas emitted by the site can be determined.

Data on the atmospheric wind speed and direction are also required to determine the emitted fluxes. To achieve this, an array of wind sensors is deployed wherever possible during the measurements, as indicated in Figure 4. 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 telescopic masts, which can be raised by up to 30 metres in elevation;

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

A simple model is also available which calculates, as a function of various parameters (such as the roughness of the terrain), the variation of wind speed with height. This is used to supplement the meteorological measurements. In addition, 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 effectively 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 in the downwind measurement plane(s), and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location.

(b) This product is computed for all points within the spatial concentration profile in the measurement plane, to form a two-dimensional array of data.

(c) This array of results is then integrated over the complete downwind concentration profile to produce a value for the flux in the measurement plume.

(d) The flux emitted by the industrial plant is taken to be the same as that in the measurement plant just downwind of the sources, since no deposition is likely to occur in this timescale, and the mass flux is therefore conserved.

The wind field over the complete spatial concentration profile in the measurement plane must be determined from a limited set of measurements. This is done either by linear or non-linear interpolation of the anemometer results, weighted by the distances that the anemometers are from any given point in the spatial profile. In addition, where appropriate, the variations of the anemometer measurement 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. (nb: this may be either the 30 m anemometer or that attached to the tethered balloon).

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 meterological 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 Carrington, the wind speed and direction were, wherever practical, monitored at elevations of 1-2 m and 3-5 m above ground level, with a third measuring system at about 18 m above ground level. In addition, a tethered balloon, with an anemometer attached, provided higher altitude wind speed and direction up to about 100 m above ground level. This procedure enabled an accurate estimate of the variations of wind speed with altitude to be determined up to elevations above the top of the plant.

All of these anemometers were carefully calibrated by NPL and intercompared before the measurement exercise. The instruments were set up, as noted above, as close to the DIAL lines-of-sight as possible - ie not necessarily close to the emission sources. These measured wind speeds were used with the concentration fields measured by the DIAL facility. Combinations of the anemometer results were generally used, where appropriate, for the determination of the emitted fluxes.

4.4 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, but are not part of the measurement strategy (eg CH_4, SO_2, NO_x, CO).

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 the 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 prepared gravimetrically at NPL. Accurate spectroscopic data for all the gaseous species relevant to this project were already on the NPL database. For this measurement exercise, the DIAL wavelengths were selected:

- to monitor the target species specifically (in this case usually ethylene, propylene and pentane) without interference from other gaseous species which may be present due to fugitive emissions from this plant or from other industrial plant located upwind (see Section 4.3). (However, it should be noted that ethylene and pentane represented the dominant emissions from these process plants.)

- 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, except for the flare study where excess concentrations above ambient were measured.) However, it should be noted that no significant concentrations of methane were emitted by this plant, as it is not part of the feedstocks or the products.

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 beam in the receiving telescope which collected the atmospherically-scattered radiation, 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 on different occasions 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 set of national facilities have now been developed, which utilise long-path optical gas cells and nationally-traceable gas mixtures of accurately-known concentrations. These enable different remote long-path and range-resolved measurement techniques to be calibrated and their performance characteristics validated, as they become available. They have already been employed to assess the performance characteristics of a double-ended open path monitor manufactured by OPSIS AB, Sweden [11], and to demonstrate the measurement accuracy of an infrared DIAL facility [12].

5 REVIEW OF THE INDUSTRY LOSS ESTIMATION PROCEDURES

5.1 OVERVIEW

This Section summarises the industry-standard procedures which are employed for the estimation of fugitive losses of volatile organic compounds (VOCs) emitted to atmosphere by petrochemical and oil refinery processing plant. These procedures were first produced by the Synthetic Organic Chemical Manufacturing Industry (SOCMI) of the USA [5], which is an association of the different USA companies involved in producing organic chemicals. They are now prepared under the auspices of the United States Environmental Protection Agency (EPA) [13]. This Section also outlines the way in which these estimation procedures have been improved over the years, summarises the measurements on which the procedures are based, and reviews their applicability to different petrochemical plant. We also discuss potential uncertainties which may occur in the accuracies of the results obtained using these procedures.

Leaks of VOCs to atmosphere occur in petrochemical process plant through the wide range of gas and liquid valves, pump and compressor seals, pressure-relief and other valves, sampling and other connections, flanges, and open-ended lines, which are contained within the plant. The EPA/SOCMI procedures that have been developed for leak estimation rely on an accurate knowledge of two basic sets of information:

(a) the total inventory of all valves, flanges, seals, connectors etc which are present in the plant;

(b) the relationships between VOC concentration measurements which are made in the atmosphere adjacent to the leaking components (known as source screening measurements), and the mass of VOCs lost to atmosphere by that component. This mass loss may be determined for different types of component, as explained in more detail below, by surrounding each selected 'leaking' components with a gas-tight container, and measuring the build-up of VOCs within the container. This VOC mass-loss measurement is known as 'bagging' the component. Details of the procedures for implementing this bagging measurement are given elsewhere [13].

Four different EPA/SOCMI procedures have currently been developed, which draw on the above information in different ways. These may be summarised as:

(i) **Average emission factors**: These use emission factors pre-defined for each type of component, which are combined with a complete inventory of all components to calculate the total emissions from the plant.

(ii) **Screening measurements**: These use measurements of the VOC concentrations which are present in the atmosphere around the different types of components in the process unit, to define whether these components leak (concentrations measured above a specified level) or do not leak (below the specified level). This screening procedure is therefore often known as the leak/no leak method. The measured data obtained is then used with prescribed procedures to calculate the total emissions from the plant.

(iii) **EPA-specified correlation procedure**: This allows an additional refinement to be applied to the VOC emission estimation procedure from equipment leaks, by providing an equation which relates the mass emission rate from a given component to the concentration obtained from the screening measurement on that component. The results are then used with the component inventory to calculate the total emissions from the plant.

(iv) **Process-Unit-Specific Correlation Procedure**: This is the most complex of the four EPA/SOCMI procedures. It requires an accurate experimental determination of the relationships between the masses of VOCs emitted to atmosphere from individual components of the selected process plant, and the concentrations measured during screening tests on that specific plant. This relation is then used with the inventory of all components to calculate the total plant emissions.

These are shown schematically in Figure 5.

The methodology whereby the EPA/SOCMI emission factors noted above have been derived over a number of years from different sets of measurements is summarised below. More details of the four procedures outlined above are presented in Section 5.3.

5.2 DEVELOPMENT OF THE EMISSION FACTORS FOR ESTIMATING LEAKS TO ATMOSPHERE FROM PROCESS PLANT

5.2.1 Overview

Different studies carried out over a number of years have been used to collect data on the leakage to atmosphere of VOCs from different equipment within petrochemical and at refinery process plant. These studies, which were carried out predominantly in the USA, have been used to define equipment emission factors and the correlation between screened concentrations and mass emissions. They have been reported in detail [13]. Refineries, natural gas and other gas processing plant, and process units within the SOCMI industry were all covered. As a result, emission factors, and data on the correlation between the screened concentration value of a component and its mass loss, have been produced for the following equipment - valves, pumps, compressors, pressure relief valves, connectors and open-ended lines. These have been revised as new studies were carried out. A summary of the studies carried out to develop the required emission factors, and the screened concentration to mass correlations, is given below.

5.2.2 First Refinery Assessment Study

In the late 1970s, EPA initiated the Petroleum Refinery Assessment Study. Equipment leak data from thirteen refineries were determined during this study and the results were collated into one database [14, 15]. All the different types of equipment were screened and the majority of sources that had screening values over 200 ppmv were bagged. Bagged equipment emission rates were reported as emission rates for non-methane organic compounds. Average emission factors and correlations between screened concentrations and mass emissions were developed for each equipment type, based on the screening and bagging data collected in this study.

This Refinery Assessment Study included an investigation of the correlations between equipment leaks and process variables for all types of compound. The only process variables which were found to correlate with mass emission rates in a statistically significant manner were:

(i) the phase (gas or liquid) of the process stream;

(ii) the volatility of the liquid in the process stream;

These findings led to a separation of the measured data on valves, pumps, and pressure-relief valves into their different applications. Three service (application) categories were defined:

- Gas/vapour - material in a gaseous state at the operating conditions of the plant;
- Light liquid - material in a liquid state in which the sum of the concentration of individual constituents with a vapour pressure of over 0.3 kilopascals at 20°C is greater than or equal to 20% by weight of the total process stream;
- Heavy liquid - ie components not in gas/vapour or light-liquid service.

5.2.3 Gas Plant Studies

A total of six natural-gas processing plants were screened in two studies which were reported in 1982 [16]. Four were screened by the United States Environmental Protection Agency and two by the American Petroleum Institute. Average emission factors were developed, and information was obtained on the percentage of equipment which was present with screened concentration values of hydrocarbons equal to or greater than 10,000 ppmv. It should be noted that these average factors included emissions of ethane and methane, which are clearly hydrocarbons, but were not classified in these studies as VOCs.

5.2.4 Original SOCMI Average Emission Factors and Correlations

In 1980, two studies, coordinated by the EPA, were carried out to collect data from SOCMI process units. These studies were known as the 24-Unit Study, and the 6-Unit Study. In the 24-Unit Study, screening measurements were taken from equipment containing organic compounds at 24 individual chemical process units. These were chosen to represent a cross-section of SOCMI process plant. In the 6-Unit Study, bagging measurements were carried out on components of six of the process units within the 24-Unit Study. These were used to determine the effect of maintenance on equipment leak emissions. Most of the bagging data of the Six-Unit Study collected in this study were from equipment with screened concentration values above 1,000 ppmv. From these results, correlations were developed between screened concentrations and mass emissions for light-liquid pumps and valves, and gas valves.

The results of these studies were not published separately. However, these SOCMI average emission factors were first presented in a combined report [17]. In this document, the data from the previous Refinery Assessment Study noted in 5.2.2 were also discussed and analysed further to develop "leak/no leak" factors for use with the EPA/SOCMI procedures. (A "leak" was defined in these studies as having a screened concentration value of greater than or equal to 10,000 ppmv of VOCs.) The original SOCMI average-emission factors were developed (with the exception of gas valves) using:

(i) the leak/no-leak emission factors developed from the Refinery Assessment Study data;

(ii) the leak frequencies which were found in the screened concentration value data set produced by the SOCMI 24-Unit Study. These indicated that the most significant statistical characteristic that distinguished equipment in SOCMI facilities from that in refineries was not the leak rate for a given screening value, but the fraction of equipment that had screening values greater than or equal to 10,000 ppmv.

For gas valves, the collected data indicated that for a given screened concentration measurement, the leak rate at a SOCMI facility was not consistent on a statistical basis with the leak rate of a similar component at a refinery. Therefore, data from the 6-Unit Study were used to develop the gas-valve average emission factors for the SOCMI industry.

5.2.5 Revised SOCMI Emission Factors and Correlations

In 1987 and 1988, screening measurements were made on 19 ethylene oxide and butadiene plants, and in 1990 bagging data were collected from 16 of these process units. In this study, the screening and bagging measurements covered emissions from light-liquid pumps, gas valves, light-liquid valves, and connectors. A specific goal of this programme was to bag equipment that had screening values of less than 1,000 ppmv. The bagging data were combined with the data previously collected in the 6-Unit Study, and this combined bagging data set was then used to revise the SOCMI correlations. In addition, the new screening data obtained in this study were combined with screening data previously collected in the 24-Unit Study, and this combined screening data set was used with the revised correlations to generate new SOCMI emission factors [13].

5.2.6 SOCMI Emission Factors and Correlations Derived from the Studies

As noted above, the SOCMI studies outlined in Sections 5.2.4 and 5.2.5 have been reviewed to produce the most appropriate values both for the average emission factors, and for the correlations between mass loss and screened concentration values for all types of components. Figures 6 to 9 show the measurements on which these emission factors and correlation values are based, for connectors, light-liquid pumps, gas valves, and light-liquid valves respectively.

From these results it can be seen that:

(i) The data sets in Figures 6 to 9 each contain typically 100-200 individual measurements. This clearly limits the statistical applicability of these results to other process equipment. The statistical limitations of these data sets have been examined [15].

(ii) The measured data have considerable scatter (typically two orders of magnitude) at all screened concentrations. This implies that for similar equipment populations, individual component emissions could be in error by at least an order of magnitude.

(iii) The average best straightline fits to the measured data (on a log-log scale) are also shown in the Figures, for the old and new results (Section 5.2.4 and 5.2.5) and where possible, for the data sets combined.

The average emission factors and the correlations between screened concentration values and VOC mass emissions are also derived from these best fitted straight lines. These are summarised in Tables 4 to 6. Their method of application is discussed further below.

5.3 EPA/SOCMI PROCEDURES USED FOR ESTIMATING EQUIPMENT LEAK EMISSIONS

The previous Section summarised the methods used in the SOCMI industry to determine the required emission factors, and the correlations between mass emissions and the screened concentrations.

The four EPA/SOCMI procedures which utilise the derived emission factors and mass loss/screened concentration correlations were summarised in Section 5.1 Figure 5 shows how these different data collection and analysis procedures can be used to develop a total equipment VOC emission inventory. In the Section below each of the approaches used for estimating equipment leak emissions are discussed further to provide a clearer understanding of their advantages, limitations, and accuracies.

5.3.1 Average Emission-factor Approach

One accepted approach for estimating emissions uses the average emission factors developed by the EPA for the industry, in combination with unit-specific data that are relatively simple to obtain. These data include:

(1) the total number of each type of component in a process unit (valves, connectors etc);

(2) the application (service) that each component is in (gas, light liquid, or heavy liquid);

(3) the VOC concentration of the process stream;

(4) the time period that the component has been in service.

The average emission factors for SOCMI process units, refineries, and natural gas plants are presented in Tables 4, 7 and 8 respectively. However, it should be noted that the average emission factors for the SOCMI processes and gas plants predict the total organic compound emission rates, whereas the average refinery factors predict non-methane organic compound emission rates. It should also be noted that limited data was collected on the leak rates of agitators, and, until additional data are collected for emissions from agitator seals, it is recommended that the average factor for light-liquid-pump seals is used to estimate the emissions from agitators.

The concentrations of the VOCs within the equipment, expressed as a weight percent, is needed to estimate emissions using the Average Emission-factor Approach. An explanation of the method for doing this is published [13]. This should clearly not include any inorganic compounds. Also, some organic compounds (eg methane and ethane) are not classified as VOCs, and these compounds should not generally be included in the determination of the VOC concentrations within the equipment of an oil refinery, but should be included in the case of SOCMI processing plant. Equipment may then be grouped into "streams" where all the equipment within the stream has approximately the same VOC weight percent. The procedures to be employed subsequently when treating these different VOC concentrations in a process stream are also discussed in [13].

It is important to note that, although the average emission factors prescribed for use in this Approach are expressed in units of kilograms per hour per individual source, these factors are only statistically valid for estimating the emissions from a large population of such equipment, and are not intended to provide an accurate estimate of the emission rate from a single piece of equipment. This can be seen from the data obtained by SOCMI and the EPA, which indicated that the range of possible leak rates from individual pieces of equipment spans several orders of magnitude. As a result, the majority of total emissions from a population of equipment at any given time will normally be produced by a small percentage of the total equipment - ie the average emission factors account for the span of possible leak rates but, as a result, they are not necessarily an accurate indication of the mass emission rate from an individual piece of equipment. Furthermore, these average emission factors do not reflect different site-specific conditions among process units within a source category, although site-specific factors can have considerable influence on leak rates from equipment. Nevertheless, in the absence of screening data, the average emission factors can provide a semi-quantitative approach to equipment leak rates from the equipment in a given process unit.

5.3.2 Screening Ranges Approach

The Screening Ranges Approach (also known, as indicated in Section 5.1, as the leak/no-leak procedure) offers a refinement over the Average Emission-factor Approach, allowing for some adjustments to be made for individual unit conditions and operations. This Approach and the two other approaches outlined below all require that screened concentration measurements be made on the equipment in the process unit. This screening data are then an indication of leak rates. The Screening Ranges approach, for example, assumes that components which have screening values of greater than 10,000 ppmv have different average emission rates than components with screening values of less than 10,000 ppmv.

This Approach may therefore be applied when simple screening VOC concentration data are available for components as either "greater than or equal to 10,000 ppmv" or as "less than 10,000 ppmv". The emission factors to be used for SOCMI plants, for these two ranges of screening values, are presented in Table 5. It should be noted that, as with the average emission-factors approach, these SOCMI screening-range factors predict total organic compound emissions, whereas the refinery screening-range factors predict non-methane organic compound emissions. It should also be noted that there are no screening range factors for sampling connections, because the emissions from sampling connections occur when the line is purged, and are thus independent of any screening value. Also, as with the average emission factors, the screening range factors for light-liquid pumps should be applied to agitators.

The Screening Ranges Approach is applied in a similar manner to the Average Emission-factor Approach, in that equipment counts are multiplied by the applicable emission factors. However, in the Screening Ranges Approach, no adjustment is made for inorganic compounds in the equipment, because the screening value on which emissions are based is a measurement of organic compound leakage only.

The screening-range emission factors represent a potentially better indication of the actual leak rate from individual equipment than the average emission factors. A screened concentration value of greater than or equal to 10,000 ppmv is particularly useful because the full scale readout of many of the screening instruments is 10,000 ppmv. For screened concentrations above this the actual screening value could only be determined by adding a dilution probe to the instrument, which represents an additional complication. Thus the greater than or equal to 10,000 ppmv factor is usually applied.

5.3.3 Stratified Emission Approach

One extension of the Screening Ranges (leak/no leak) Approach uses a slightly more complex procedure, known as the stratified emission factor approach, whereby the screened concentration values are divided into high (> 10,000 ppm) medium (10,000 - 1,000 ppm) and low (< 1000 ppm) and a different emission factor is used for each of these. The factors to be applied in this Approach [18] are presented in Table 15.
Despite the potential improvements of these procedures, over the average emission-factor approach, however, some of the available data indicate that measured mass emission rates for individual components may vary considerably from the rates predicted by the use of these screened concentration measurements.

5.3.4 EPA Correlation Approach

This Approach offers an additional refinement for estimating emissions from equipment leaks by providing an equation to predict mass emission rate as a function of screened concentration value for particular equipment types. Correlations developed by EPA which relate the screened concentration values to mass emission rates for SOCMI process units and refineries are presented in Tables 6 and 9, respectively. As noted previously, the SOCMI correlations predict total organic compound emission rates, whereas the refinery correlations predict non-methane organic compound emission rates.

The EPA Correlation Approach is preferred when actual measured screened concentration values are available. This Approach involves entering the screening values into a correlation equation, which predicts the mass emission rate. Correlations for SOCMI plant are available for gas valves, light-liquid valves, connectors, and light-liquid pump seals. Limited bagging data have also been obtained at SOCMI plants for compressors and pressure-relief devices.

By comparison, correlations for refineries are available for gas valves, light-liquid valves, connectors, and heavy-liquid pump seals, and there is a single equation for light-liquid pump seals, compressor seals and pressure-relief valves. The single refinery correlation for liquid pump seals, compressor seals, and pressure-relief valves arises because statistical tests performed on the bagging data collected from these equipment types during the Refinery Assessment Study indicated that one correlation could represent these component types.

Limited mass loss data have been obtained for compressors and pressure relief devices at SOCMI plants. However, statistical tests performed as part of the Refinery Assessment Study, noted above, indicated that emissions from light-liquid pumps, compressors and pressure relief valves could be expressed with a single correlation. Therefore until additional data are collected, the SOCMI equation for light liquid pump seals should be applied to estimate emissions from compressor seals and pressure-relief valves in SOCMI process units. Bagging results are also unavailable for agitator seals for refineries and SOCMI process units. Compared to those equipment types that have correlations, agitators most closely resemble light-liquid pumps, and, for this reason, the applicable light-liquid pump correlation should be used to estimate agitator emissions. Simililarly, the SOCMI light-liquid pump correlation should be used to estimate emissions from SOCMI heavy-liquid pumps.

Correlations can be used to estimate emissions from the entire range of non-zero screening values, from the highest potential screened value to the screened concentration value that represents the minimum detection limit of the monitoring device. All non-zero screening values can then be entered into the correlation to predict emissions associated with the screened value.

The "default-zero" leak rate is defined as the mass rate which is associated with a screened concentration value of zero. It should be noted that any screening value that is less than or equal to ambient (background) concentration is considered as zero, and that the EPA/SOCMI correlations mathematically predict zero emissions for zero screening values. However, data collected by the EPA show that this prediction may be incorrect. Mass emissions have been measured from equipment which has a screened value of zero. Therefore, one of the specific objectives when producing the revised SOCMI correlations was to collect mass emissions data from equipment that had a screened value of zero. These data were then used to determine a default-zero leak rate associated with equipment which has zero screening values.

Table 10 lists the default-zero leak rates obtained from SOCMI facilities for each of the equipment types. These default-zero lead rates are applicable only when the minimum detection limit of the portable monitoring instrument is 1 ppmv or less above background. However, these leak rates are based on the best available data and are considered applicable to all source categories.

The portable monitoring devices used to define the default-zero data in the original study were as noted above, sufficiently sensitive to indicate a screening value of 1 ppm or less. However, in cases where a monitoring instrument has a minimum detection limit greater than 1 ppmv the default-zero leak rates presented in Table 10 are not applicable. For these cases, an alternative approach for determining a default-zero leak rate should be used. One method is to determine one-half the minimum screening value of the monitoring instrument, and enter this screening value into the applicable correlation to determine the associated default-zero leak rate.

The EPA correlation approach also provides data on the mass emission values to be assigned to equipment with screened concentration values > 10,000 ppm. A procedure for this has been published [13]. The values used in this Report are given in Table 15.

The final procedure for determining the total emissions from these calculations is to determine the sum of the emissions associated with each equipment type from each of the screened concentration values, (assuming all the organic compounds are classified as VOCs). Each piece of equipment with a screening value of zero is then assigned the default-zero leak rate. For all equipment with a non-zero screening value, the screening value associated with each individual piece of equipment is entered into the applicable correlation to predict the emissions. (Each individual screening value must be entered into the correlation to predict emissions from an individual piece of equipment. It is not valid to average the screened concentration values and then enter the average value into the correlation to estimate the emissions.)

5.3.5 Unit-specific Correlation Approach

It is possible to develop unit-specific correlations by determining the correlations between the screened concentration values and the corresponding mass emissions data (ie bagging data) on the equipment of the specified process unit. The equipment selected for bagging should be screened at the time of bagging. The mass emission rate determined by bagging, and the associated screening value, can then be used to develop a leak rate/screening value relationship (ie correlation) for that specific equipment type in that process unit. The correlations should be developed on the specific process unit to minimize errors associated with differing leak rate characteristics between units. A detailed procedure for doing this has been published [13]. However, as this approach was not used in the exercise reported here, it will not be discussed further.

6 WORK PROGRAMME CARRIED OUT AT SHELL CHEMICAL WORKS

A work programme has been carried out to realise the objectives noted in Section 2. An outline of this work is given below.

6.1 The Shell Chemicals UK Ltd, Carrington Manufacturing Complex was identified as a suitable location for a measurement exercise which utilised the NPL mobile remote monitoring DIAL facility and ancillary instrumentation. This was partially because this petrochemical works is involved with the production of a range of petrochemical products including, for example, the manufacture of polyethylene from ethylene feedstock, polypropylene from propylene, and polystyrene from styrene, and it was considered that these processes involving light organics could emit significant amounts of volatile organic compounds to atmosphere.

6.2 Preliminary visits to the petrochemical works were carried out with the aim of:

- establishing in more detail the industrial processes occurring within the works, and the potential sources of the highest emissions;

- assessing the magnitude and the uncertainties in the emissions of different VOCs to atmosphere, as currently estimated by Shell personnel. (note: Table 2 indicates the initial estimates of emissions produced by Shell UK Ltd;)

- establishing suitable locations for using the DIAL facility to monitor the emissions from selected plant which are potentially the largest sources of fugitive (diffuse) VOC losses;

- defining the potential locations of the ancilliary meteorological and other instrumentation;

- agreeing a work programme to be carried out by Shell personnel in order to derive the emission estimates based on the EPA/SOCMI procedures for the plant.

- taking an initial air sample about 50 m downward of the polyethylene plant for analysis by NPL, in order to obtain an initial estimate of the main species emitted, and to determine whether there were additional species present in the atmosphere which could interfere with the DIAL measurement process. (The results of the analysis of the hydrocarbon concentrations in this sample are given in Table 11.)

6.3 A measurement exercise was carried out by NPL, using the DIAL facility and ancillary instrumentation, during the period 23rd January-4th February 1994, at the Shell Carrington Works. The industrial processes measured within the Works were:

(i) The polyethylene plant, which was monitored for 6½ days.

(ii) The polystyrene plant with its associated liquid-pentane storage tanks, which were monitored for 3 days.

(iii) The site industrial flare, which was monitored when olefins were being combusted, for ½ day.

As noted in Section 4.3, measurements were made of the concentration profiles of VOCs in the atmosphere downwind and upwind of each process. These measurements were combined with the meteorological data (see below) measured simultaneously, to determine the fluxes of the selected VOCs emitted from the processes.

6.4 Meteorological parameters, specifically wind speed and direction and atmospheric temperature and humidity, were monitored continuously throughout all the DIAL measurements using accurately calibrated instrumentation placed at selected locations. These were supplemented by measurements using instruments suspended from a tethered balloon, which provided data on the vertical profiles of the wind speed and direction around the plant being monitored.

6.5 Atmospheric samples were taken at appropriate times and places during the measurement exercise. These were taken by drawing ambient air into passivated gas cylinders (in the case of NPL), and into glass flasks through small orifices (in the case of Shell). These were subsequently analysed by the organisation which took these air samples by using gas-chromatographic techniques to identify and quantify the range of hydrocarbons which were present in the ambient air. These samples provided data on the concentrations of VOCs not targeted by the DIAL facility, and also provided an independent check that no significant cross-interference problems occurred during the DIAL measurements.

6.6 A work programme was carried out by Shell personnel, (both from the Carrington complex and from Thornton Research Centre). This work programme entailed measurements and computational work to estimate the emissions from the LDPE-3 plant by using the EPA/SOCMI procedures discussed in Section 5. This work complemented the NPL measurements and had the objective of facilitating the application of the results of this work programme to other similar petrochemical processing sites. This complementary work is discussed in more detail Section 7.5.

6.7 NPL personnel liased with appropriate Shell personnel during the measurement exercise. This included regular contacts on which area was being monitored, and an exchange of information on the initial results of the measurements. This assisted in the rapid identification of anomalous emissions and other problems, and ensured the optimum utilisation of NPL and Shell resources.

6.8 Technical discussions were carried out between all the organisations concerned in order to interpret and compare all the results obtained. All the results are presented in Section 8.

6.9 NPL scientists assist experts from the UK National Environmental Technology Centre in the identification and quantification of significant emission sources in the oil, petrochemical and chemical industrial sectors, and participating in discussions with representatives from these industries with a view to:

- improving the UK VOC emission inventory;
- recommending improved monitoring techniques and control technologies.

7 MEASUREMENT METHODOLOGY EMPLOYED DURING THE SHELL CARRINGTON EXERCISE

7.1 GENERAL METHODOLOGY FOR DIAL MEASUREMENTS AT THE SHELL CARRINGTON COMPLEX

Three industrial areas were identified for DIAL measurements by Shell Carrington personnel as being most likely to produce emissions to atmosphere, and these industrial processes within the Works were monitored during the measurement exercise, as noted in Section 6.3. Figure 10 shows all the locations where the DIAL facility made measurements during the monitoring exercise at the Shell Carrington Works. Table 12 shows the positions where the DIAL facility was located around the Polyethylene Plant during this period, the measurement dates and times, the wind speeds and directions, and the lines-of-sight used. Table 13 provides the same information covering the measurements made around the Polystyrene Plant and the associated road-tanker loading area.

It should be noted that, as outlined in Section 4, the NPL DIAL facility has the capability for range-resolved concentration measurements along any chosen line-of-sight. It is therefore possible to separate plumes originating from several sources, given suitable wind directions and the ability to locate the DIAL facility appropriately so that the chosen lines-of-sight intersect the plumes from these sources in the atmosphere before they merge together. In some cases therefore, it was possible during this measurement exercise to separate out the emissions of, for example, the LDPE-2 and LDPE-3 polyethylene plants from each other and from the degassing bunker vents. The total emissions were then obtained by summing the fluxes from these three sources. However, as the DIAL measurements were necessarily made some distance downwind of the plant in order to obtain valid values for the emitted fluxes, it was not always possible to delineate accurately the exact boundary between these sources. In these cases, the assignment of the emissions to a particular unit was subject to some uncertainty. The total measured fluxes, however, were not subject to the same uncertainty.

7.2 METHODOLOGY FOR DIAL MEASUREMENTS OF THE POLYETHYLENE PLANT

The polyethylene production plant, as described in Section 3, consisted of two units, a 'new' LDPE-3 unit to the west of the 'old' LDPE-2 original unit. Table 14 lists the throughputs of feedstock to each of these units which occurred during the measurement exercise. Shell Carrington personnel supplied an inventory of known and potential ethylene sources in the vicinity of these polyethylene production plant. These are shown in Figure 11. The potential sources identified are principally vents, and the heights at which they emit are also recorded below the Figure.

The VOC concentration profiles measured with the DIAL facility downwind of the complete plant were obtained typically over 15-20 minute periods. These profiling scans were repeated a number of times, in order to average out short-term fluctuations which might occur in the emitted concentrations, and to reduce DIAL measurement uncertainties orginating from atmospheric turbulence.

DIAL measurements were also made of the concentration profiles upwind of the plant under study, generally by moving the facility intermittently upwind. These determined the fluxes arising from upwind sources. They were generally repeated whenever significant changes in wind direction occurred. In addition, the possible effects of upwind sources was checked more regularly when the DIAl facility was monitoring downwind. This was done by choosing specific lines-of-sight in the atmosphere where there was no contribution from the source under study. Repeated measurements were then carried out to ensure that these concentrations remained zero.

During some of the DIAL measurement scans carried out in this exercise, significant changes in the atmospheric wind speed or direction occurred. The results of these measurements could potentially be in error and are thus not included in this Report.

As noted in Section 4.3, the wind speed and direction and the atmospheric temperature and humidity were monitored during all the measurements using calibrated instruments at representative locations. These allowed the pattern of the wind field in the measurement planes to be determined.

The measured data were analysed by NPL in order to derive the emitted fluxes during each scan, and averaged to produce approximately hourly-mean values for the emitted VOC fluxes. These hourly-average emissions were then converted to annual estimated emissions by using a multiplication factor of 8000. (This factor was proposed by the plant operators to allow for a realistic operating downtime of the plant - corresponding to about 9% per year.) The results obtained are presented in Section 8.

7.3 METHODOLOGY FOR DIAL MEASUREMENTS OF THE POLYSTYRENE PLANT

Two key measurement areas on this plant were identified by Shell personnel. These were:

(i) the area around the liquid-pentane storage tanks;

(ii) the region covered by the styrocell processing plant;

The main organic compound emitted to atmosphere was generally considered by the plant operators to be pentane. This was confirmed by atmospheric sampling (Section 7.6). Pentane is stored in fixed-roof tanks and is piped to the styrocell plant where it is used as a process additive. It was anticipated the pentane would leak fugitively from this plant. It was also expected that pentane would diffuse from the manufactured styrofoam whilst it is stored in the warehouse. The largest storage warehouse is located to the south of the styrocell plant (Figure 22).

The specific objectives of the polystyrene plant measurements were therefore:

(i) to measure gaseous pentane emissions occurring during transfer of liquid pentane from road tankers to the storage tanks;

(ii) to investigate steady-state fugitive emissions from the storage tanks when no road tankers were present;

(iii) to investigate fugitive and other pentane vapour emission sources in the area around the styrocell processing plant, including the storage warehouse.

The results obtained are presented in Section 8.3.

7.4 METHODOLOGY FOR FLARE MEASUREMENTS USING THE DIAL FACILITY

The flare located at the Shell Carrington Manufacturing Complex was usually operated with very low flows of input gases. In these cases, test measurements made using the DIAL facility demonstrated that the emissions were below the levels where accurate DIAL results could be achieved (typically <0.1 kg/hr^{-1} for methane and <0.03 kg/hr^{-1} for other volatile organic compounds). Instead, a further measurement exercise was planned. This entailed storing selected process gas in a pressurised container throughout the period when the DIAL facility was being used to monitor the emissions from the polyethylene plant. It was intended that the accumulated gas would then be vented to the flare in a controlled manner, at a significantly greater release rate than that which would generally ocur operationally. Propylene gas was stored for this purpose with the intention of carrying out DIAL tests on the plant flare for greater than two hours. Two types of test were scheduled:

(a) measurements of the residual flux of propylene which was emitted to atmosphere after flare combustion had taken place (known as gas 'slippage');

(b) measurements of any excess amount of gaseous methane generated, above atmospheric background levels, as a product of partial combustion of the propylene in the flare.

In both the above sets of tests, the DIAL system was scanned in the atmosphere downwind of the flare, in the manner outlined in Section 4.3, to determine the fluxes of the target gases emitted by the flare. The results obtained are summarised in Section 8.4.

7.5 METHODOLOGY FOR DETERMINING EMISSIONS USING THE INDUSTRY LOSS ESTIMATION PROCEDURES

7.5.1 Overview

Section 5 outlined the four industry-standard procedures used to estimate fugitive leaks from petrochemical and refinery plant. The equipment used during this measurement exercise at Shell Carrington, and the different procedures used to scale up the sample measurements to provide an estimate of the total emissions, are summarised below.

7.5.2 Instruments Used

Ethylene concentration measurements (screening tests) were carried out around potential fugitive leak points with one of two point-sensing instruments which employed the flame-ionisation detection (FID) technique - the well-established Foxboro OVA model 108, and the more recently produced Thermo-Electron HVM 680. It should be noted that the response of the HVM instrument was more heavily damped than that of the OVA instrument, although both met the EPA-recommended response time of less than 30 seconds.

7.5.3 Instrument Calibration

The accuracy of the instruments were checked by drawing known-concentration methane samples, which were contained in Tedlar bags, through the instruments. These standard calibration gas mixtures were supplied by Phase Separations Ltd. Instrument calibrations were carried out daily. However, this frequency of checking appeared to be unnecessary as no significant drifts in calibration were detected. (An initial check carried out prior to the present work after the OVA had been in service for several years without calibration showed a concentration measurement error of less than 20%).

The Thermo Electron HVM 680 instrument has not been available for a sufficiently long period to check its long-term drift. However, an initial calibration carried out at Shell Thornton Research Centre was within 3% of the calibration carried out by the manufacturers. Therefore, as other sources of uncertainty in the procedure for estimating the emissions are much larger than would result from this uncertainty in the instrument calibration, this calibration uncertainty was not corrected for.

Although both instruments had been set up to provide a linear response to methane concentrations, they were actually used to measure ethylene. Tests were therefore carried out to check their linearity when used for these ethylene measurements. This entailed producing a multi-point calibration curve for ethylene for both instruments. This was done using known-concentration gas samples drawn from Tedlar bags. The results are shown in Figure 12. It can be seen that the responses of both these instruments are non-linear for ethylene. However, their responses may be represented approximately by a linear factor of 0.71 (the measured ethylene concentration divided by its actual concentration) when calibrated with methane. This response factor was used throughout the Shell Carrington exercise.

7.5.4 Measurement and Analysis Procedures

Screening tests were carried out during this measurement exercise around potentially leaky components according to SOCMI/EPA recommended procedures [5,18]. The results were then interpreted in terms of emission rates using the published emission factors and correlation coefficients [13, 18] as outlined in Section 5. Tables 15 and 16 give the different emission factors which were actually applied when using the different types of estimation procedure. It should be noted that the figures in these Tables are different from those in Tables 4, 5 and 6 because of the calibration procedures used during this exercise (see Section 7.5.3 above).

Screening concentration measurements were taken first with the OVA instrument and, four months later, with the HVM instrument. The OVA measurements were made in the same time period as the DIAL measurements. The results, which gave emission rates in kg/hr, were then annualised initially using the factor 8.76 tonnes/yr for each measured kg/hr. This scale factor assumes an annual emission rate which is based on 100% plant operating time. However, this rate was then corrected for the average operating time of the plant throughout the year, which is estimated at 91%, to obtain a more accurate annual emission figure.

The emissions were also estimated more simply from component counts and from the published average emission factors [13, 18], as outlined in Section 5.3.1, in addition to estimating the emissions from the plant from the screened concentration values. The factors used in this procedure, which was summarised in Section 5.3, are given in Table 16.

In previous studies, the process plant component count has often been subject to significant uncertainties. For example, in the USA, where annual screening tests are mandatory, it is not unusual for component numbers to increase by 25% per year [19]. Therefore, in an attempt to overcome this, we collaborated with the plant process engineers to obtain an accurate count of appropriate valves and flanges. This was done both by studying process-flow diagrams and isometric drawings, and by touring the plant. Care was taken to ensure that no nitrogen, water or steam lines were included in the component count, and that the component concerned was pressurised at the time of measurement.

Both the paper studies and the plant visits were found to be essential for obtaining an accurate count. The first estimates of the number of each type of component, which were suggested by site personnel, were increased as a result of these more detailed investigations by almost factor of three.

7.5.5 Components Measured

Measurements were made on the LDPE-3 plant and covered only valves and flanges, because the vents associated with the compressor seal leaks were generally too high and inaccessible. It was also impossible to gain access to the high-pressure-reactor components, as these are enclosed in a concrete cell. Therefore, it was only possible to screen valves and flanges in the compression and extrusion stages of the process. This restriction meant that about 73% of the valves and 11% of the flanges on the LDPE-3 plant were measured. The consequences of this less than complete sampling are discussed in Section 8.5. However, it should be noted that the compression area of the plant contains both high and low-pressure components, and therefore the screening tests carried out in this area should be at least approximately representative of the whole plant.

7.6 METHODOLOGY FOR GROUND-LEVEL POINT-SAMPLING MEASUREMENTS

7.6.1 Overview

One of the secondary aims of the measurement exercise at Shell Carrington was an assessment of the validity of the procedure used previously by Shell personnel to estimate losses of VOCs to atmosphere (see Section 3.8). This employs a combination of atmospheric dispersion modelling and point-sampling techniques [8,9]. The point-sampling technique utilises a linear array of passive atmospheric samplers near ground level downwind of the plant.

Shell Carrington and NPL used different methods for passively sampling the ambient air downwind of the plant near ground level. NPL then carried laboratory analyses of its samples and Shell Carrington carried out similar analyses on theirs. The methods for carrying out the samples and the analyses are summarised below.

7.6.2 Shell Procedure

The Shell Carrington methodology for carrying out ground-level measurements to estimate the mass emissions from the plant has already been described [8, 9]. In summary, it entails using a glass flask, previously filled with water, which is slowly drained through a capillary tube at the bottom. As the water drains out, the atmospheric air is sucked into the flask through a silicone-rubber tube at the top. When the flask had been drained of water and contained ambient air, both ends of the flask are sealed with taps. Its contents are subsequently analysed by using gas chromatography. The Shell method sampled ambient air for 30-40 minutes, which was generally longer (by a factor of three) than that of the NPL method (see below). Direct comparisons of the Shell and NPL downwind array methods were carried out on three occasions.

The air samples obtained were analysed in the laboratory within 12 hrs of being taken. 4 ml of sample was introduced by a gas sample valve onto a 3.5 m x 3 mm column packed with 160 - 180 micrometre particles of activated alumina at 90°C. The components were separated using nitrogen carrier gas at 30ml/min and measured by a flame-ionisation-detector, the output signal of which was connected to a computer-based data analysis system. The instrument had been previously calibrated for ethane, ethene, propane and propene against traceable standards. The concentrations were reported in units of microlitres of component per cubic metre of air sample, with a minimum detection limit of 2 μl and a precision of ±10% relative.

The Shell sampling methodology outlined above (and the screening method discussed in Section 7.5) were used during this measurement exercise to provide data which was directly comparable with the DIAL results. In particular, the downwind monitoring measurements were focussed during this period only on the polyethylene plant, rather than the usual procedure which entailed monitoring the whole Carrington Manufacturing Complex. This enabled a direct correlation to be made with the DIAL measurements around the polyethylene plant. The results of these point-sample measurements are given in Section 8.6.

7.6.3 NPL Procedure

The NPL procedure used previously-evacuated gas cylinders which had specially-passivated internal walls to ensure that their interiors were inert to the chemical species being sampled. Atmospheric samples were taken using an array of these cylinders, arranged in a horizontal line across the gas plume in the atmosphere downwind of the plant near ground level (~1m above ground). The procedure entailed opening the cylinder valve so that the flow rate into the 10 litre capacity cylinder was about 0.5 l/min. The integration time for an individual measurement was therefore typically 10-15 minutes. The cylinder valve was then closed. These cylinders were then returned to NPL and their contents analysed using a gas chromatograph (detection sensitivity achievable ~2 parts in 10^{11}). This then determined the concentrations of all atmospheric hydrocarbon constituents present. The results of these measurements are given in Section 8.6.

8 RESULTS OF THE MEASUREMENT EXERCISE AT SHELL CARRINGTON COMPLEX

8.1 RESULTS OF NPL METEOROLOGICAL MEASUREMENTS

It is necessary to determine accurately the pattern of the wind-field in the plane of the DIAL measurements, in order to provide valid measurements of the fluxes of gases emitted to atmosphere. To this end, an array of "ground level" anemometers (~3 metres above ground level) were deployed on a routine basis, and these were re-located when significant changes in wind direction occurred. In addition, an 18 m high mast attached to the DIAL facility enabled higher altitude measurements to be made. All the measurements of wind speed and direction were logged continuously during the exercise. A summary of wind speed and direction data, which correspond to the DIAL measurement times, is given in Table 17.

Further meteorological measurements to define the wind-field were made by monitoring the vertical profiles of wind speed and direction with an anemometer attached to a tethered balloon. This was flown up to an altitude of greater than 90 m, which was significantly above that of the tallest plant in the Complex. This balloon was flown on eight occasions. These results have been combined with the continuous aenomometer measurements noted above to provide a more accurate representation of the wind field at higher altitudes. Examples of the vertical wind speed profiles measured on January 31st during both the ascent and descent of the balloon are shown in Figure 13. This data was combined with the other meteorological measurements to provide the wind field up to the heights required for the DIAL measurements.

8.2 RESULTS OF DIAL MEASUREMENTS ON POLYETHYLENE PLANT

8.2.1 Overview of DIAL Polyethylene Plant Measurements

As noted in Section 6.1, the emissions from the polyethylene plant were monitored using the DIAL facility for seven days, from January 25th to 31st. The locations of the DIAL facility on each of these days are indicated in Figures 14 to 20 respectively. The numbered positions and the respective lines-of-sight for each day shown in these figures correspond to those listed in Table 12. This Table also shows the measurement times and the meteorological conditions. Table 14 gives the ethylene throughput of the two plants which occurred during this measurement period.

As noted in Section 7.1 three major separable sources of hydrocarbon emissions were identified from the DIAL measurements - the old plant, the new plant and the vents from the degassing bunker (Section 3.5). The locations of the known vent emissions within these are indicated in Figure 11. Table 18 indicates the proportions of emissions measured by the DIAL facility at different times from each of these three sources, using the procedure outlined in Section 7.1.

A summary of the DIAL measurements carried out on each day and the results obtained are presented below.

8.2.2 DIAL Measurements on 25 January

The performance characteristics of the DIAL facility, including its alignment and calibration, were verified by a series of prescribed tests on 24 January, following its transport to Shell Carrington.

The NPL DIAL facility was then located at position #1 (Figure 14) using the line-of- sight as shown. The wind direction was from about 260° with a speed of about 5 ms^{-1}. Meteorological monitoring stations were deployed along the line-of-sight and a series of DIAL measurements were made which provided the total flux emitted from both the polyethylene process units. However, on this occasion it was not possible to measure accurately the emitted VOC fluxes from the degassing bunker vents, as the DIAL facility was located within the plume from this source.

The total emissions from the two polyethylene units (excluding the degassing bunker vent) were measured to be 59 kg hr^{-1}.

8.2.3 DIAL Measurements on 26 January

The wind direction throughout the day was between about 225° and 260° (Figure 15). As a result, two DIAL measurement positions were employed, #3 and #4. These used lines-of-sight 3A and 4A respectively. Eight vertical scans, each consisting of more that ten line-of-sight measurements were obtained, with all except one providing range-resolved data for the emissions from the three main sources in the area of the polyethylene plant. The exception was scan 261B when the wind direction meant that the emissions from the new process plant could not be measured.

The average value for the total polyethylene plant emissions was 60 kg hr^{-1}, which included a contribution of 4 kg hr^{-1} from the degassing bunker vents.

8.2.4 DIAL Measurements on 27 January

Most of the DIAL measurements carried out were from position #5 along line-of-sight 5A, (Figure 16) as the wind was mainly from about 270°, with speeds of 5-9 ms^{-1}. It was not possible to separate out the emissions from the old and new plants. However, it was possible to separate the emissions of the degassing bunker vents from the combined emissions of the two process units. The total plant emissions, were measured as 56 kg hr^{-1}, with an additional contribution of 4 kg hr^{-1} from the bunker vents.

This wind direction also meant that measurements could readily be made of the emissions from the new plant alone. This was achieved by moving the DIAL facility to position #6 and scanning vertically along line of sight 6A. Three partially spatially-resolved plumes were observed during these scans, which originated from sources significantly above ground level. These were assigned to vents at the southern and northern ends of the new plant. However, the measurements were made too far downwind to identify the specific vents which produced these emissions.

The total emissions from the new plant measured during these scans were 28 kg hr^{-1}. The concentrations of VOCs near ground level ($\leq$ 3 m) at this location were below the DIAL detection limits.

8.2.5 DIAL Measurements on 28 January

The DIAL facility was positioned at #7 using line-of-sight 7A (Figure 17) for the entire day. The wind speed was 7 to 10 ms^{-1}. This meant that it was not possible to separate the emissions from the three areas since the plumes from the two processing plants were completely merged, and that from the degassing bunker vents were blended with those from the plants. Seven valid scans were obtained.

The total emissions from the old and new plants and the degassing bunker vents were 63 kg hr^{-1}.

8.2.6 DIAL Measurements on 29 January

The wind direction was variable, from 200° to 250°. To accommodate this, as shown in figure 18, three lines-of-sight were used, 8A, 2A and 9A, from DIAL locations #8, #2 and #9 respectively.

The data obtained from positions 2 and 8 enabled measurements to be made of the emissions from the old plant and the degassing bunker vents. This provided a value of 35 kg $hr^{-1}$for the total emissions from these two areas.

Measurements from position 9 produced an average value for the total flux emitted by all three sources of 60 kg hr^{-1}. It was only possible from some of these measurements to separate out, with any accuracy, the emissions from the different units.

8.2.7 DIAL Measurements on 30 January

The measurement locations and lines-of-sight are shown in Figure 19. The wind direction was initially 270°. The DIAL facility was located at positions #10, #3 and #11, using lines of sight 10A, 3A and 11A respectively. Average emissions from the degassing bunker vents were 4 kg hr^{-1} and the total emissions from the complete polyethylene plant was 61 kg hr^{-1}.

8.2.8 DIAL Measurements on 31 January

Measurements of the polyethylene plant were made from positions #12 and #7 (Figure 20) with an approximately south-westerly wind. As a result, the emissions from the degassing bunker vents were merged with those of the old plant. However, these were generally separated from the new plant emissions. The average emissions from the new plant were 27 kg hr^{-1}. Those from the bunker vent and old plant combined totalled 31 kg hr^{-1}. The total measured emissions were therefore 58 kg hr^{-1}.

In addition to the above measurements of the complete polyethylene plant, a number of DIAL scans were made from position #7. These were made specifically to measure the emissions from the high-pressure reactor cell (Section 3.4) located at high elevations in the new plant. Ethylene emissions were monitoring downwind - mainly from the top of the north wall of the cell. These were measured to be about 3 kg hr^{-1} - ie about 11% of the total emissions from this new plant.

The wavelengths of the DIAL facility were then adjusted in order to enable the measurements on the polystyrene plant to be made, and the standard calibration checks were carried out to verify the DIAL measurement accuracy.

8.2.9 Summary of DIAL Measurements on the Polyethylene Plant

DIAL measurements were made on a total of seven days in order to study the VOC emissions from the Polyethylene Plant. A summary of all the measurement periods is given in Table 12. The individual results of the DIAL measurements obtained are presented in Table 18. Table 19 summarises the results of these DIAL measurements on a daily basis, presenting where possible, the emissions from the three principle source areas separately as well as giving the total emissions. The emissions from the new Plant (LDPE-3) were about 10% lower than those of the old plant over the measurement period. From this data it is calculated that the measured emissions from the new LDPE-3 plant were 0.18% by mass of its throughput, and that of the LDPE-2 plant were 0.36% (excluding degassing emissions). The only other significant source of emissions of ethylene was the degassing bunker vents, which emitted 4 kg/hr, corresponding to about 0.02% of total plant throughput. A correlation between the total emissions and the total plant throughput during this exercise has also been produced, as shown in Figure 21. This showed that no significant variations in the VOC emissions occurred during the measurements as the total plant throughput varied by a small amount.

8.3 RESULTS OF DIAL MEASUREMENTS ON THE POLYSTYRENE PLANT

8.3.1 Overview of the Polystyrene Plant Measurements

The emissions in the vicinity of the Polystyrene Plant were measured over a period of three days, with pentane measured as the dominant species. The two principal sources of these emissions were the area containing the pentane storage tanks, and the polystyrene processing plant/warehouse complex. The locations of these potential sources are shown in Figure 22. The locations and the lines-of-sight of the DIAL facility which were used to determine these emissions during the measurement periods are shown in Figures 23 to 25 respectively. The numbered positions and the respective lines-of-sight correspond to those listed in Table 20. Table 20 also give all the individual results obtained.

A summary of the DIAL measurements carried out each day, and the associated results obtained, are presented below.

8.3.2 DIAL Measurements on 1 February

The DIAL facility was positioned at #13, using line-of-sight 13A (Figure 23). The wind was at about 9 ms^{-1} and 180°. This allowed both upwind and downwind measurements of the pentane storage tank area to be made from the same location. A road tanker began unloading at 10.40 hrs and a first attempt was made at monitoring emissions during the loading of the tanks from this tanker. However, the road tanker moved away after ten minutes of measurements. Subsequent measurements carried out on the storage tank area following this showed no emissions above the detection limit of the DIAL technique ($\leq$ 0.03 kg hr^{-1}).

The DIAL facility was moved to position #15. The wind direction was at this time about 240°. Measurements of the emissions from the styrocell plant and warehouse were made along line-of-sight 15A. Three measurement scans were made from this position before the wind changed. The DIAL facility was then moved to position #16. Emissions from the styrocell plant itself were observed both at low elevations, (ie up to 8 m above ground level), and from the plant vents. The results are shown in Table 20.

8.3.3 DIAL Measurements on 2 February

A road tanker was scheduled to unload liquid pentane into the storage tanks commencing at 10.00 hrs. The wind direction was from 210° at about 2 ms^{-1} at this time. The DIAL facility was placed at position 13 (Figure 24) and small fluxes of pentane were measured until 10.30 hrs. Large pentane emissions were then measured from 10.35 hrs. This was subsequently found to be due to the disconnection of the pipes connecting the road tanker to the tank filling port, as the road tanker had commenced unloading an hour earlier than scheduled. Following this, several scans downwind of the pentane tanks, interlaced with upwind scans, measured emissions which were below the DIAL detection limits (Table 20).

The DIAL facility was then moved to position #17 in order to monitor the emissions from the polystyrene plant. Two scans were made from this position before the wind changed. Low elevation emissions from the plant and significant emissions from the vents at high elevations were measured with more than half the emissions on this occasion orginating from the higher-level vents.

8.3.4 DIAL Measurements on 3 February

The wind was from 90°. The DIAL facility was positioned at #18 (Figure 25) in order to monitor the emissions which occurred when a pentane road-tanker was unloading into the tanks. A measurement downwind of the storage tanks was made before the tanker arrived and a second measurement made as the tanker began to unload. Very large emissions were seen during the initial two minutes of unloading, gradually reducing during the loading cycle. The relationship between measured emissions and the time when unloading started is shown in Figure 26. It is believed that some of these emissions at the beginning of the process could have originated from a pentane spill which took place during the coupling of the road tanker to the storage tanks. However, as noted above, a similar release occurred during disconnection of the loading pipes on 2 February.

8.3.5 Summary of DIAL Measurements on the Polystyrene Plant

DIAL measurements were made over a period of three days in order to study the pentane emissions associated with the polystyrene plant. The areas studied, the emissions measured, and the times over which the measurements were made, are listed in Table 13. The results are summarised on a daily-averaged basis in Table 21. The daily average emissions listed in Table 21 represent those principally from the polystyrene plant. The emissions measured from the plant were significant near ground level up to a height of typically 10 m. However, greater than 70% of the emissions produced were from the high level vents ($\geq$ 20 m).

No significant emissions were measured during this exercise from the warehouses or from the area around the pentane storage tanks under normal operating conditions, compared with those from the plant itself. However, during the transfer of 17.2 tonnes of pentane from a road tanker to Tank 804A on the 3rd of February large emissions were recorded. These corresponded to about a 7.5 kg loss, or 0.04% loss of throughput during the process of loading the liquid pentane into the storage tanks.

It should be noted that these results are for the total emissions of pentane (ie including all isomers). The contribution of each pentane isomer to the total is determined through the whole-air samples (Section 8.6.7).

It was not possible to obtain information on the total polystyrene plant thoughout during the period.

8.4 FLARE MEASUREMENTS

As noted in Section 7.4, it was anticipated that sufficient propylene had been stored to enable the flare to operate for up to two hours, with the DIAL facility first set up to monitor methane resulting from hydrocarbon cracking in the flaring process, and subsequently to monitor direct propylene emissions from slippage. In the event, the stored propylene allowed the flare to be operated for about fifteen minutes, and only one complete set of valid measurements were obtained. These indicated very low level of hydrocarbons above ambient within this flare. When this result is combined with the lower detection limits for methane and propylene estimated from these measurements, the flare efficiency on this occasion was calculated to be $\geq$98%.

8.5 RESULTS OBTAINED USING THE INDUSTRY LOSS ESTIMATION PROCEDURE

8.5.1 Overview

As discussed in Section 7.5.1, the industry loss estimation procedures entail specifying the complete component count for the plant, carrying out screening concentration measurements using hydrocarbon monitoring instruments, and scaling up the results to provide the total emissions. Table 22 gives the component count obtained for the LDPE-3 polyethylene plant at Carrington. Section 5 described the procedure which may be applied to derive loss estimates from this average emission-factor approach and the screening measurements, where applicable. Table 23 gives the estimates for the combined annual emissions obtained from valves and flanges obtained using these procedures - the simplest average emission-factor approach using only a component count, and the three methods based on screening measurements (leak/no leak, stratified emission factor, and correlation procedures).

8.5.2 Results of Measurements Obtained Using the OVA Instrument

Table 23 gives the results obtained from the three EPA/SOCMI measurement-related procedures using the OVA instrument. The emission rates from the valves and flanges in the plant are calculated to be 12 to 14 tonnes/year. These results (in line with common experience) are significantly lower than the emission estimate obtained using the average emission-factor approach of 23 tonnes/year, which is also shown in Table 23. It should be noted that in this case, the biggest contribution to these emissions arise from the flanges. This is not the usual experience in petrochemical process plant, where the biggest contribution normally arises from valves.

At first sight the agreement between the three measurement-based API/SOCMI emission estimates might suggest the results may be accurate. However, a closer scrutiny reveals that, in each case, about 90% of the emissions arise from a small number of components (3 flanges and 6 valves measured with the OVA instrument) which are classified as major leakers (i.e. those screened at greater than the full scale deflection of the analyser of 10,000 ppmv). These components are treated in the three measurement methods in the same way - ie by assigning an identical "pegged source" emission factor to each source. Thus the procedures differ only in their treatment of the residual 10% of the emissions which arise from the 'non-leaking' components. It is therefore not surprising that there is (fortuitous) agreement between these results.

Notwithstanding the apparent agreement between the estimation methods, there is a large uncertainty in the emission estimates obtained. These arise because the emissions at Shell Carrington occur, as noted above, almost entirely from a few components which have large leaks, with the total emission rates estimated by multiplying the measured number of leaking components of each type by the relevant global average emission factors. The uncertainty attributable in this measurement exercise to this process has been calculated, and upper and lower (95% confidence level) emission limits have been estimated for the emission rates obtained in this exercise. These are also given in the last two columns of Table 23. These emission limits include uncertainties arising from:

a) The variations of the actual emission factors of individual components about their tabulated mean values;

b) The incomplete coverage of the measurements of the components of the plant;

The former uncertainty is common to all tests on similar plant and the uncertainty attributable to this was calculated by standard statistical techniques. The latter is specific to the measurements reported here. The uncertainty arising from this incomplete sampling was estimated by assuming a hypergeometric distribution. (The hypergeometric distribution represents a sampling procedure without replacement, which is equivalent to the test procedures carried out during this exercise). This was then used to calculate the uncertainty in the total number of leakers at the plant, given the number observed in the measured sample. There are also other possible sources of uncertainty that are not as easily quantified. These are discussed further in Section 8.5.7 and in Appendix C.

The results obtained were also used to estimate the total emissions from the LDPE-3 polyethylene plant. This was carried out by scaling up the results presented in Table 23 by the ratio of the total emission rate obtained from the average emission-factor approach for all components, to that obtained when applying the average emission-factor approach to the valves and flanges which were measured. This method of processing the results attempts to account for the emissions from compressor seals and other vents which were not accessible to these measurements (Section 3.3). It therefore corresponds to the application of the average emission-factor approach to the total plant, corrected by the ratio of the leak/no leak measurement results to the average emission-factor estimates for the valves and flanges which were measured.

The above results are clearly only approximate. At the Carrington LDPE-3 plant a large proportion of the additional emissions (which could not be screened because they were inaccessible and have thus been estimated by scaling) were not emitted directly to atmosphere. Instead, they were either collected and recycled, or directed to the flare or the high-level vents (Section 3.3.). The overall estimates for the LDPE-3 plant are therefore likely to be inaccurate. However, for completeness they are given, in Table 24.

The upper and lower (95% confidence level) emission limits for these results are also given in Table 24. These are derived by direct scaling of the limits in Table 23. The uncertainties derived from this procedure cover the range from 0.19 to 3.6 times the mean value.

8.5.3 Results of Measurements Obtained Using the HVM Instrument

The emission rates determined from the HVM instrument (Table 23) were considerably lower than those determined from the OVA instrument even though both were calibrated correctly.

However, the HVM measurements were taken at a later date, and consequently the differences could have been affected by different operational conditions in the plant, and by any intervening maintenance activity. Operational changes which result in variations in the emissions from valves (due to their different stem positions etc). could also lead to a significant lack of correlation between one set of measurements and another taken subsequently. In the data obtained during this exercise for example, some initially leaking valves gave low readings when retested, and some initially gas-tight valves showed leaks when re-tested. In addition, maintenance of some valves had taken place between the two sets of measurements and this would be expected to reduce the emissions from these valves systematically. Despite these factors, much of the observed differences are considered to be related to an instrumental difference. This is indicated, for example, by the results for flanges (see below) which produced significantly smaller readings with the HVM instrument than those obtained by the OVA instrument, even though they had not been influenced by operational variations or plant maintenance activities.

It would therefore have been valuable to carry out simultaneous comparisons to determine the ratio of the OVA to HVM readings when used for field measurements. This was not done because it was not realised in advance that there would be such a significant difference between the responses of the two types of instrument to a given leak. However, in the absence of simultaneous OVA and HVM tests, a correction factor has been estimated for the HVM readings. This was done by:

(a) determining the ratio of the OVA to the HVM readings for each component;
(b) discarding very large or very small values of this ratio (<0.1 or >10), on the assumption that they were inaccurate or caused by plant variations;
(c) taking the mean of the remaining ratios.

The overall mean ratio obtained by this procedure is 3.3. (It should be noted that it was not possible to take the mean of all the measurements because many HVM readings were zero, whilst the OVA gave finite results, and this would clearly give an OVA/HVM ratio of infinity.)

If the above approach is applied to the valves only the correlation factor is 2.3. If it is appplied to flanges only, the correction factor is > 5.2. This correction factor for flanges is given as a lower limit because the OVA readings obtained in these cases were at their maximum values of 10,000 ppm. However, because these flanges have no moving parts, and were mostly undisturbed between the two sets of tests, it was decided to use the correction factor derived from the flange readings only. This view is supported by the fact that there was a significantly better correlations between the OVA and HVM readings for flanges than for valves. (For example, the highest readings of each instrument were found for the same flanges). With this approach, and using a correction factor of 5.2, the HVM readings resulted in a revised estimate of 3 leaking flanges and 1 leaking valve, compared to the corresponding OVA results of 3 flanges and 6 valves. For comparison, applying the correction to just the HVM readings obtained for the valves that had moderate OVA/HVM ratios (between 0.1 and

10), and which are therefore considered to be not significantly affected by maintenance, resulted in one leak for the HVM measurements. There was also one leak indicated from the same subset of valves by the OVA. This suggests that the residual difference in the number of leaky valves probably reflects both changes in the plant operating conditions and the systematic effect of maintenance activity. There is thus some evidence that the above correction obtained using flanges only is not unreasonable.

An alternative approach would have been to simply scale the HVM data by the factor required to produce the same number of leakers as the OVA measurements. This produces a scale factor of 315. However, because there was maintenance activity between the OVA and HVM tests, this provides an upper limit for the correction factor. In addition, this scale factor seems unrealistically high, and this approach was therefore rejected.

8.5.4 Comparisons of Results Obtained Using the Two Different In-situ Instruments

The instrumental differences arise mainly because of the different response times of the instruments. They occur because, according to EPA procedures, the maximum screening value should be recorded. However, the OVA instrument is very lightly damped and the needle responds rapidly to transients, whereas the HVM is more heavily damped and approaches the maximum indicated concentration without overshoot. Consequently the HVM is less responsive to transients and reads lower in actual tests, which generally involve fluctuating gas concentrations. It is, however, more repeatable as a result of its slower response, and it has the additional practical advantage that it records the maximum screening value t measures automatically.

It should also be noted that, although the correlations and emission factors were originally developed by EPA and SOCMI using 'maximum' readings, it is not clear as to what extent transient fluctuations were included when the correlations were produced. In the current case, care was taken to record the maximum OVA reading observed, although this may have been a short transient. The readings should thus represent the maximum that could be recorded. Other operators could take a different view of what is a significant transient concentration and record only more sustained readings. This would reduce the screening values obtained. The range of uncertainty which might be produced by different operator interpretations of OVA readings is probably indicated by the difference between the OVA readings and the more heavily-damped HVM readings observed in this project - about a factor of five.

8.5.5 Comparisons of Results Obtained with Average Emission-factor Approach and Screening Measurement Methods

The emission rate which was estimated using the pre-defined average emission factor approach was a factor of 1.7 higher than those that were estimated from the screening measurements. This may be understandable since the screening measurement methods should give lower values where improved maintenance practices are in place, as these should result in a smaller proportion of leaking components occurring than would have been the case when the original emission factors were developed. A ratio of larger than unity may thus, to some extent, be an indicator of improved plant operating conditions.

8.5.6 Comparisons of Results Obtained Using Different Analysis Methods

The authors of this Report believe that the stratified emission factor approach is generally the most relevant method to be applied in cases such as the Shell Carrington exercise. This is because the extra effort required to carry out the correlation procedure may not produce a sufficient increase in accuracy to be considered worthwhile. This is the case in the present work, where the emissions were dominated by major leakers. Under these circumstances there was little justification for using procedures that were more complex.

8.5.7 Additional Sources of Uncertainty Arising from the Use of the Industry Estimation Procedures

Further potential sources of error may be:

a) Uncertainties in the original determinations of the EPA/SOCMI emission factors and correlation coefficients.

b) Differences in the nature of the equipment tested during this exercise and that used to derive the emission factors and correlation coefficients.

In the first case, the determinations of the emission factors were based on measurements obtained with similar numbers of components to those involved in this project (see Section 5). Therefore random uncertainties of a similar magnitude would be anticipated. The discussion in Section 5 suggested that this could be up to an order of magnitude. The latter uncertainties are harder to quantify. However, the possible magnitude of this could be judged by considering differences between the emissions of similar components which are used for different types of operation. Some examples of the different average emission factors that have been prescrived for use in different industrial applications are given in Table 25. It can be seen, for example, that the valve emission factors for gases vary by a factor of 134 between applications, and the flange/connector emissions vary by a factor of 61. It might therefore be concluded that because the emission factors vary by these amounts between different applications, it is likely that there will be significant uncertainties associated with the emission factors that are present at any particular plant. A further discussion of the possible uncertainties in these procedures is presented in Appendix C.

8.6 RESULTS OF GROUND LEVEL POINT-SAMPLING MEASUREMENTS

8.6.1 Preliminary sample

An evacuated passivated cylinder was, as noted in Section 5, sent by NPL to Shell Carrington in order to obtain an initial sample of the ambient air downwind of the polyethylene plant. The valve of this gas cylinder was opened downwind of this plant in a region close to the expected emitted plume centre, in order to estimate the approximate concentrations of gases emitted by the plant, in preparation for measurements by the NPL DIAL facility. The cylinder was opened at position B (Figure 27) with the wind blowing from the south-west. The results obtained at NPL by gas chromatographic techniques are shown in Table 11. It can be seen that ethylene was the predominant species measured, at 244 ppb. (However it can also be seen that significant methane and ethane concentrations are present above ambient background levels. There were subsequently attributed to a natural-gas storage plant which was upwind of the Shell plant on this occasion). The DIAL facility was thus adjusted to avoid interferences from methane and ethane, and its sensitivity was also adjusted during this measurement exercise to enable measurements of ethylene in the range 40-2000 ppb to be made over the spatial extent of the plume.

8.6.2 Point-sampling Measurements on 26 January

Two separate sets of ground-level point-monitoring measurements were made by NPL. The second set of these was coordinated with Shell Carrington point sample measurements (see Section 8.6.8). Both NPL sets were carried out at ground level along a line-of-sight of, and simultaneously with, the DIAL measurements. The distribution of gas sample cylinders for Set 1 is shown in Figure 27. The wind was from 250° at about 3.5 ms^{-1}. They were therefore downwind of the north-east corner of the polyethylene plant at ground level. The cylinder valves were opened at 13.51 hrs, and the sampling was terminated at 14.05 hrs when they reached atmospheric pressure.

The results obtained are shown in Table 26, for all the hydrocarbons analysed. The maximum concentration of ethylene of 1130 ppb was measured in cylinder no. NPL 372, - the remaining two indicating 873 and 565 ppb respectively in the northern wing of the plume.

A second set was taken about one hour later, with three NPL evacuated cylinders sampling at the same positions as three of the Shell Carrington sampling tubes. The samples were arranged along the northern boundary of the polyethylene plant as shown in Figure 28. The wind was from 230° at about 5.5 ms^{-1}. All samples were started at 15.40 hrs. The NPL sampling was completed at 15.48 hrs. Shell Carrington samples were complete at 16.10 hrs.

The NPL results for all the hydrocarbons analysed are shown in Table 27. Cylinder NPL 148 contained the highest ethylene concentration of 782 ppb. The results obtained by Shell Carrington are shown in Table 28.

8.6.3 Point-sampling Measurements on 27 January

One complete set of measurements were made. This set included direct intercomparisons between three NPL sample cylinders and three of the Shell Carrington samplers, as noted in

Section 7.6. The samples were arranged in a north-south line to the east of the polyethylene plant as shown in Figure 29. The wind direction during these measurements was from about 245° with speeds of about 6 ms^{-1}. The starting times for the NPL and Shell sampling was synchronised at 14.34 hrs. The NPL cylinders were filled within 10-15 minutes. The Shell Carrington samples were not sealed off until about 15.00 hours. The results obtained are shown in Tables 29 and 30.

8.6.4 Point-sampling Measurements on 28 January

Shell Carrington carried out a point-sampling exercise along the line-of-sight of the DIAL facility from 15.20 to 16.10 hrs. The results obtained are shown in Table 31.

8.6.5 Point-sampling Measurements on 30 January

NPL sample cylinders were placed to the east of the plant at ground level, at the positions indicated in Figure 30, along the line-of-sight of the DIAL measurements. The wind was from 275° at about 4 ms^{-1}. The results showed a peak concentration for ethylene of 744 ppb at the centre of the line of samplers and values of 291 ppb and 183 ppb nearer the edges. The sampling period was from 16.45 to 16.55 hrs. The results are shown in Table 32.

8.6.6 Point-sampling Measurements on 31 January

A set of sample cylinders were placed along the line-of-sight of the DIAL facility at ground level, to the north of the polyethylene plant as shown in Figure 31. The wind direction was from about 210°. The measurement period was from 15.51 to 16.09 hrs. However, the wind changed to about 230° during the measurements and the most easterly cylinder (N207) recorded the largest ethylene concentration (480 ppb). The results are shown in Table 33.

8.6.7 Point-sampling Measurements on 2 February

These measurements were made in the vicinity of the pentane storage tanks. The sample cylinders were placed to the north of the pentane tanks, spaced by about 25 m, as shown in Figure 22. The wind was from 180° at about 2.3 ms^{-1}. The point-sample measurement period was from 10.25 to 10.34 hrs, which coincided with the final minutes of transfer from road tanker to the tanks. Any spillage due to the disconnection of filling pipes between the road tanker and the storage tanks would therefore have been detected during this measurement. The results are shown in Table 34. These also provided measured data on the actual ratio of normal to iso-pentane in the atmosphere. This was used to confirm the isotopic ratio which had been assumed when carrying out the DIAL calibrations, and thereby confirms that the DIAL measurements correctly produce the total emissions of all sources of pentane.

8.6.8 Comparison of Shell and NPL point-sampling results

On three occasions, (on 26 January and 27 January) Shell Carrington personnel took samples of ambient air using their sampling flasks (Section 7.6) along the atmospheric lines-of-sight used by the NPL DIAL facility. On each occasion twelve Shell sampling flasks were arranged in a linear array along the line-of-sight at about 20 m intervals. (In addition, three Shell sampling flasks were arranged at similar intervals approximately parallel to the same line, but about 100 m upwind of the polyethylene plant.)

During two of these three sets of measurements, side-by-side intercomparisons were undertaken between the NPL and Shell Carrington ambient air samplers. However only one, that of 27 January, was an exact comparison. In this case the entrance orifices of the NPL and Shell sampling devices were taped together to monitor the same volume of air. (The samples taken on 26 January monitored ambient air using entrance orifices which were typically 100 mm apart.)

Table 30 shows the correspondence between NPL and Carrington ambient air samples on 27 January. The NPL values are higher by up to 20% in regions where there are the high ethylene concentrations, but lower by about 7% near the edges of the plume. There is no explanation for these discrepancies, beyond that arising from the slightly different sampling times.

8.7 EMISSIONS FROM THE POLYPROPYLENE PLANT

The measurements carried out during this exercise were not aimed at determining the VOC emissions from the Shell Carrington polypropylene plant, since insufficient time was available to do this. However, some of the measurements carried out fortuitously provided an approximate indication of the emissions which might originate from this plant:

(i) Measurements were made on some occasions using the mobile DIAL facility at locations which were upwind of the polypropylene plant but downwind of the polypropylene plant. In these cases, although the DIAL laser wavelengths was not optimised for propylene, the measurements made gave an approximate indication of the propylene emissions present on these occasions.

(ii) The whole-air samples taken by both NPL and Shell personnel gave information on the concentrations of propylene which were present mainly originating from the polypropylene plant, together with the ethylene concentrations present which originated from the polyethylene plant.

If the limited set of results obtained as indicated above are inspected, an approximate estimate of the emissions to atmosphere from the propylene to polypropylene processing plant can be derived. This corresponds to emissions to atmosphere in the region of 0.07% to 0.2% as a percentage of mass, of propylene through the plant.

9 COMPARISONS OF THE DIAL MEASURED EMISSIONS WITH THE INDUSTRY ESTIMATION PROCEDURES

The total emissions obtained from the DIAL measurements of the LDPE-3 polyethylene processing plant (Table 19) may be compared with those obtained by the industry estimation procedures (Tables 23 and 24). The emissions measured by the DIAL facility, however, included significant contributions from high-level vents and vents external to the plant which carried, for example, the emissions from the compressor cooling oil and the de-gassing silos. These emissions were not determined by the screening measurements discussed in Section 8.5, because the vents were inaccessible to the *in-situ* instruments. The procedure for scaling the emissions shown in Table 23 in order to achieve the total estimated emissions in Table 24 aimed to include at least some of these vent and other emissions. However, clearly the scope for error is increased by the extrapolation. The uncertainties within the industry estimation procedures used here, and the further uncertainty due to extrapolation, mean that caution should therefore be applied when comparing the results in these Tables with the measured DIAL data.

The DIAL results gave the total emissions of ethylene from the combination of the LDPE-2 and LDPE-3 plants as 478 ± 32 tonnes/yr. Of this, 212 ± 20 tonnes/year was measured as originating from the LDPE-3 plant. These DIAL results include both the fugitive emissions from valves and flanges at low levels within the plant (for which comparative emission estimates were obtained by using the screening measurements and the EPA/SOCMI procedures) and the emissions from the inaccessible high-level vents, (for which there was no comparable data).

A direct comparison of the total emissions measured by DIAL from the LDPE-3 plant, with the best estimate obtained using the EPA/SOCMI procedures, produces a ratio for the DIAL to the EPA/SOCMI results of 5.9. However, the DIAL results are only a factor of 1.7 above the overall upper emission limit (95% confidence level) of the EPA/SOCMI procedure estimated for this application.

Out of the total DIAL measured emissions, approximately 38 tonnes/yr were identified, on the basis of the height of the emission sources, as arising from valve and flange fugitive losses. Thus, if approximately two thirds of the overall valve and flange emissions, arise from the LDPE-3 plant on the basis of its throughput, a value of about 25 tonnes per year is obtained for the contribution of the LDPE-3 plant valves and flanges, estimated by DIAL measurements. This result is a factor of 1.9 higher than the most probable emission rate estimated from the screened concentration point-sensor results for the same valves and flanges - which is 13 tonnes per year (Table 23). However, it is well within the (95% confidence level) upper and lower emission limits calculated for the industry estimation procedure, of between 2.5 and 50 tonnes per year.

It is also possible to attempt to estimate the fugitive emissions from the LDPE-3 plant valves and flanges, by subtracting the process vent emissions (which had been estimated approximately by Carrington personnel) from the overall NPL measured emission data. However, it should be noted that the Carrington estimates for the compressor emissions are significantly higher than those obtained by the average emission-factor approach for this plant. (The reason for this may lie the high pressures involved in the Carrington process which might be expected to produce higher-than-average leak rates per unit). If the Carrington estimates for the compressor and vent contributions are subtracted from the overall emission rate measured by the DIAL facility the fugitive emission rate for all the valves and flanges of the LDPE-2 and LDPE-3 plants combined is 15 (+45, -15) tonnes per year. The uncertainty in this result is clearly too large to permit quantitative comparison with the estimates obtained from the EPA/SOCMI procedures. However, the approximate agreement between the NPL overall emission measurements and the Carrington estimates of known process emissions provide an indication that the *in-situ* measurements would not have given significantly larger estimates for the measured components than those which were obtained by the DIAL technique, provided the derived upper (95% confidence level) emission limit was used (50 tonnes per year -Table 23) rather than the most probable emission estimate.

The overall emissions in Table 24 estimated by scaling the valve and flange point-sensor data are also significantly lower than the DIAL measurements because the extrapolations used to estimate the other non-screened contributions to the emissions may underestimate the true emissions.

10 SUMMARY AND CONCLUSIONS

10.1 DIAL MEASUREMENTS

(i) Measurements were made using the NPL DIAL facility to determine the total fugitive emissions of volatile organic compounds from the polyethylene production units at the Shell Carrington Complex. The best estimate of the total fugitive ethylene emissions obtained during the measurement exercise corresponds to 60 kg/hr. If this is scaled proportionally, taking into account the plant utilisation rate and the annual throughput of ethylene, this measured hourly rate corresponds to an annual emission of 478 tonnes per year.

(ii) The measured DIAL emissions were in the range 55-63 kg/hr on a daily averaged basis, which when scaled up to equivalent annual emissions, correspond to a range of about 440-500 tonnes per year.

(iii) Polyethylene is manufactured at Shell Carrington using two process plants. The older of the two process plants (LDPE-2) has a nominal capacity of 65,000 tonnes per year, whilst the newer plant (LDPE-3) has a capacity of about 107,000 tonnes per year. The measured emissions from the old and new plant were 30 kg/hr and 26.6 kg/hr respectively (excluding the degassing bunker vents) corresponding to annualised emissions of 212 tonnes per year and 234 tonnes per year. The total annual emission losses from the older process plant are therefore equivalent to about 0.36% of its throughput. The total fugitive emissions from the new process plant correspond to 0.18% of its throughput. The additional emissions from the degassing bunker vents correspond to 0.017% of the total ethylene throughput.

(iv) The total measured ethylene losses from the plant, including those from the degassing bunkers corresponded to 0.26% of the total throughput during the period, with the polyethylene process having a production capacity of 170,000 tonnes per year.

(v) Low emissions were measured from the new polyethylene plant near ground level, with the vast majority of the emissions from this plant emanating from high-level sources including the vent stacks. However, a higher proportion (~25%) of emissions from the old plant were measured at low levels, below the heights of the vent stacks.

(vi) The measured fugitive emissions arising from the polyethylene processing units are at the lower end of the range estimated previously by Shell Carrington personnel from mass balance calculations and from downwind sampling measurements (250-4300 tonnes per year).

(vii) The average measured fugitive emissions of pentane from the styrene processing plant and its associated polystyrene storage warehouse were 18 kg/hr. If this is scaled proportionally, taking into account the plant utilisation rate and the annual throughput, this measured hourly rate is equivalent to an annual emission of 147 tonnes per year. This corresponds to a loss of about 4.8% of the pentane throughput to the process. The majority of these emissions were from vent stacks at high elevations on the process unit. It was not possible to obtain accurate information on the production of polystyrene during the measurement period.

(viii) DIAL measurements were also made of the fugitive losses of pentane to atmosphere from the area around the pentane storage tanks. Measurements made during periods when pentane was being loaded from road tankers into these storage tanks indicated a loss of 0.04% by mass of pentane transferred. If this loss represented the annual rate, it would correspond to an emission of 1.2 tonnes per year. Measurements made when no road tanker loading was taking place, gave no detectable fugitive losses. An upper limit on the losses of VOCs when no loading occurs can therefore be derived, which corresponds to $\leq$ 0.3 tonnes per year.

(ix) DIAL measurements on the emissions from the industrial flare at the site, indicated that the efficiency of this flare was $\geq$ 98% during the period of the tests.

(x) All the results obtained using the DIAL facility are summarised in Table 35.

10.2 RESULTS OBTAINED USING THE INDUSTRY-STANDARD ESTIMATION PROCEDURES

(i) Industry-standard procedures were used to estimate the emissions from part of the processing plant at the Shell Carrington Works. The total fugitive emissions from the LDPE-3 plant, estimated using an incomplete sample of point-sensing screening measurements, and analysed by the EPA/SOCMI leak/no leak method, were 36 tonnes per year. Additional analyses carried out using the stratified emission-factor and EPA- correlation procedures gave almost identical values. This is because the emissions in this plant were dominated by a few large leakage sources which are treated in the same way by each procedure. The component count method gave higher results (56 tonnes per year).

(ii) A statistical analysis of the uncertainty in the results of the industry estimation procedures gave lower and upper emission limits (95% confidence level) of 6 and 125 tonnes per year respectively.

(iii) The annual emissions from only the valves and flanges measured on the LDPE-3 plant was estimated to be 14 tonnes per year, with lower and upper 95% confidence limits of 2.5 and 50 tonnes per year respectively.

(iv) When only around a few hundred components are tested, point-sampling emission-rate estimates are intrinsically subject to uncertainties of at least a factor of three. These arise partly from the statistical uncertainties in the measurements when this relatively small number of components are used to obtain the emission factors. These could be reduced by measuring larger numbers of components. Further uncertainties arose in this exercise because only a proportion of the plant components were measured. These factors clearly show the desirability of near complete sampling of a large number of components. This type of measurement may also be subject to significant uncertainties which arise from the fact that the prescribed EPA/SOCMI correlation coefficients and emission factors may not be correct for this industrial application.

(v) New FID instruments may, in principle, be improvements on older designs for these industry procedure measurements. However, instrumental differences, in particular their transient response characteristics, will influence the readings obtained in the field. In this exercise the ratio between the emission rates derived from a Thermo Electron instrument and those derived from the OVA instrument was estimated to be between 0.17 and 0.5. Consequently, before new instruments can be used for reliable emission rate estimates, it is necessary either to develop new emission factors and correlations to interpret their readings, or to develop correction factors which use existing factors to relate the new instrument readings to equivalent OVA readings. An approximate correction factor of 5 was derived by a field comparison of the Thermo Electron instrument with an OVA instrument, and if this was applied more consistent results were obtained. However, the accuracy of the comparisons was limited because they made use of measurements taken on different occasions. Further work to compare simultaneous OVA and HVM readings would be required to determine whether this correction factor approach is viable in other applications. However, this variability in the emissions estimated using different instruments may be indictive of the accuracy achievable with the EPA/SOCMI methods.

(vi) The uncertainties in the emission rates which arise from all aspects of these industry procedures should be assessed thoroughly by users of the methodology.

10.3 COMPARISONS OF DIAL MEASUREMENTS WITH EPA/SOCMI RESULTS

(i) The valve and flange emissions only from the LDPE-3 plant were estimated from the DIAL data to be about 25 tonnes/yr. This was higher than the most probable emission rate of 13 tonnes/year, determined by the industry procedure, by a factor of 1.9, but is within the range 3-50 tonnes per year calculated by a statistical analysis of the point-sensor data. The true uncertainties of the point-sensor results are probably greater than this, but it was not possible to quantify the additional uncertainties.

(ii) DIAL measurements carried out simultaneously with the *in-situ* screening measurements gave emission rates for the whole LDPE-3 process plant which were about 6 times higher than those estimated by the EPA/SOCMI procesures. This difference may partly be attributable to:

- known process emissions, for example outgassing of ethylene from the polyethylene storage bunkers. However, the emissions from the polyethylene storage bunker vents were generally measured separately from the process plant emissions by the DIAL technique, and are in the range 29-36 tonnes per year. They are not therefore the cause of this difference;

- higher-than-average compressor-seal emissions, possibly arising from the high operating pressures in this plant, and large emissions to the vent stacks from other sources in the plant.

- the EPA/SOCMI emission factors may be inaccurate for these industrial applications, particulary with respect to different inspection and maintainance practices.

10.4 SCALING THE RESULTS TO DEFINE CONTRIBUTIONS TO THE UK VOC EMISSION INVENTORY

10.4.1 Polyethylene Production

The total production of polyethylene in the UK was estimated to be 445 ktonnes in 1991 [20]. The current estimate is 460 ktonnes per year, with ≥ 40% being of the low density type manufactured by the Shell Carrington Complex. The volatile organic compounds emitted to atmosphere from both the Shell processing plant and its associated storage facilities, measured by the DIAL techniques, correspond to 0.26% of the throughput of ethylene to the plant. An estimate can be made of the total emissions to atmosphere from all UK polyethylene plant, using this factor. This corresponds to 1200 tonnes per year. An estimate can also be made of the uncertainty in this value of the annual emissions. If the uncertainties in the annual production of polyethylene in the UK, the variations in processing plant conditions and operating procedures, and the DIAL measurement uncertainties, are taken into account, it is estimated that the emissions to atmosphere from polyethylene production in the UK lie in the range 840-1550 tonnes per year. It should be emphasised that these emissions arise from the process which is used to convert the process feedstock (ethylene) to polyethylene and does not include the emissions produced by process plant manufacturing these feedstocks (see Section 10.5.3 below) which will contribute to further atmospheric emissions of VOCs.

10.4.2 Emissions of Other VOCs

Measurements were made during this exercise by the DIAL facility and other point-sampling techniques of some of the other petrochemical process emissions on the Carrington site. Other estimates of losses have also been carried out by Shell Carrington personnel.

The results obtained around the propylene to polypropylene processing plant indicated that the emissions to atmosphere from this process were between one third and one times those emitted by the polyethylene plant, as a percentage of the mass throughput of propylene. If this is the case elsewhere in the UK, an estimate can be made of the contribution from polyethylene processing to the UK VOC emission inventory. The annual UK production of polypropylene is about 420 ktonnes per year. The losses from this are thus estimated to be to 500-1000 tonnes per year. As noted above, this estimate covers the emissions that are used to convert process feedstock into polyethylene but not those emitted during the manufacture of the feedstocks.

DIAL measurements were also carried out, as summarised in Table 35, to determine the VOC emissions from the polystyrene processing plant. However, this is a batch (ie not continuous) process and the operating conditions vary significantly. The VOC emissions measured from the Shell polystyrene plant have therefore not been scaled up to produce a UK estimate of the emissions from this process. Further work on this is underway.

10.4.3 Comparisons with Oil Refinery VOC Emission Estimates

Ethylene is manufactured, as noted above, from bi-products of the oil refinery industry, (eg ethane and naphtha). It is therefore of interest to compare the results obtained with the estimates of oil refinery VOC emissions. A number of DIAL measurement surveys have been carried out by NPL on a number of oil refineries in the UK and throughout the rest of Europe. Table 36 summarises the results obtained from these surveys for the total emissions of VOCs to atmosphere. It can be seen that the average VOC emissions from this ensemble of oil refineries with different sizes, ages and type of processing equipment, correspond to 0.19% by mass of crude oil throughput, with a range between 0.12% and 0.3%. Table 37 also breaks down these total emissions measured by the NPL DIAL technique into VOC emissions by refinery area, showing that the process unit of this 'ensemble-averaged' oil refinery emits 0.05% of VOCs to atmosphere by mass of refinery crude oil throughput.

These NPL DIAL results are consistent with the average VOC emissions from oil refineries estimated by two other authors [22, 23] by carrying out mass-balance calculations on all UK oil refineries. It should also be noted that the total VOC oil refinery emissions measured using the NPL DIAL facility are consistent with those contained within the 1993 Emission Inventory [21] of 180 ktonnes per year, which are summarised in Table 38. However a more recent estimate produced by the oil industry gave VOC emissions of 100 ktonnes per year.

These DIAL measured emission values of 0.19% and 0.05% of throughput for the total oil refinery and for the process unit, may be therefore compared with the results obtained during the exercise for the VOCs losses from the old and new polyethylene process units of 0.18% and 0.36% respectively (mean value 0.26%). These two sets of results are not disimilar in their emissions of VOCs to atmosphere as a percentage of feedstock throughput.

11 ACKNOWLEDGEMENTS

The authors of this Report would like to acknowledge the Department of the Environment, Air Quality Division for their sponsorship of this work. We would also like to thank Mr M Woodfield and Dr I Marlowe of the National Environmental Technology Centre for their continuous interest and enthusiasm throughput the project. We are grateful to scientists from Shell Thorton Research Centre for their technical contributions to the project. We would finally like to thank Shell UK plc for their cooperation during the project, and the staff at the Shell Carrington Complex for their continued asssistance.

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APPENDIX C

C1 Distribution of "pegged" source emission rates for gas/vapour valves.

C2 Upper and lower 97.5% confidence limits for emission rate as a function of the number of leaks

TABLE 1: Estimated Ranges of Ethylene Loss per Annum

Emissions to atmosphere through vents etc	255 - 450 t/a
Estimated loss to flare	1120 - 2450 t/a
Inferred total fugitive emissions	255 - 4250 t/a

TABLE 2: Estimate made by Shell Carrington of Total Emissions of Certain Gaseous Species to Atmosphere before the Measurement Exercise

Substance	Total Emission (t/a)		Previously Measured Concentrations* $\mu g/m^3$
	Prob.	Range	
Ethylene	1200	600 - 5000	50 - 300
Propylene	600	300 - 4000	5 - 100
i-octane	1200	1100 - 1300	n/a
Ethylene/Propane oxides	400	250 - 600	15 - 50
Styrene	300	150 - 500	n/a

*Results obtained by Shell Carrington personnel, before the measurement exercise reported here, using the glass flask samplers (Section 7.6.2)

TABLE 3: **Examples of Detection Sensitivities Attainable with NPL Remote Monitoring Facilities**

Tunable diode-laser system			Ultraviolet/visible DIAL system			Infrared DIAL system (range 300 m; range resolution 10 m)		
CO	0.5	ppb	NO	5	ppb	CH_4	10	ppb
CH_4	1	ppb	NO_2	5	ppb	C_2H_2	20	ppb
NH_3	5	ppb	SO_2	4	ppb	C_2H_4	15	ppb
C_2H_4	5	ppb	O_3	2	ppb	C_2H_6	20	ppb
C_2H_6	1	ppb	Hg	0.5	ppb	Higher Alkanes Alkenes Alkynes	25	ppb
C_2H_2	2	ppb	Benzene	3	ppb	H_2S	2	ppm
H_2S	1	ppm	Toluene	5	ppb	OCS	50	ppb
N_2O	0.2	ppb	Xylenes	10	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 4: SOCMI Industry Average Emission Factors

Equipment type	Service	Emission factor (kg/hr/source)
Valves	Gas Light liquid Heavy liquid	0.00597 0.00403 0.00023
Pump seal	Light liquid Heavy liquid	0.0199 0.00862
Compressor seals	Gas	0.228
Pressure relief valves	Gas	0.104
Connectors	All	0.00183
Open-ended lines	All	0.0017
Sampling connections	All	0.0150

Notes: The emission factors presented in this table for gas valves, light-liquid valves, light-liquid pumps, and connectors are the revised SOCMI average emission factors.

These factors are for total organic compound emission rates.

TABLE 5: SOCMI Industry Screening-Value Emission Factors

Equipment type	Service	≥10,000 ppmv Emission factor (kg/hr/source)	<10,000 ppmv Emission factor (kg/hr/source)
Valves	Gas Light liquid Heavy liquid	0.0782 0.892 0.00023	0.000131 0.000165 0.00023
Pump seals	Light liquid Heavy liquid	0.243 0.216	0.00187 0.00210
Compressor seals	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Connectors	All	0.113	0.0000810
Open-ended lines	All	0.01195	0.00150

Notes: The emission factors presented in this table for gas valves, light-liquid valves, light-liquid pumps, and connectors are the revised SOCMI emission factors for concentrations less than and greater than 10,000 ppmv.

These factors are for total organic compound emission factors.

TABLE 6: SOCMI Correlations between Screened Concentration Values and Leak Rates

Equipment type	Correlation
Gas valves	Leak rate (kg/hr) = 1.87×10^{-6} $(SV)^{0.873}$
Light-liquid valves	Leak rate (kg/hr) = 6.41×10^{-6} $(SV)^{0.797}$
Light-liquid pumps	Leak rate (kg/hr) = 1.90×10^{-5} $(SV)^{0.824}$
Connectors	Leak rate (kg/hr) = 3.05×10^{-6} $(SV)^{0.885}$

Notes: The correlations presented in this table are the revised SOCMI correlations.

SV = Screened concentration value

These correlations predict total organic compound emission rates.

The correlation for light liquid pumps can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps.

TABLE 7: Oil Refinery Average Emission factors

Equipment type	Service	Emission factor (kg/hr/source)
Valves	Gas Light liquid Heavy liquid	0.0268 0.0109 0.00023
Pump seals	Light liquid Heavy liquid	0.114 0.021
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.16
Connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.0150

Notes: These factors are for non-methane organic compound emission rates

The light liquid pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE 8: Gas Plant Average Emission Factors

Equipment type	Service	Emission factor (kg/hr/source)
Valves	All	0.020
Pump seals	Liquid	0.063
Compressor seals	All	0.204
Pressure relief valves	All	0.188
Connectors	All	0.0011
Open-ended lines	All	0.022

Note: These factors are for total organic compound emission rates
The pump seal factor can be used to estimate the leak rate from agitator seals.

TABLE 9: Correlations between Screened-concentration Values and Leak Rates for Refineries

Equipment type	Correlation[b,c]
Gas valves	Leak rate (kg/hr) = 2.18×10^{-7} $(SV)^{1.23}$
Light liquid valves	Leak rate (kg/hr) = 1.44×10^{-5} $(SV)^{0.80}$
Light liquid pumps, compressors, pressure relief valves[d]	Leak rate (kg/hr) = 8.27×10^{-5} $(SV)^{0.83}$
Connectors	Leak rate (kg/hr) = 5.78×10^{-6} $(SV)^{0.88}$
Heavy liquid pumps	Leak rate (kg/hr) = 8.79×10^{-6} $(SV)^{1.04}$

[b]SV = Screening value
[c]These correlations predict non-methane organic compound emission rates
[d]This correlation can be applied to agitators

TABLE 10: Default-zero Emission Rates for SOCMI Facilities

Equipment type	Default-zero emission rates (kg/hr/source)
Gas valve	6.56×10^{-7}
Light liquid valve	4.85×10^{-7}
Light liquid pump	7.49×10^{-6}
Connectors	6.12×10^{-7}

Note: The light liquid pump default zero value can be applied to compressors, pressure relief valves, agitators, and heavy liquid pumps.

TABLE 11: Analysis of Pre-Trial Air Sample taken Downwind of Polyethylene Plant

Sample No: Cylinder No: A165 Date: 15/12/93	Concentration (ppb)
ethane	13.1
ethene	296
propane	4.2
cyclopropane	0.83
propene	28.8
2-methyl propane	0.61
ethyne	2.20
n-butane	1.6
trans-2-butene	0.05
1-butene	0.11
isobutene	0.24
cis-2-butene	*
2-methyl butane	0.96
n-pentane	0.46
1,3-Butadiene	*
trans-2-pentene	*
pentenes	*
cis-2-pentene	*
cyclic C6 unidentified	*
dimethyl butane	*
2-methyl pentane} 3-methyl pentane}	0.61
n-hexane	0.23
isoprene	
n-heptane	0.11
benzene	0.44
C8 HCs unidentified	4.62
methyl benzene	1.38
C9 HCs unidentified	0.86
ethyl benzene	0.31
1,3-dimethyl benzene	1.61
1,2-dimethyl benzene	0.51
1,3,5-trimethyl benzene	*
1,2,4-trimethyl benzene	*

* below detection limit ~0.05 ppbv

TABLE 12: Overview of DIAL Measurements Carried out Around the Polyethylene Plant at Shell Carrington Chemical Works

Day	Position	Times	Wind Speed Lower m/s	Wind Speed Upper m/s	Wind Direction degrees	File	LoS	Scan
25th January Tuesday	P1	16.20-17.17	5.09	5.21	259	jan251	1	A
26th January Wednesday	P3	13.03-13.34	3.80	4.55	254	jan261	3	A
		13.53-14.09	4.00	4.44	246			C
	P4	15.18-15.31	4.00	4.47	229	jan262	4	A
		15.39-16.15	4.72	6.37	235			B
		16.26-16.54	4.50	6.06	238	jan263	4	A
		17.03-17.26	4.92	6.20	249			B
		17.54-18.21	4.35	6.37	240	jan264	4	A
		18.26-18.50	4.16	5.79	237			B
27th Janaury Thursday	P5	11.30-11.48	5.15	8.19	254	jan271	5A	A
		12.06-12.25	6.00	6.00	261			B
		13.53-14.18	5.33	7.20	252	jan272		A
		14.26-15.04	6.19	6.61	245			B
		15.23-15.50	6.55	7.62	244	jan273		A
	P6	17.01-17.50	4.95	5.88	284		6A	B
		18.03-18.50	6.60	8.16	275	jan274		A

Day	Position	Times	Wind Speed Lower m/s	Wind Speed Upper m/s	Wind Direction degrees	File	LoS	Scan
28th January Friday	P7	11.56-12.17	6.33	7.94	297	jan281	7A	A
		12.21-12.41	6.51	8.85	298			B
		13.19-13.42	6.30	8.21	305	jan282		A
		13.53-14.43	5.66	7.51	298			B
		15.13-16.04	5.30	7.23	299	jan283		A
		17.07-17.42	2.81	3.81	293			B
		17.47-18.10	3.67	5.42	283	jan284		A
29th January Saturday	P8	11.58-13.01	2.69	3.10	210	jan291	8A	A
	P2	16.04-16.27	3.95	4.49	236		2A	B
	P9	17.32-17.48	5.53	7.92	247	jan292	9A	A
		17.55-18.13	5.19	7.72	244			B
30th January Sunday	P10	13.26-14.20	7.10	8.10	285	jan301	10A	A
	P3	14.47-15.36	6.06	6.73	280		3A	B
	P11	16.03-16.32	4.89	5.90	278	jan302	11A	A
		16.44-17.21	4.74	5.60	276	jan303		A
		17.27-17.57	3.70	4.40	266			B
		18.11-18.37	4.50	5.00	269	jan304		A
		18.42-19.01	4.18	5.00	264			B

Day	Position	Times	Wind Speed		Wind Direction	File	LoS	Scan
			Lower m/s	Upper m/s	degrees			
31st January Monday	P12	11.48-12.38	3.21	3.70	225	jan311	12A	A
	P7	14.39-15.27	2.65	3.31	209			B
		15.49-16.22	2.61	3.10	221	jan312	7A	A
		17.01-17.27	3.28	3.30	195			C

TABLE 13: Overview of DIAL Measurements Carried out Around the Road-Tanker Delivery Area and the Polystyrene Plant

Day	Position	Times	Wind Speed Lower m/s	Wind Speed Upper m/s	Wind Direction degrees	File	LoS	Scan
1st February Tuesday	P15	15.00-15.12	4.70	5.60	237	feb011	15A	C
		15.19-15.54	6.24	7.40	244	feb012		A
		16.08-16.46	6.98	7.00	265			B
	P16	17.00-17.39	6.02	6.88	254	feb013	16A	A
2nd February Wednesday	P13	10.09-10.27	1.50	2.75	210	feb021	13A	A
		10.29-10.51	2.00	2.11	170			B
		11.10-11.27	2.30	3.27	185			D
		11.29-11.45	2.16	3.57	180			E
		13.16-13.32	1.80	3.00	170	feb022		A
		14.07-14.30	1.37	2.30	184		17A	B
	P17	15.01-15.47	1.81	2.28	157			C
		15.50-16.26	0.97	1.79	147	feb023		A
3rd February Thursday	P18	09.40-09.55	9.26	9.89	103	feb031	18A	A
		10.08-10.27	9.26	9.89	103			B
		10.34-10.47	9.19	9.90	103			C
		10.52-11.07	9.16	9.70	105			D
		11.10-11.26	9.20	10.00	101			E
		11.32-11.53	8.50	9.00	104			F
		12.12-12.26	8.56	9.10	103	feb032	18B	A

TABLE 14: Daily Throughput of the Polyethylene Plant during the Measurement Period

Date	New Plant (LPDE 3) Tonnes/day	Old Plant (LDPE 2) Tonnes/day	Total Tonnes/day
25/1/94	352	202	554
26/1/94	367	208	575
27/1/94	345	201	546
28/1/94	354	192	546
29/1/94	305	194	499
30/1/94	356	187	543
31/1/94	356	203	559
Mean daily throughput	348	198	546

Table 15: EPA/SOCMI Emission Factors and Correlation Coefficients Used in the Carrington Study

Component	API/SOCMI		
	Screening (kg/hr)	Stratified (kg/hr)	Correlation* (kg/hr)
Valve, gas/vapour (GV)	leak = 0.0451 no leak - 0.00048	high = 0.0451 medium = 0.00165 low = 0.00014	pegged source factor = 0.0451 default zero factor = 0.000033 slope = 0.693 intercept = 5.35 sbcf = 3.766
Valve, light liquid (LL)	leak = 0.0852 no leak = 0.00171	high = 0.00852 medium = 0.00963 low = 0.00028	pegged source factor = 0.00852 default zero factor = 0.000451 slope = 0.47 intercept = 5.34 sbcf = 8.218
Flange	leak = 0.0375 no leak = 0.00006	high = 0.0375 medium = 0.00875 low = 0.00002	pegged source factor = 0.0375 default zero factor = 0.0000928 slope = 0.818 intercept = 4.73 sbcf = 2.02

* Leak rate = sbcfx $10^{intercept}$X $ppmv^{slope}$ kg/h for components screeing between 8 and 10000 ppmv (with methane calibration), leak rate = default zero, kg/h for components screening <8 ppmv and leak rate = pegged source factor, kg/h for components screening > 10000 ppmv

TABLE 16: EPA/SOCMI Component Count Emission Factors used in the Carrington Study

Component	Emission Factor (kg/hr/per unit source)
Valve gas/vapour (GV)	0.0056
Valve light liquid (LL)	0.0071
Flange	0.00083
Relief valve	0.104

TABLE 17: Shell Carrington Wind Summary

Day	Scan	LoS	Times	Wind Speed Lower m/s	Wind Speed Upper m/s	Wind From degrees
25th January	251A	1A	16.26-17.17	5.09	5.21	259
26th January						
	261A	3A	13.03-13.34	3.80	4.55	254
	261C		13.53-14.09	4.00	4.44	246
	262A	4A	15.18-15.31	4.00	4.47	229
	262b		15.39-16.15	4.72	6.37	235
	263A		16.26-16.54	4.50	6.06	238
	263B		17.03-17.27	4.92	6.20	249
	264A		17.54-18.19	4.35	6.37	240
	264B		18.26-18.50	4.16	5.79	237
27th January						
	271A	5A	11.30-11.48	5.15	8.19	254
	271B		12.08-12.25	6.00	6.00	261
	272A		13.53-14.18	5.33	7.20	252
	272B		14.26-15.04	6.19	6.61	245
	273A		15.23-15.50	6.55	7.62	244
	273B	6A	17.01-17.50	4.95	5.88	284
	274A		18.03-18.50	6.60	8.16	275
28th January						
	281A	7A	11.56-12.17	6.33	7.94	297
	281B		12.21-12.41	6.51	8.85	298
	282A		13.19-13.42	6.30	8.21	305
	282B		13.53-14.43	5.66	7.51	298
	283A		15.13-16.04	5.30	7.23	299
	283B		17.07-17.42	2.81	3.81	293
	284A		17.47-18.10	3.67	5.42	283
29th January	291A	8A	11.58-13.01	2.69	3.10	210
	291B	2A	16.04-16.27	3.95	4.49	236
	292A	9A	17.32-17.48	5.53	7.92	247
	292B		17.55-18.13	5.19	7.72	244

Day	Scan	LoS	Times	Wind Speed Lower m/s	Wind Speed Upper m/s	Wind From degrees
30th January	301A	10A	13.26-14.20	7.10	8.10	285
	301B	3A	14.47-15.36	6.06	6.73	280
	302A	11A	16.03-16.32	4.89	5.90	278
	303A		16.44-17.21	4.74	5.60	276
	303B		17.27-17.57	3.70	4.40	266
	304A		18.11-18.37	4.50	5.00	269
	304B		18.42-19.01	4.18	5.00	264
31st January	311A	12A	11.48-12.38	3.21	3.70	225
	311B	7A	14.39-15.27	2.65	3.31	209
	312A		15.49-16.22	2.61	3.10	221
	312C		17.01-17.27	3.28	3.30	195
1st February	011C	15A	15.00-15.12	4.70	5.60	237
	012A		15.19-15.54	6.24	7.40	244
	012B		16.08-16.46	6.98	7.00	265
	013A	16A	17.00-17.39	6.02	6.88	254
2nd February	021A	13A	10.09-10.27	1.50	2.75	210
	021B		10.29-10.51	2.00	2.11	170
	021D	13A	11.10-11.27	2.30	3.27	185
	021E		11.29-11.45	2.16	3.57	180
	022A		13.16-13.32	1.80	3.00	170
	022B		14.07-14.30	1.37	2.30	184
	022C	17A	15.01-15.47	1.81	2.28	157
	023A		15.50-16.26	0.97	1.79	147
3rd February	031B	18A	09.40-10.27	9.26	9.89	103
	031C		10.34-10.47	9.19	9.90	103
	031D		10.52-11.07	9.16	9.70	105
	031E		11.10-11.26	9.20	10.00	101
	031F		11.32-11.53	8.50	9.00	104
	032A	18B	12.12-12.26	8.56	9.10	103

TABLE 18: Results of Individual DIAL Measurements Around the Polyethylene Plant

Day	Postion	Times	File	LoS	Scan	Flux (kg/hour)				Flux (equivalent tonnes/a)				Vent Measured?	Old/New Plants Overlap?	Average Wind Speed m/s
						Vent	Old	New	Total	Vent	Old	New	Total			
25th January Tuesday	P1	16.20-17.17	jan251	1	A2	(4)	59		63	(32)	470		502	no	yes	5.1
26th January Wednesday	P3	13.03-13.34	jan261	3	A	4	29	19	52	32	232	152	416	separated	partly	4.2
		13.53-14.09			B	3	53		56	24	424		468	separated	yes	4.2
	P4	15.18-15.31	jan262	4	A	3	35	24	62	24	280	192	496	separated	no	4.2
		15.39-16.15			B	3	33	27	63	24	264	216	504	separated	partly	5.5
		16.26-16.54	jan263	4	A	5	44	26	74	40	352	208	592	separated	partly	5.3
		17.03-17.26			B	4	32	25	61	32	256	200	488	separated	partly	5.6
		17.54-18.21	jan264	4	A	4	27	23	54	32	216	184	432	separated	partly	5.4
		18.26-18.50			B	5	24	25	53	40	192	200	424	separated	partly	5.0
Daily average =						4	32	24	60	31	256	193	477			
27th January Thursday	P5	11.30-11.48	jan271	5A	A	3	60		63	24	478		502	separated	yes	6.7
		12.06-12.25			B	5	44		49	40	351		391	separated	yes	6.0
		13.53-14.18	jan272		A	3	48		51	24	383		407	separated	yes	6.3
		14.26-15.04			B	2	53		55	16	422		438	separated	yes	6.4
		15.23-15.50	jan273		A	5	51		56	40	407		447	separated	yes	7.1
Daily average =						4	51		55	29	382		438	separated	yes	
	P6	17.01-17.50		6A	B			27				216		n/a	no	5.4
		18.03-18.50	jan274		A			29				232		n/a	no	7.4
Daily average =								28				224				

Day	Postion	Times	File	LoS	Scan	Flux (kg/hour)				Flux (equivalent tonnes/a)				Vent Measured?	Old/New Plants Overlap?	Average Wind Speed m/s
						Vent	Old	New	Total	Vent	Old	New	Total			
28th January Friday	P7	11.56-12.17	jan281	7A	A	(4)	56		60	(32)	446		478	no	partly	7.1
		12.21-12.41			B	(4)	61		65	(32)	486		518	no	partly	7.7
		13.19-13.42	jan282		A2	(4)	52		56	(32)	414		446	no	partly	7.3
		13.53-14.43			B	(4)	57		61	(32)	454		486	no	partly	6.6
		15.13-16.04	jan283		A	(4)	74		78	(32)	590		622	no	partly	6.3
		17.07-17.42			B	(4)	55		59	(32)	438		470	no	partly	3.3
		17.47-18.10	jan284		A	(4)	57		61	(32)	454		486	no	partly	4.5
Daily average =						(4)	59		63	(32)	469		502			
29th January Saturday	P8	11.58-13.01	jan291	8A	A		34	ni	34		272	ni	360	inc.in old plant	no	3.0
	P2	16.04-16.27		2A	B		33	ni	33		264	ni	248	inc.in old plant	no	4.2
	P9	17.32-17.48	jan292	9A	A		59		59		470		470	not separated	yes	6.7
		17.55-18.13			B		61		61		486		486	not separated	yes	6.5
Total emissions daily average =									60				478			
30th January Sunday	P10	13.26-14.20	jan301	10A	A		82		82		650		650	included	yes	7.6
	P3	14.47-15.50		3A	B	4	63		67	32	506		538	separated	partly	6.4
	P11	16.03-16.32	jan302	11A	A	3	46		49	24	369		398	separated	partly	5.4
		16.44-17.21	jan303		A	5	60		65	40	482		522	separated	partly	5.2
		17.27-17.57			B	4	50		54	32	398		430	separated	yes	4.0
		18.11-18.37	jan304		A	5	52		57	40	418		458	separated	partly	4.7
		18.42-19.01			B	6	46		52	48	370		418	separated	partly	4.6
Daily average =						4	57		61	36	451		487			

Day	Postion	Times	File	LoS	Scan	Flux (kg/hour)				Flux (equivalent tonnes/a)				Vent Measured?	Old/New Plants Overlap?	Average Wind Speed m/s
						Vent	Old	New	Total	Vent	Old	New	Total			
31st January Monday	P12	11.48-12.38	jan311	12A	A		30	29	59		240	232	472	inc.in old plant	partly	3.5
	P7	14.39-15.27			B		32	27	59		256	216	472	inc.in old plant	no	3.0
		15.49-16.22	jan312	7A	A		29	26	55		232	208	440	inc.in old plant	partly	2.9
Daily average =							30	27	58		243	218	461			
		17.07-17.27			C	high pressure cell		3	3	high pressure cell		24	24			3.3

notes i) ni: not included in measurement set

ii) numbers in brackets (for the degassing vents) are average values measured on other occasions

TABLE 19: Summary of DIAL Measurements Around the Polyethylene Plant

Date	New Plant				Old Plant				Degassing Bunker Vent				Total			
	Flux kg/hr	Range kg/hr	Flux t/a	Range t/a	Flux kg/hr	Range kg/hr	Flux t/a	Range t/a	Flux kg/hr	Range kg/hr	Flux t/a	Range t/a	Flux kg/hr	Range kg/hr	Flux t/a	Range t/a
25 January	-	-	-	-	-	-	-	-	(4)	-	(32)	-	63	-	502	-
26 January	24	19-27	193	152-216	32	24-44	256	192-352	4	3-5	31	24-40	60	52-74	477	416-592
27 January	28	27-29	224	216-232	23	-	187	-	4	2-5	29	16-40	55	49-63	438	391-502
28 January	-	-	-	-	-	-	-	-	(4)	-	(32)	-	63	56-78	502	446-622
29 January	26	-	211	-	29	-	235	-	-	-	32	-	60	59-61	478	470-486
30 January	-	-	-	-	-	-	-	-	4	3-6	36	24-48	61	46-82	487	392-650
31 January	27	26-29	218	208-232	-	-	-	-	-	-	-	-	58	55-59	461	440-472
MEAN	26.6	24-28	212	193-224	30	-	234	-	4	3-6	32	29-36	60	55-63	478	438-502

Notes : ni: indicates that plume not included in measurements
: - indicates merged plumes
: the numbers in brackets for the degassing vents are estimated average values measured directly on other occasions

TABLE 20: Results of Individual DIAL Measurements Around the Polystyrene Plant and the Road-Tanker Loading Area

Day	Position	Times	File	LoS	Scan	Average wind speed	Flux (kg/hr)	Flux (equivalent) tonnes per annum	Area studied
1st February	P15	15.00-15.12	feb011	15A	C	5.2	16	128	Polystyrene plant
		15.19-15.54	feb012		A	6.8	18	144	
		16.08-16.46			B	7.0	16	128	
	P16	17.00-17.39	feb013	16A	A	6.5	19	152	
							Day average = 17	Day average = 138	
2nd February	P13	10.09-10.27	feb021	13A	A	2.1	1	8	Road tanker delivery area
		10.29-10.51			B	2.1	1	6	
		11.10-11.27			D	2.8	0	2	
		11.29-11.45			E	2.9	1	5	
			feb022		A	2.4	0	4	
		14.07-14.30		17A	B	1.8	0	1	
	P17	15.01-15.47			C	2.0	18	144	Polystyrene plant
		15.50-16.26	feb023		A	1.4	21	168	
3rd February	P18	09.40-09.55	feb031	18A	A	9.6	1	4	Road tanker delivery area
		10.08-10.27			B	9.5	10	80	
		10.34-10.47			C	9.4	5	40	
		10.52-11.07			D	9.6	5	40	
		11.10-11.26			E	8.8	3	24	
		11.32-11.53			F	9.2	2	16	
		12.12-12.26	feb032	18B	A	8.8	0	1	

TABLE 21: Summary of DIAL Measurements around the Polystyrene Plant

Date	Flux (kg/hr)	Range (kg/hr)	Flux Equivalent Emitted (t/a)	Range Equivalent Emitted (t/a)
1 February	17	16-19	138	128-152
2 February	20	18-21	156	160-188
MEAN	18	17-20	147	138-156

TABLE 22: Component Count for the LDPE-3 Plant

Area	Flanges	Valves (Gas)	Valves (light liquid)	Control Valves
General	442	61	62	9
High Pressure	420	15	0	0
Pre Comp	247	35	0	5
Hyper Comp	408	4	0	0
NBA Injection	49	0	14	0
Total	1566	115	76	14

TABLE 23: Most Probable Annual Emissions for Valves and Flanges on Carrington LDPE-3 Plant Estimated by the API/SOCMI Procedures

Average emission factor	Screening	Stratified	Correlation	Lower emission limit	Upper emission limit
23	14 (OVA) 2.6 (HVM)	12 (OVA) 4.3 (HVM)	14 (OVA) 6.3 (HVM)	2.5	50

nb: results expressed in tonnes per year, allowing for 91% plant utilisation

TABLE 24: Scaled-up Estimated Annual Emissions from the LDPE-3 Plant

Average emission factor	Leak/No Leak	Stratified	Correlation	Lower emission limit	Upper emission limit
56	36 (OVA) 9.1 (HVM)	27 (OVA) 9.1 (HVM)	36 (OVA) 18 (HVM)	6.4 (OVA)	124 (OVA)

nb: results expressed in tonnes per year, allowing for 91% plant utilisation

TABLE 25: Average Emission Factors used for Different Industrial Operations

	Valves (GV)	Flanges/connectors
Refineries	0.0268	0.00025
Chemical plants	0.00597	0.00183
Natural gas plant	0.0075-0.02	0.00046/0.0011
Pacific offshore oil & gas	0.0002	0.000099
Petroleum marketing terminals	-	0.00003
Ratio max/min	134	61

TABLE 26: **NPL Atmospheric Whole-air Sample Data**
Taken 26/1/94, 13.51 - 14.05 hours

DIAL CYL CARRINGTON SET 1			
Cylinder No:	**NPL372 ppb**	**NPL350 ppb**	**NPL249 ppb**
ethane	24.96	22.37	14.40
ethene	1133.0	873.0	565.0
propane	1.95	2.23	2.05
propene	0.57	0.48	0.49
2-methyl propane	3.53	3.37	4.05
propadiene	2.97	2.15	1.28
ethyne	2.00	2.06	2.37
n-butane	2.89	3.25	3.77
trans-2-butene	0.42	0.43	0.40
1-butene	0.57	0.59	0.58
isobutene	0.23	0.27	0.31
2-methyl butane	1.26	2.09	1.90
n-pentane	0.71	1.25	0.79
2-methyl pentane	0.79	1.42	0.33
3-methyl pentane	0.26	0.39	0.15
n-hexane	0.34	0.60	0.27
n-heptane	0.22	0.72	0.25
benzene	0.51	0.54	0.47
methyl benzene	2.18	2.41	2.10
ethyl benzene	0.32	0.37	0.31
1,3-dimethyl benzene	0.85	1.00	0.80
1,2-dimethyl benzene	0.21	0.30	0.20
1,3,5-trimethyl benzene	1.03	0.72	0.84
1,2,4-trimethyl benzene	0.38	0.44	0.39

TABLE 27: NPL Whole Air Sample Data
Taken 26/1/94, 15.40 - 15.48 hours

DIAL CYL SET 2			
CYLINDER NO:	A2R	A148	A150
LOCATION: (with respect to DIAL)	NEAR	MID	FAR
	ppb	ppb	ppb
ethane	15.1	22.1	4.4
ethene	445	781	31.5
propane	2.2	2.2	2.0
propene	0.5	0.7	0.4
2-methyl propane	0.6	0.8	0.8
ethyne	3.7	10.0	
n-butane	26.6	9.6	4.9
trans-2-butene		0.5	
1-butene		0.8	
isobutene	0.5	0.3	
cis-2-butene		0.6	
2-methyl butane	0.6	0.7	0.6
n-pentane	0.3	0.4	0.3
1,3 Butadiene		5.9	
trans-2-pentene		3.3	
pentenes?			
cis-2-pentene		1.5	
cyclic C6			
dimethyl butane			
2-methyl pentane	1.3	0.3	
3-methyl pentane		0.2	
n-hexane		0.5	
isoprene		1.8	
n-heptane	0.1	1.1	
benzene	0.5	2.3	0.4
C8 aliphatic HC			
C8 aliphatic HC			
methyl benzene	1.2	8.8	2.0
ethyl benzene	0.2	6.5	1.9
1,3-dimethyl benzene	0.7	4.2	1.3
1,2-dimethyl benzene	0.2	2.5	0.3

TABLE 28: Carrington Point-Sample Data
Taken 26/1/94, 15.40-16.10 hours

Sample	Ethane (ppb)	Ethene (ppb)	Propane (ppb)	Propene (ppb)
1	11	500	5	11
2	12	610	6	7
3	13	850	3	7
4	14	980	3	<2
5	14	790	5	<2
6	112	620	2	<2
7	10	465	3	<2
8	12	550	<2	<2
9	13	865	4	<2
10	9	490	<2	<2
11	6	115	<2	<2
12	5	80	4	<2
13	17	3	5	<2
14				
15	15	3	5	<2

TABLE 29: **NPL Atmospheric Point-sample Data Taken 27/1/94, 14.34-14.54 hours**

CYLINDER NO:	A163	A165	A166
LOCATION: (referred to DIAL)	NEAR	MID	FAR
	ppb	ppb	ppb
ethane	6.9	6.5	7.7
ethene	71.0	202.4	291.6
propane	8.6	3.4	2.7
propene	41.7	5.6	1.3
2-methyl propane	15.2	16.3	16.9
ethyne	1.2	0.0	1.1
n-butane	27.7	20.3	20.4
trans-2-butene	0.0	0.2	0.3
1-butene	0.0	0.5	0.2
isobutene	0.4	0.5	0.3
cis-2-butene	0.0	0.0	0.0
2-methyl butane	1.8	2.5	2.1
n-pentane	1.3	1.2	1.3
1,3-Butadiene	0.0	0.0	0.0
trans-2-pentene	0.0	0.0	0.0
pentenes?	0.0	0.0	0.0
cis-2-pentene	0.0	0.0	0.0
cyclic C6?			
dimethyl butane?			
2-methyl pentane	1.5	0.8	0.7
3-methyl pentane	0.3	0.3	0.3
n-hexane	0.4	0.4	0.4
isoprene	0.0	0.0	0.0
n-heptane	0.2	0.0	0.0
benzene	0.7	0.6	0.6
C8 aliphatic HC?			
C8 aliphatic HC?			
methyl benzene	1.9	1.4	1.4
ethyl benzene	0.4	0.3	0.3
1,3-dimethyl benzene	0.8	0.9	1.0
1,2-dimethyl benzene	0.2	0.2	0.2

TABLE 30: **Carrington Atmospheric Point-sample Data Taken 27/1/94 14.34-15.00 hrs**

Sample	Ethane ppb	Ethene ppb	Propane ppb	Propene ppb	Corresponding NPL Sample
1	6	230	4	<2	
2	6	230	3	4	A166
3	7	235	4	4	
4	9	22	15	87	
5	10	24	16	81	
6					
7					
8	7	56	10	50	
9	10	76	9	43	A163
10	7	100	6	27	
11	6	146	4	14	
12	7	175	4	8	A165
13					
14	3	4	<2	<2	
15	5	12	<2	<2	

TABLE 31: **Carrington Whole Air Sample Data Taken 28/1/94 15.20-16.10 hrs**

ETHYLENE IN AIR ANALYSIS - 28/1/94				
Sample	Ethane ppb	Ethene ppb	Propane ppb	Propene ppb
1	10	15	20	235
2				
3	6	41	<2	57
4	5	76	<2	19
5	8	475	<2	<2
6	9	595	3	7
7	8	410	<2	<2
8	5	145	<2	3
9	6	92	<2	<2
10	4	51	<2	<2
11	4	26	<2	<2
12	4	20	<2	<2
13	4	3	<2	<2
14	4	4	<2	3
15	7	14	17	125

TABLE 32: NPL Whole-Air Sample Data
Taken 30/1/94, 16.45-16.55 hours

CYLINDER NO:	A238	A185	A232
	ppb	ppb	ppb
ethane	6.31	19.20	6.10
ethene	290.9	744.18	182.95
propane	1.47	2.17	1.33
propene	0.51	0.47	0.32
2-methyl propane	0.78	0.74	0.45
propadiene	0.67	1.10	0.36
ethyne	1.76	4.68	1.76
n-butane	1.37	0.53	0.94
isobutene	0.38	1.28	*
cis-2-butene	*	*	*
2-methyl butane	0.75	0.73	0.55
n-pentane	0.27	0.36	0.25
1,3-Butadiene	2.34	*	*
2-methyl pentane	*	*	0.22
n-hexane	*	0.22	*
n-heptane	*	0.21	*
benzene	0.41	0.41	0.43
methyl benzene	0.81	0.99	0.84
ethyl benzene	0.29	0.29	0.14
1,3-dimethyl benzene	0.70	0.95	0.44
1,2-dimethyl benzene	0.20	0.27	0.13
1,3,5-trimethyl benzene	0.51	0.94	0.40
1,2,4-trimethyl benzene	*	*	0.26

* below detection limit ~ 0.1 ppbv

TABLE 33: NPL Whole-Air Sample Data
Taken 31/1/94 15.51-16.09 hours

DIAL CYL CARRINGTON SET 5			
CYLINDER NO:	N207	N208	N211
DATE SAMPLED: 31/1/94	ppb	ppb	ppb
ethane	23.34	13.36	6.87
ethene	476.37	54.35	13.25
propane	5.38	4.13	2.57
propene	17.20	3.21	0.76
2-methyl propane	0.90	1.01	0.92
propadiene	1.98	1.21	0.37
ethyne	2.48	2.33	2.86
n-butane	1.74	1.50	2.11
isobutene	0.41	*	0.37
2-methyl butane	0.77	0.68	0.99
n-pentane	0.40	0.37	0.42
2-methyl pentane	0.75	*	0.35
3-methyl pentane	*	*	*
n-hexane	*	*	0.15
isoprene	*	*	0.26
benzene	0.39	0.34	0.54
methyl benzene	0.90	0.63	0.92
ethyl benzene	0.16	0.18	0.17
1,3-dimethyl benzene	0.55	0.62	0.62
1,2-dimethyl benzene	0.26	0.18	0.23
1,3,5-trimethyl benzene	0.40	0.47	0.27
1,2,4-trimethyl benzene	*	*	0.30

* below detection limit ~0.1 ppbv

TABLE 34: NPL Whole Air Sample Data
Taken 2/2/94 10.25-10.34 hours

CYLINDER NO:	N212	N213	N214
DATE SAMPLED: 2/2/94	ppb	ppb	ppb
ethane	3.54	3.42	15.80
ethene	5.98	6.64	7.21
propane	2.14	2.18	5.63
propene	1.12	16.40	1.10
2-methyl propane	3.08	1.05	1.44
ethyne	2.72	1.06	4.66
n-butane	1.67	6.15	3.39
isobutene	1.05	0.29	0.35
2-methyl butane	55	191.	52
n-pentane	181.	549.	138.
1,3-Butadiene	*	*	0.62
2-methyl pentane	0.49	0.43	0.76
3-methyl pentane	0.21	0.17	
n-hexane	0.18	0.14	0.27
benzene	0.96	0.79	0.81
methyl benzene	1.52	1.47	1.37
ethyl benzene	0.70	0.70	0.52
1,3-dimethyl benzene	1.15	1.00	1.95
1,2-dimethyl benzene	0.41	0.36	1.04
1,3,5-trimethyl benzene	0.44	0.50	0.32
1,2,4-trimethyl benzene	0.35	0.32	0.28
methane ppm			2.01
Ratio iso-pentane n-pentane	0.30	0.35	0.38

* below detection limit ~0.1 ppbv

TABLE 35: Summary of VOC Emissions Measured by the NPL DIAL Facility during the Shell Carrington Exercise

Source	Target Species	Emission Flux (kg/hr)	Range (kg/hr)	Emission Flux Equivalent (t/a)	Range Equivalent (t/a)	Measured emissions as percentage of throughput
Polyethylene Plant and Storage Warehouse	Ethylene	60	55-63	478	438-502	0.26
Polystyrene Plant and Storage Warehouse	Pentane	18	17-20	147	138-156	4.8 (of total pentane)
Storage Tankage filling from Road Tanker	Pentane	7.3 kg per load	-	-	-	0.04* 0.04**
Flare	Methane/ propylene	not determined	-	-	-	≤ 2

* Based on 1993 figures for the total pentane delivered during the year
** Based on 3 deliveries/week

TABLE 36: Summary of NPL DIAL Measurements of VOC Emissions from European Oil Refineries

	Range	Average Value
Refinery throughput	4.5 - 11.9 Mt/annum	6.8 Mt/annum
Measured emissions to atmosphere	840 - 2810 kg/hr	1320 kg/hr
Hydrocarbon emissions ratio to refinery througput	(1.2 - 3.0)E-03*	1.9E-03*

* assuming measured emissions in kg/hr are scaled linearly throughout year

TABLE 37: Breakdown of NPL DIAL-measured VOC Emission by Refinery Area

Refinery Area	'Typical' Refinery DIAL Measurements kg/hr		UK Inventory Emissions Estimate kg/hr
	Measured 6.8 Mt/a	Scaled* 9.0 Mt/a	Scaled* 9.0 Mt/a
Storage of crude oil	340	450	239
Process plant	357	472	573
Storage of product/intermediate	574	760	717
Waste water treatment	51	68	549
Total	1322	1750	2078

* results scaled linearly to a refinery throughput of 9.0 Mt/annum

TABLE 38: Summary of the Oil Refinery Emission Estimate in the UK Emission Inventory

	Range	Average Value
Total UK Refinery throughput (1988)	n/a	85,660 kt/annum
Hydrocarbon emissions to atmosphere (kt/annum)	90 - 480*	180*
Ratio of hydrocarbon emissions to refinery throughput	(1.0 - 5.6)E-03	2.1E-03

* Emissions to Volatile Organic Compounds from Stationary Sources in the UK:
N R Passant, Warren Spring Laboratory Report LR1990, December 1993

Figure 1 NPL DIAL Facility on an Industrial Site.

Figure 2 **NPL DIAL Transmitting/receiving telescope.**

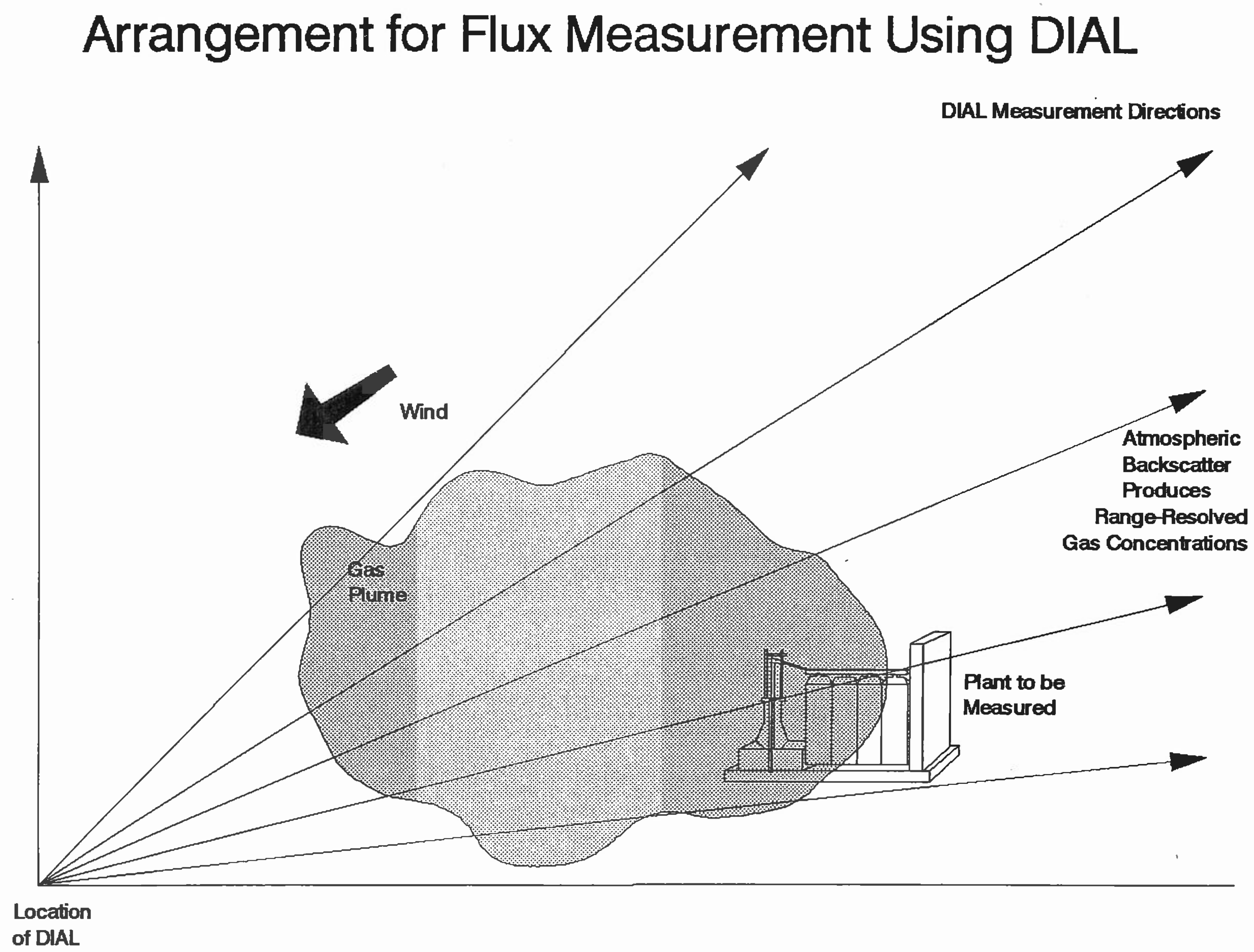


Figure 3 Arrangement for Flux Measurements using DIAL.

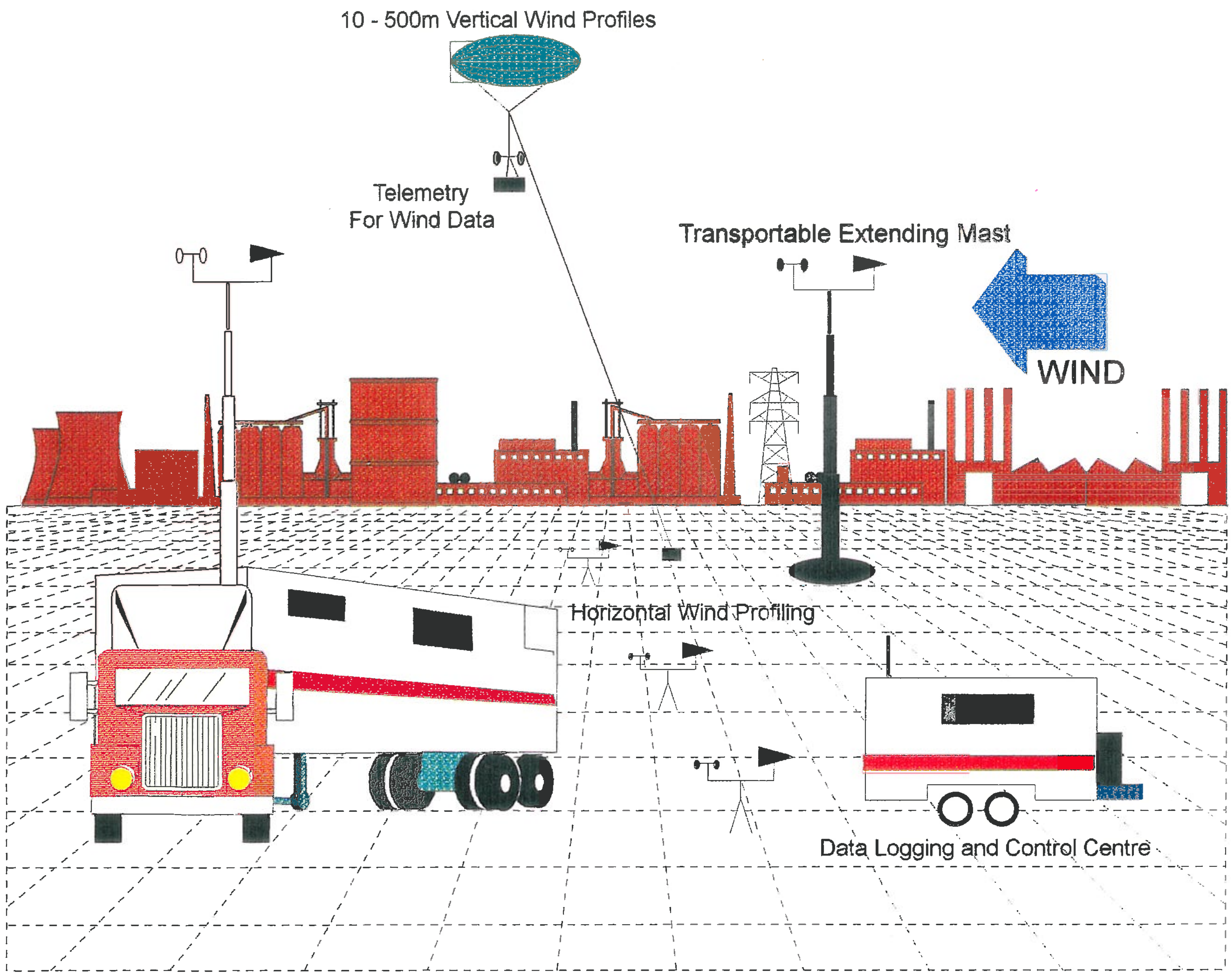


Figure4 Meteorological Equipment used in Conjunction with the NPL Mobile DIAL to measure Emission Fluxes.

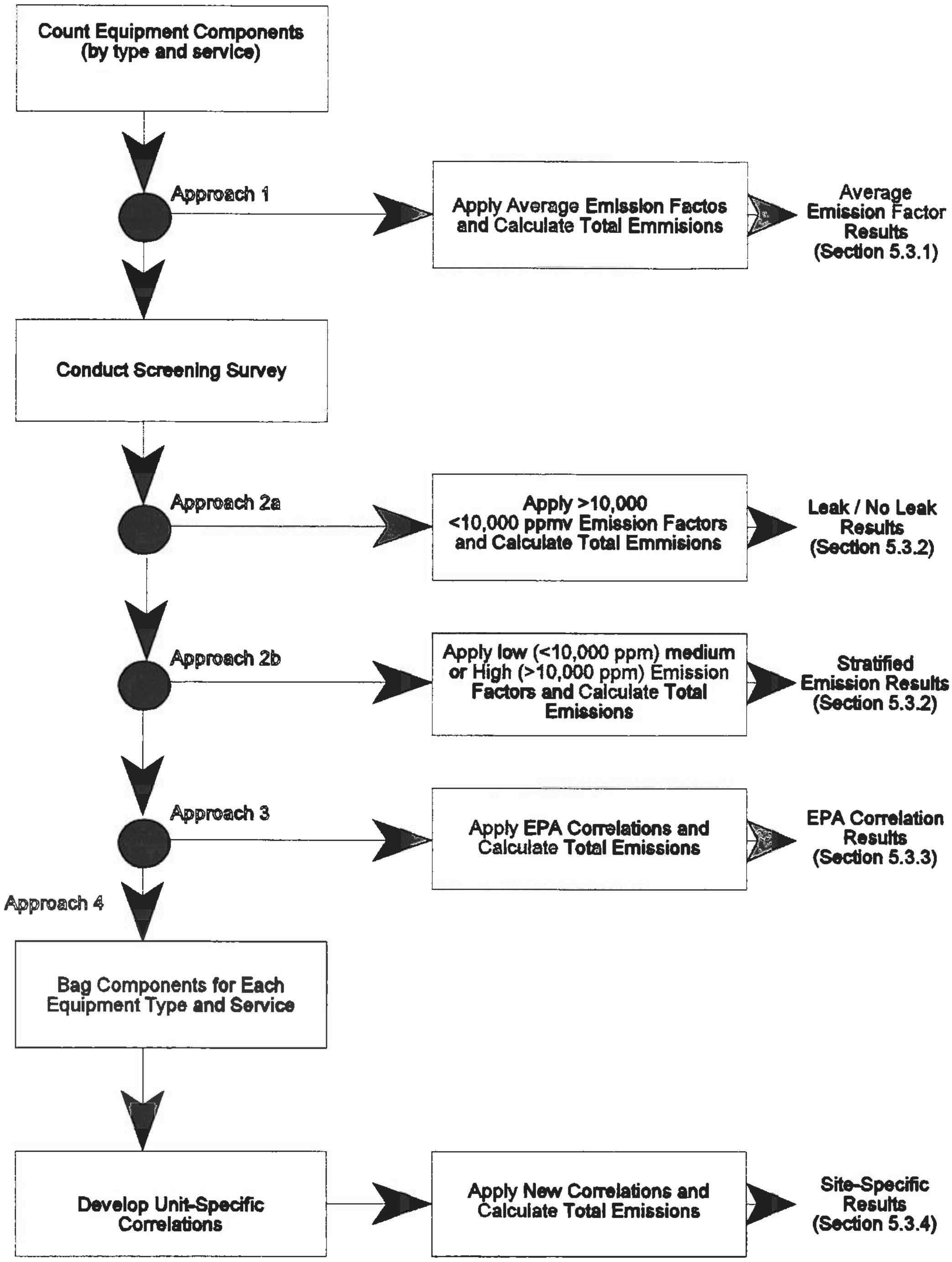


Figure 5 : Overview of the EPA Data Collection and Analysis Approaches for Developing Equipment Leak Emission Inventory

Figure 6 EPA/SOCMI Correlation Data for Process Unit Connectors.

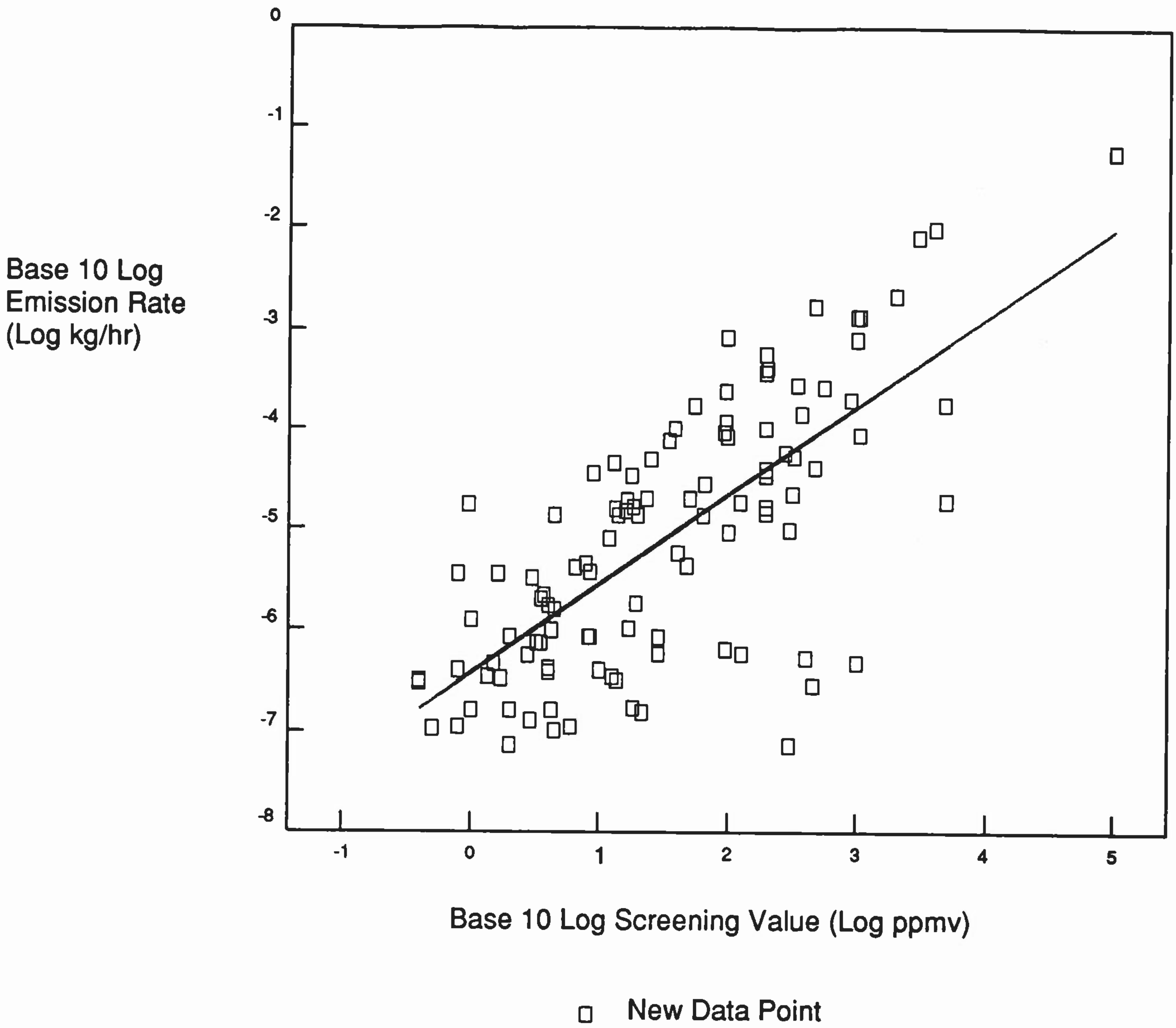


Figure 7 EPA/SOCMI Correlation Data for Process Unit Light-liquid Pumps

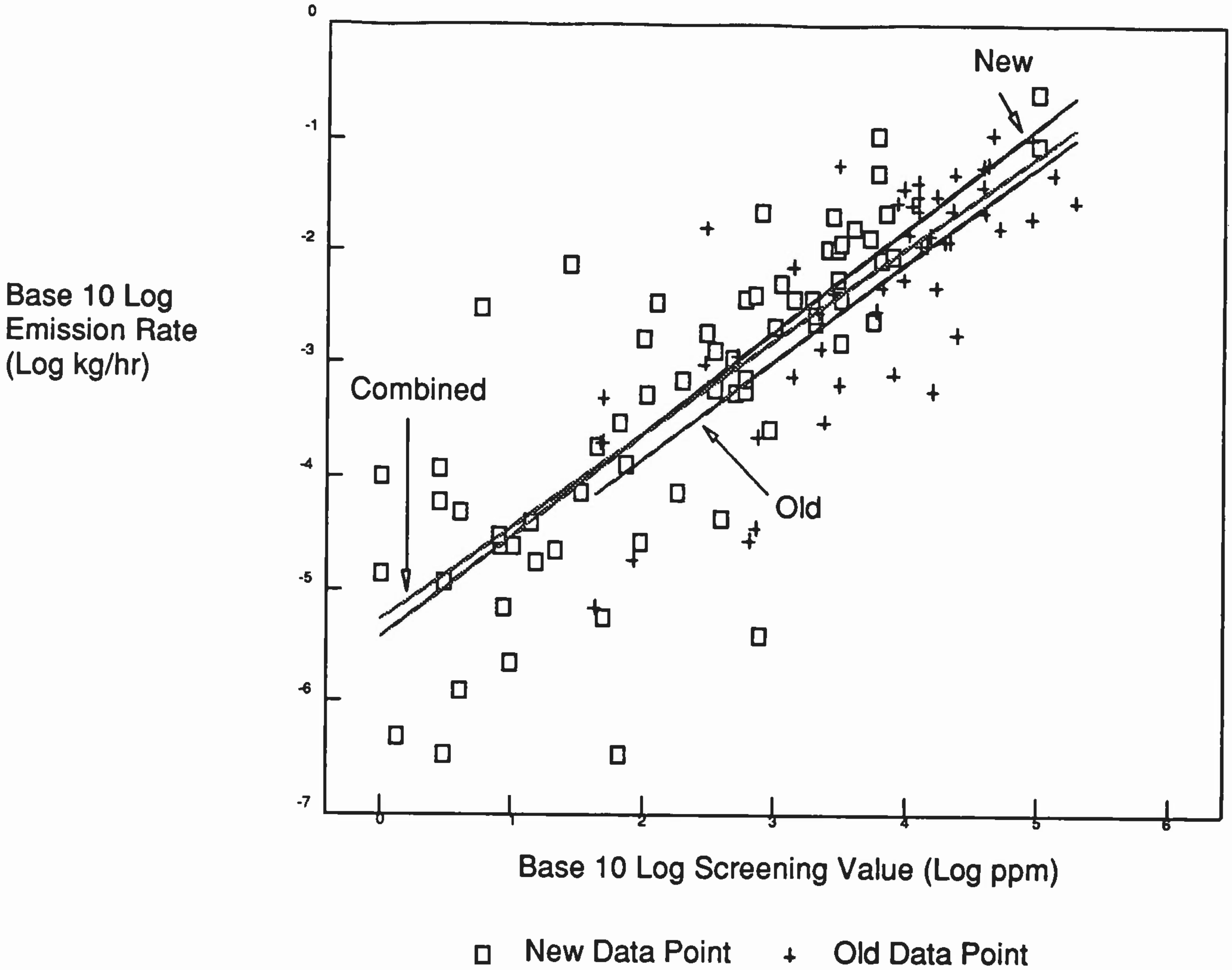


Figure 8 EPA/SOCMI Correlation Data for Process Unit Gas Valves

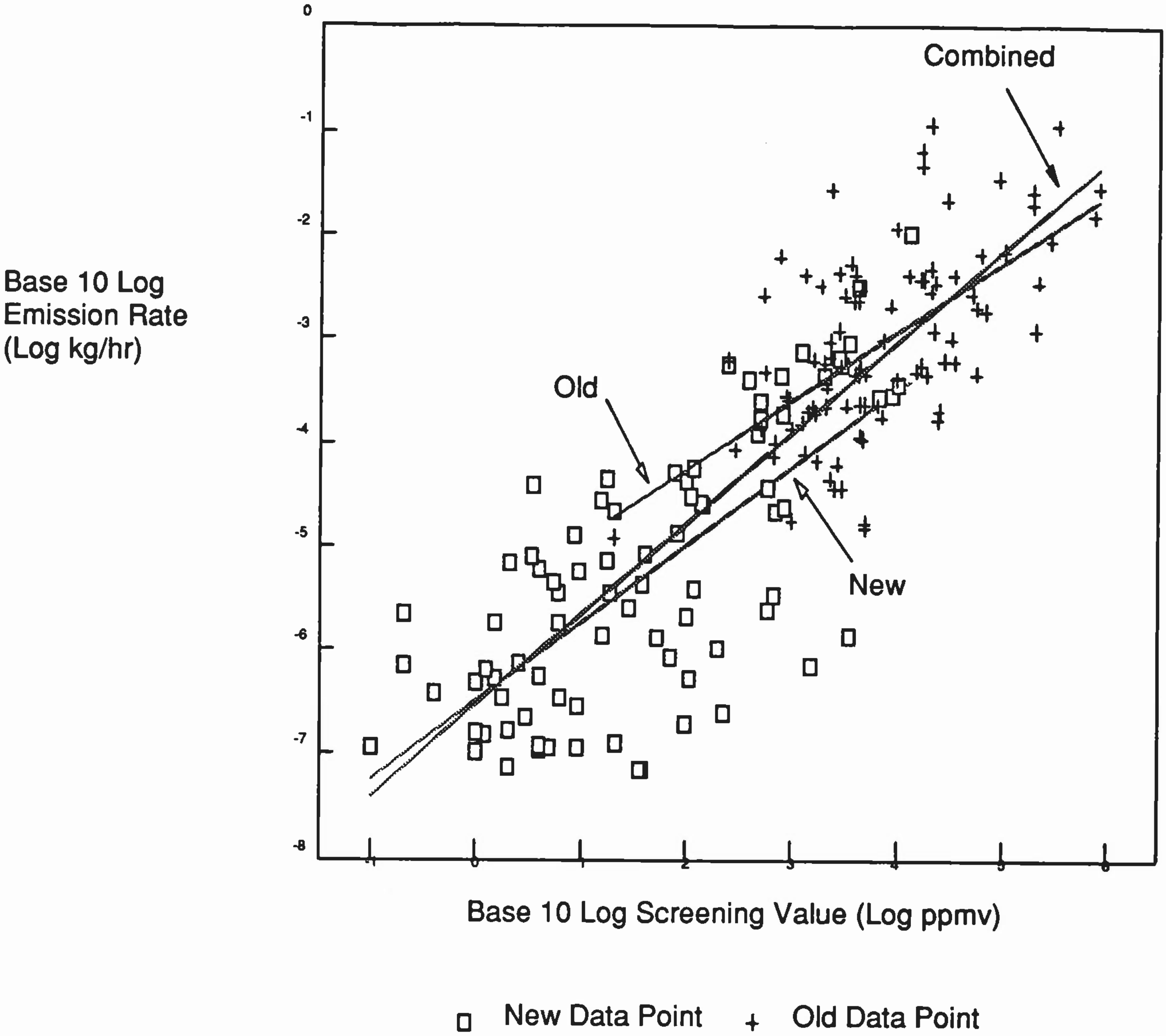


Figure 9 EPA/SOCMI Correlation Data for Process Unit Light-liquid Valves

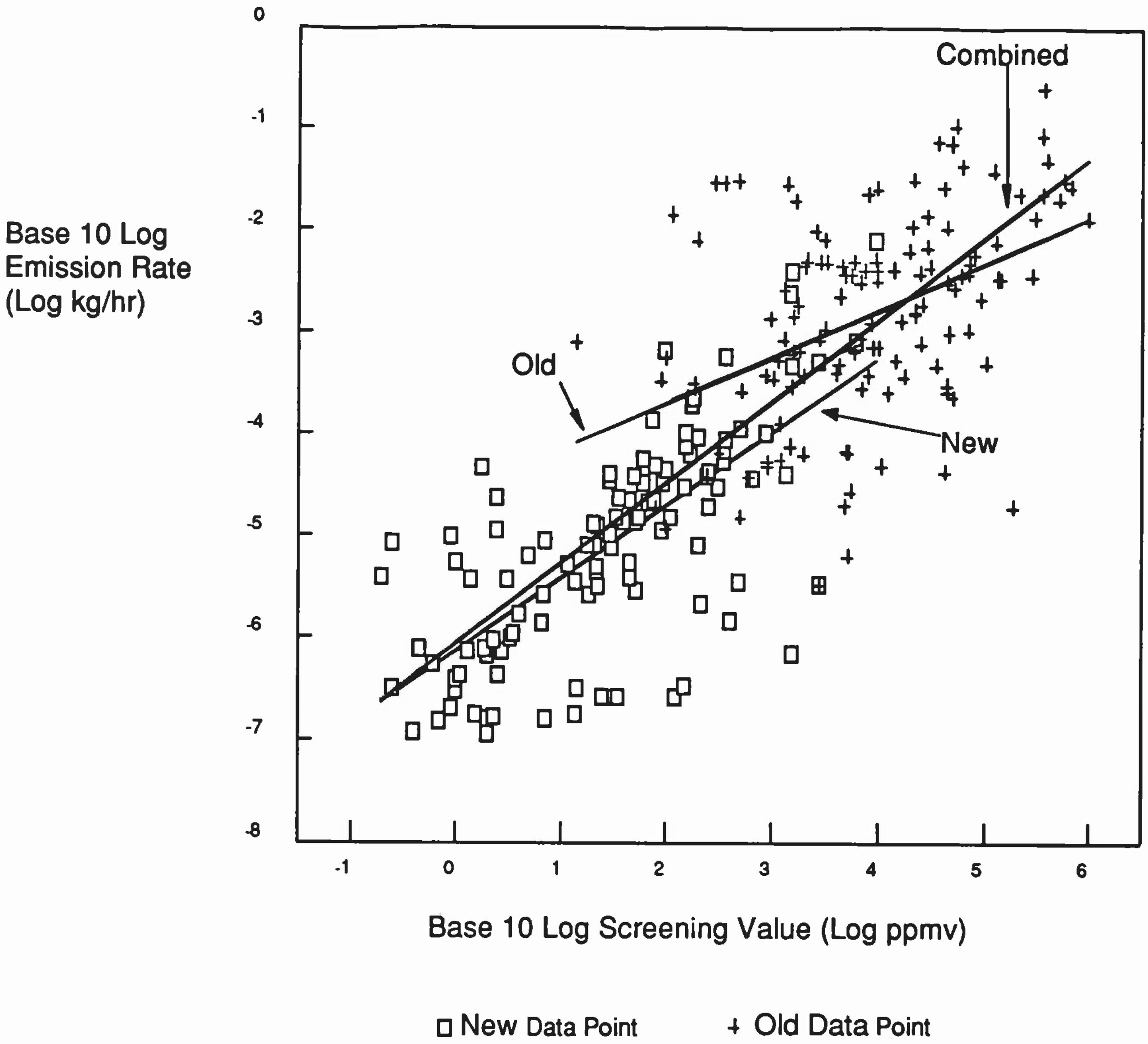
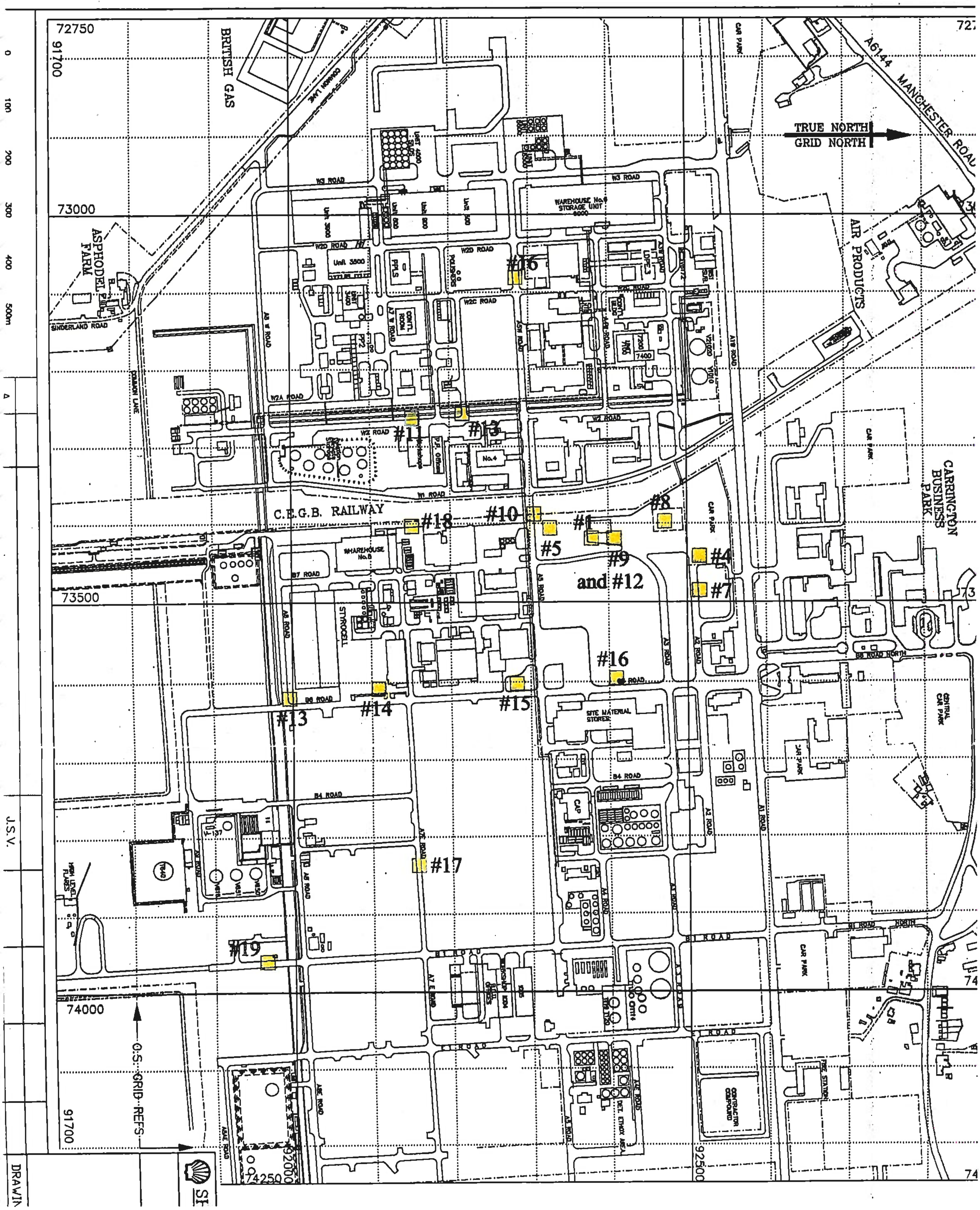


Figure 10 DIAL measurement sites during Shell, Carrington Measurement Exercise.

■ = DIAL Van position



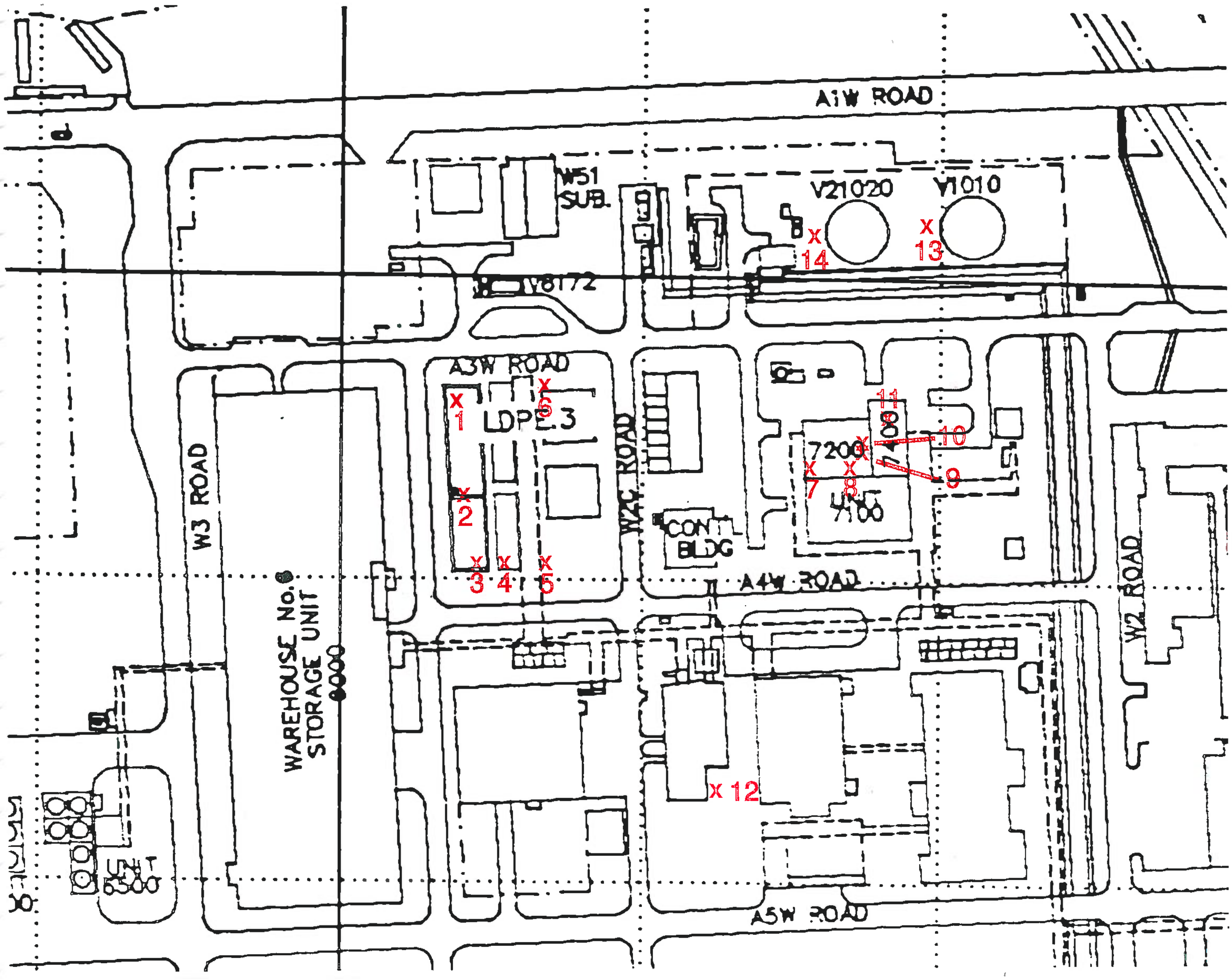


Figure 11 **Distribution of Ethylene sources in the vicinity of the Polyethylene Plant.**

KEY:

1. Hot water vents (25m)
2. Reactor emergency vents (41m)
3. HP recycle emergency vents (25m)
4. MR degassing vent (13m)
5. Compressor vents, oil vessel vents
6. Precompressor vents (25m)
7. HP recycle emergency vents (14m)
8. Compressor / recycle vents (10-25m)
9. Extruder backgland
10. Main emergency vent (33m)
11. Extruder vents (17m)
12. Degassing bunker vents (5m)
13. } Gas holder emergency vents(25m)
14. }

Figure 12 Calibration of OVA 108 for Ethylene.

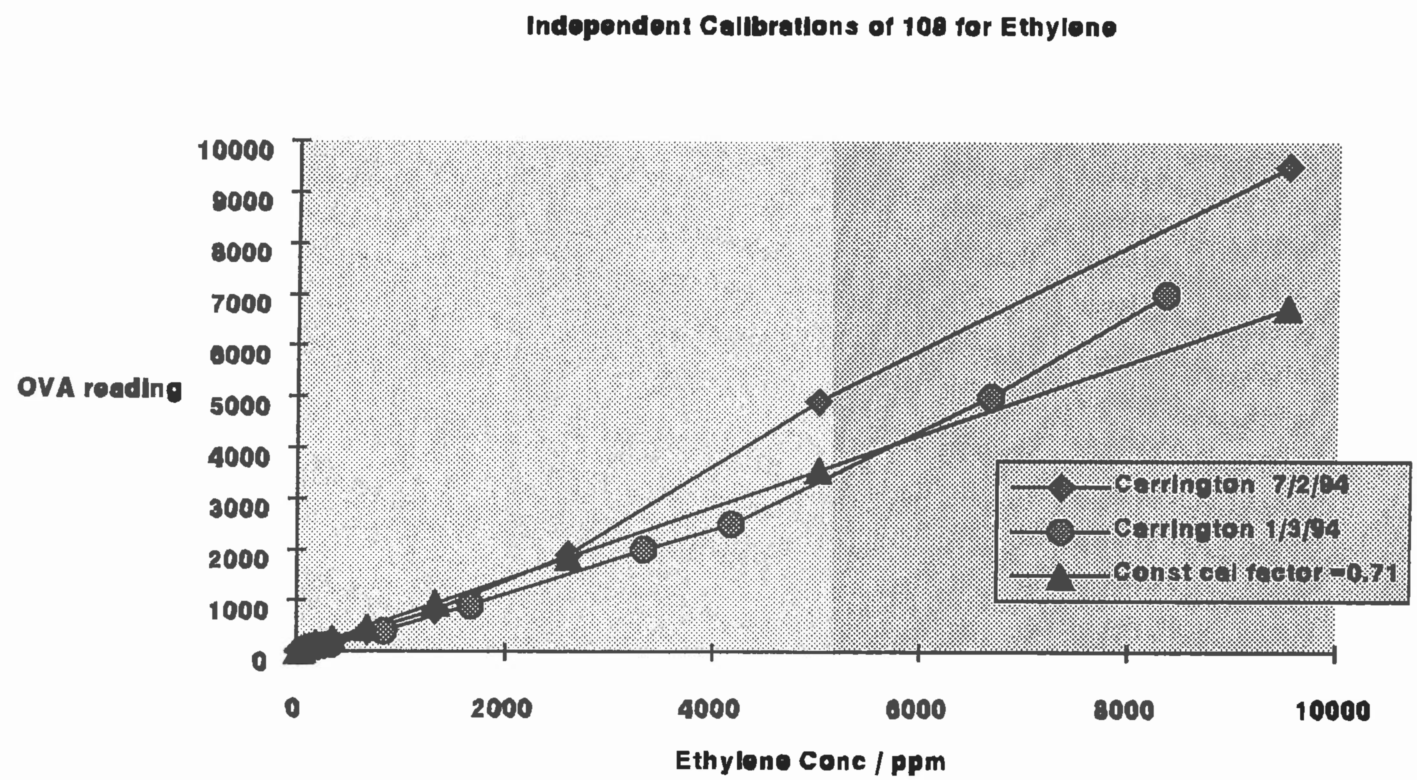


Figure 13 Shell Carrington Wind Profile 31.1.94.

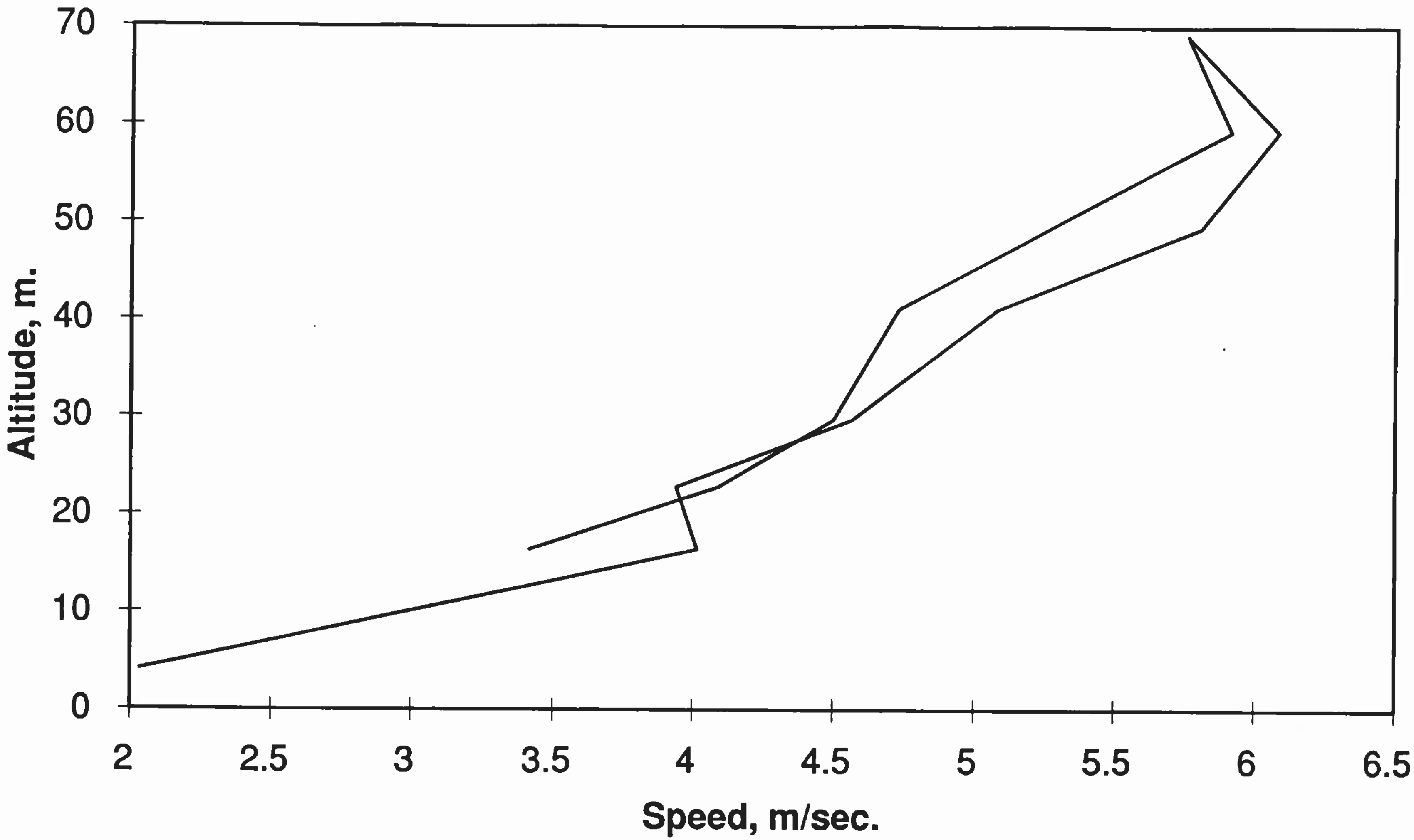
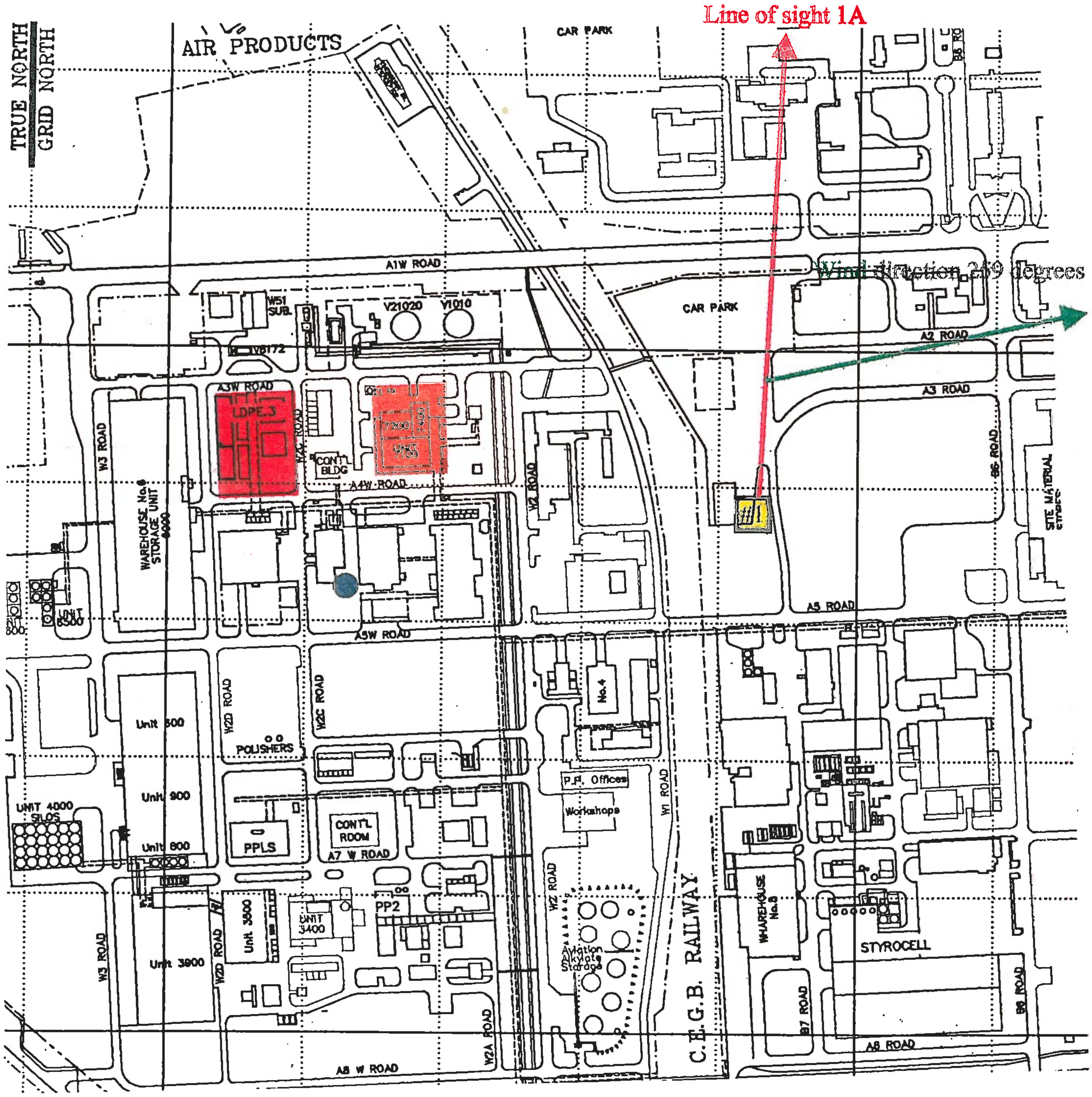


Figure 14 Polyethylene plant measurements, January 25th 1994.



KEY:

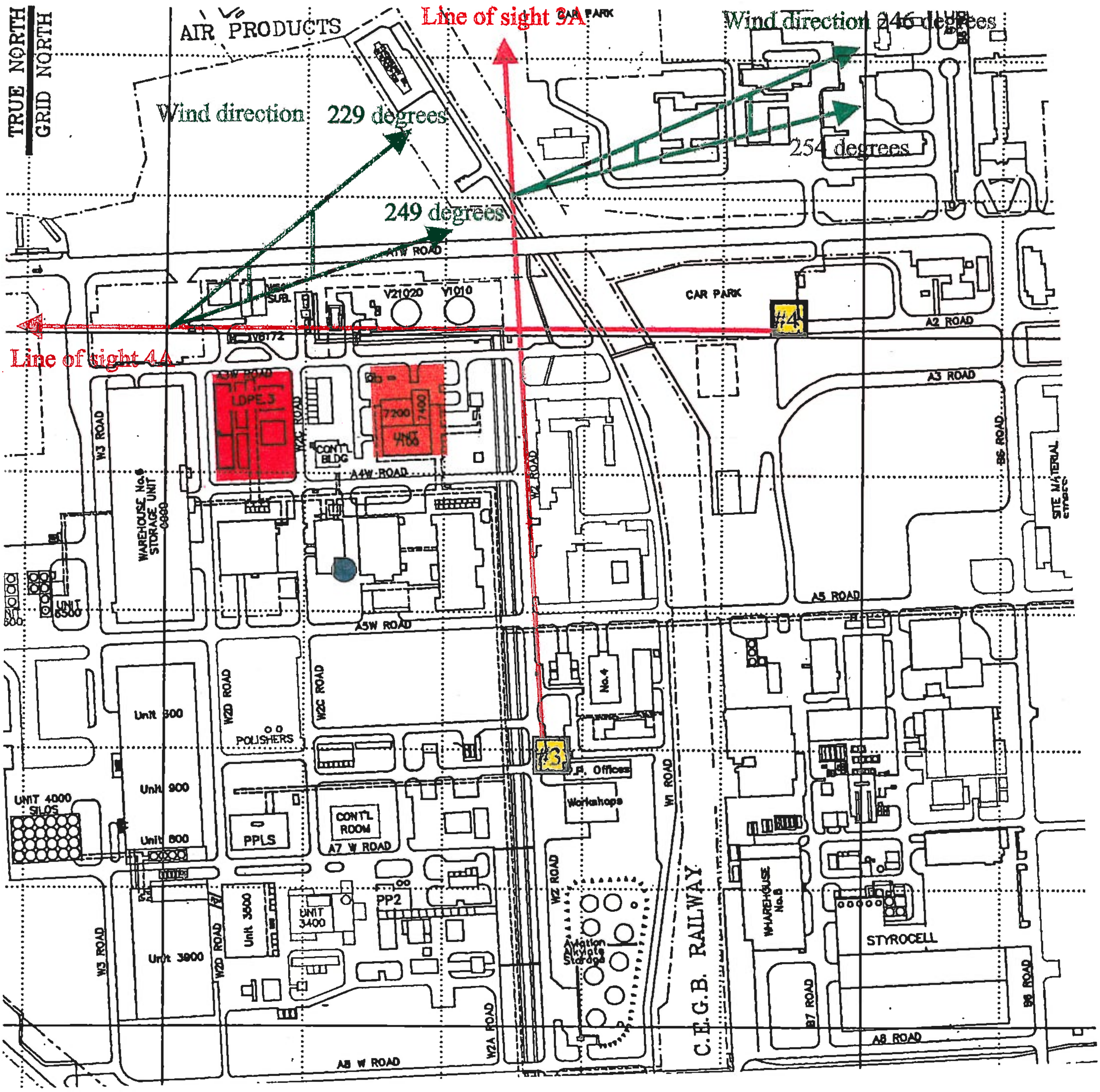
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 15 Polyethylene plant measurements, January 26th 1994.



KEY:

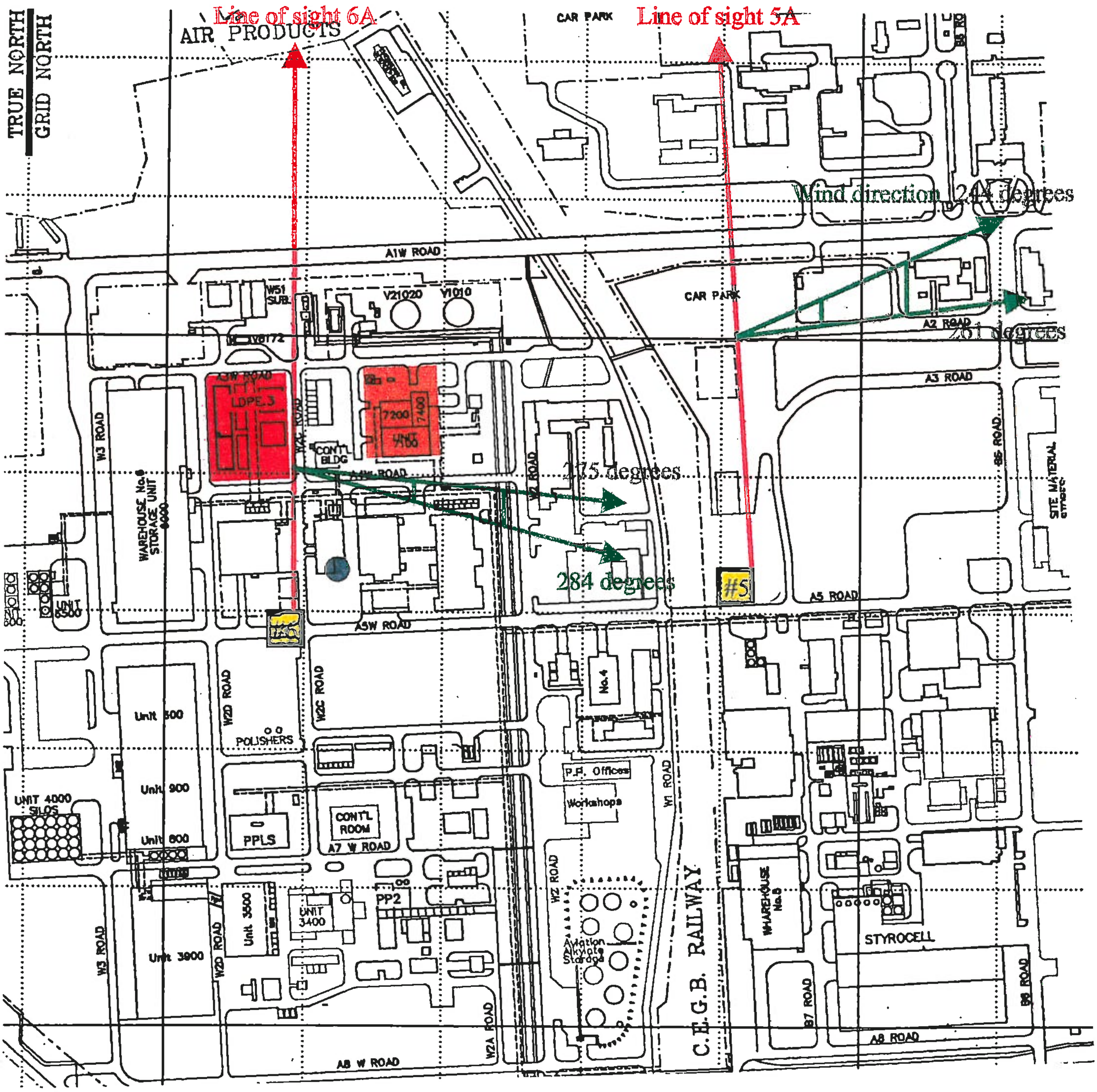
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 16 Polyethylene plant measurements, January 27th 1994.



KEY:

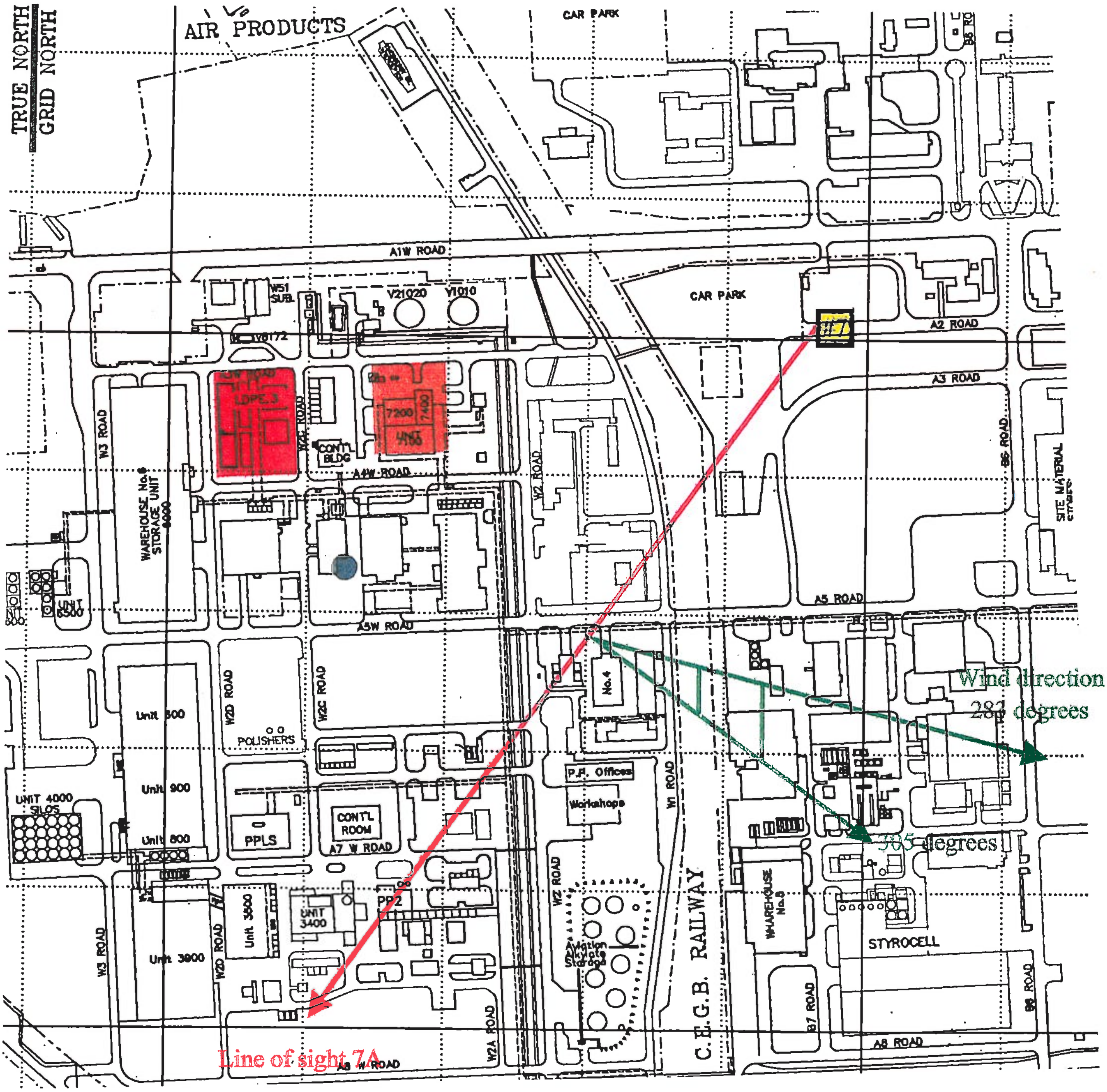
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 17 Polyethylene plant measurements, January 28th 1994.



KEY:

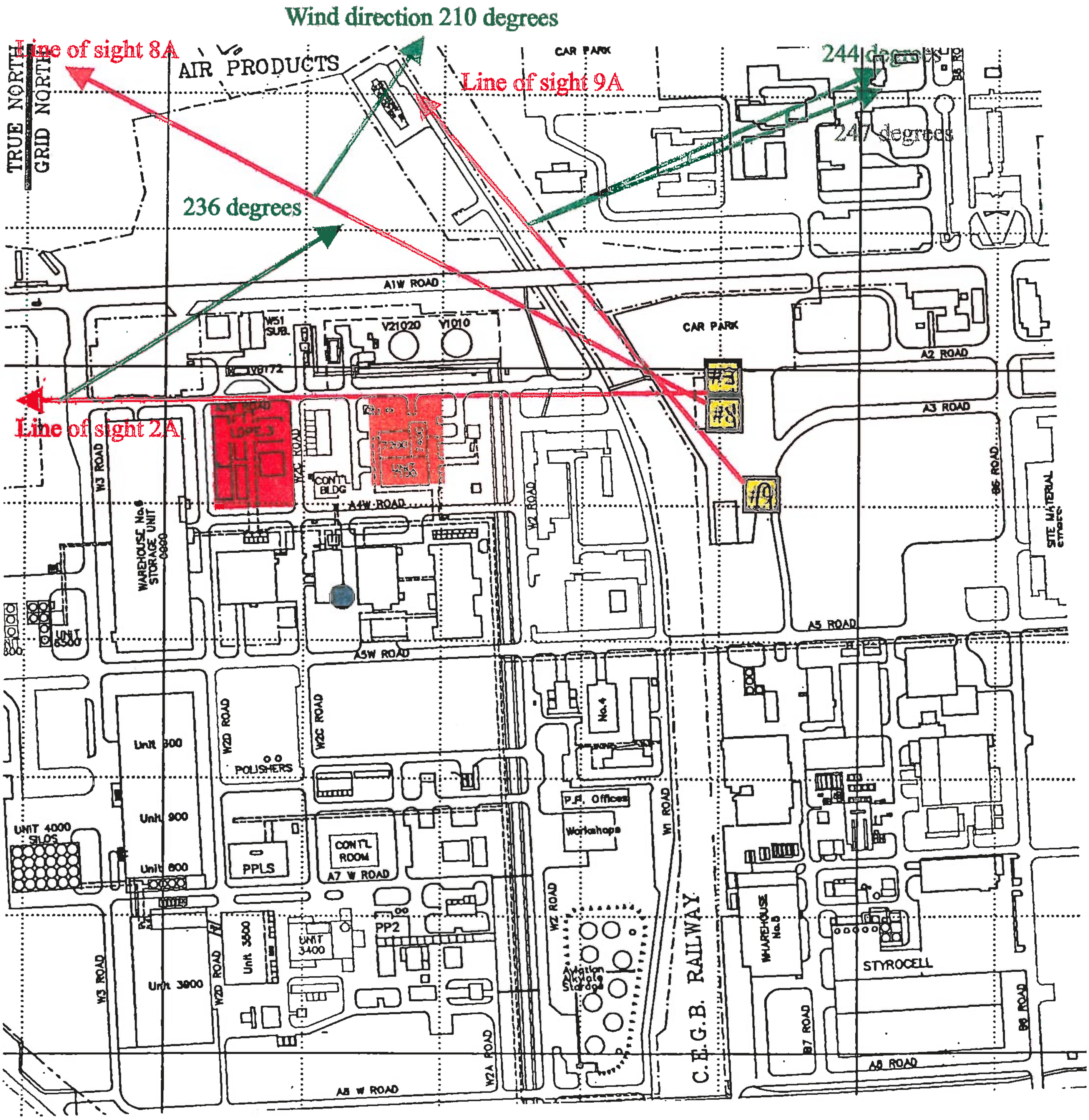
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 18 Polyethylene plant measurements, January 29th 1994.



KEY:

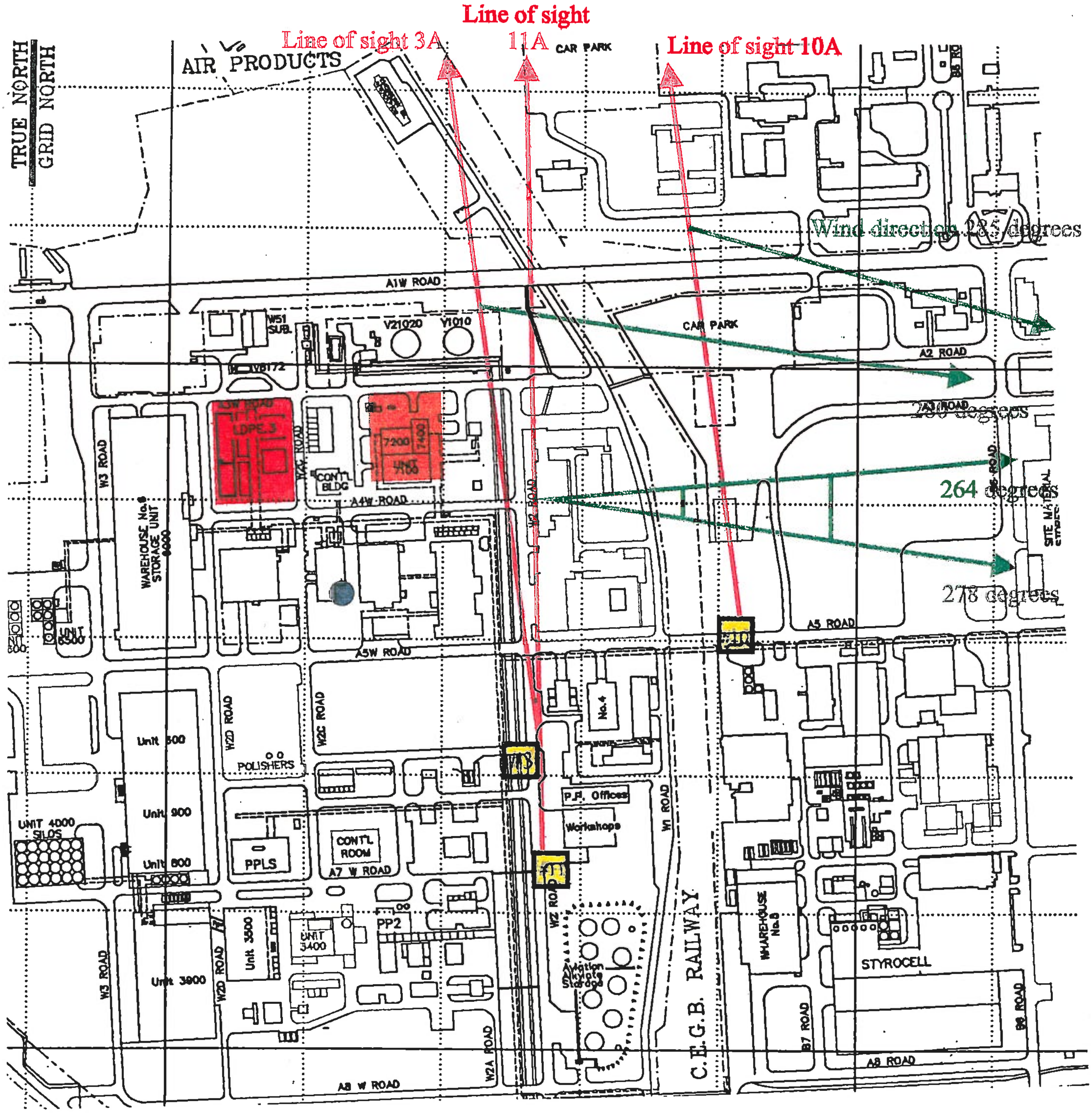
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 19 Polyethylene plant measurements, January 30th 1994.



KEY:

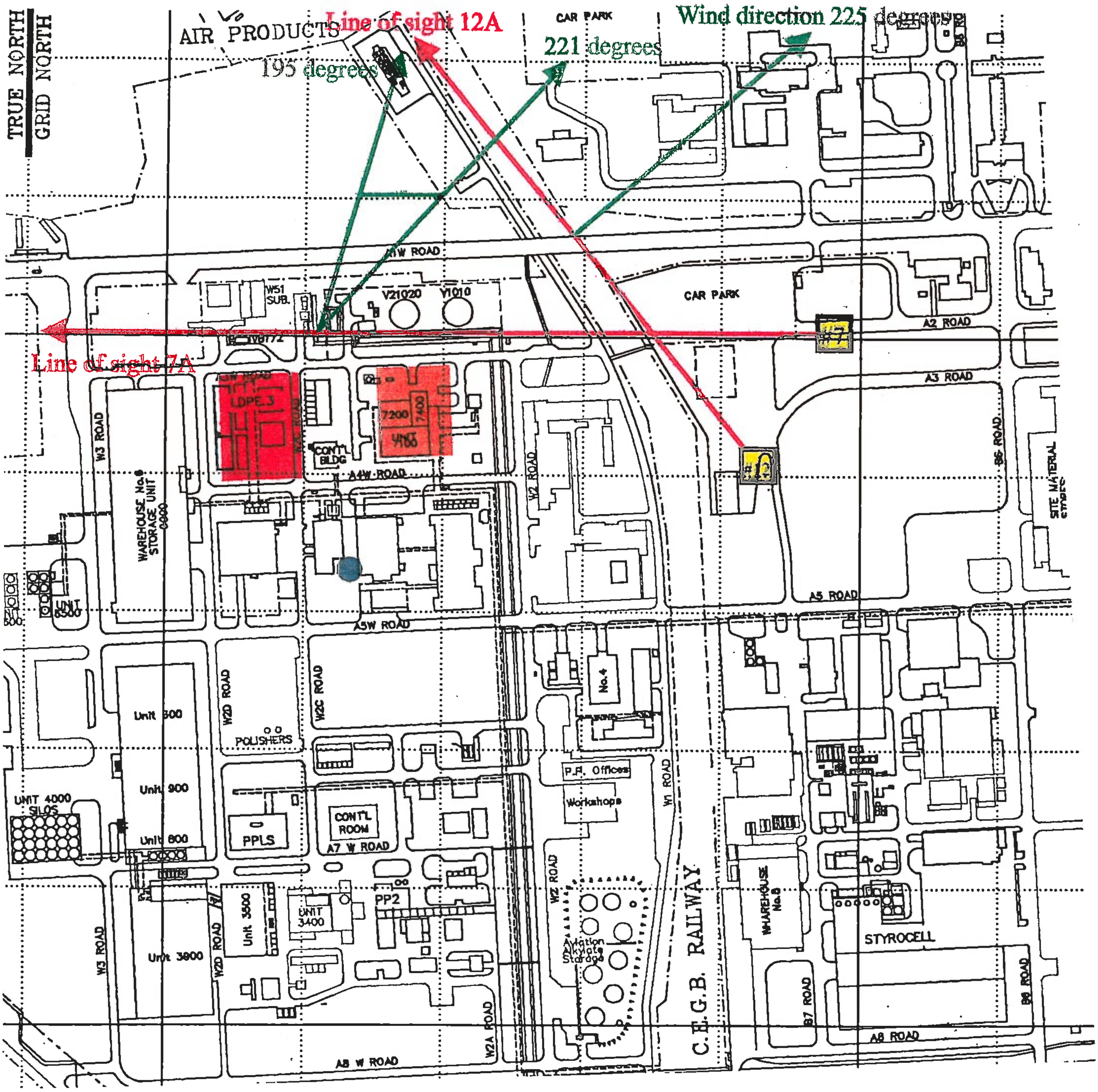
= New plant

= Old plant

= Vent source

= DIAL Van position

Figure 20 Polyethylene plant measurements, January 31st 1994.



KEY:

= New plant

= Old plant

= Vent source

= DIAL Van position

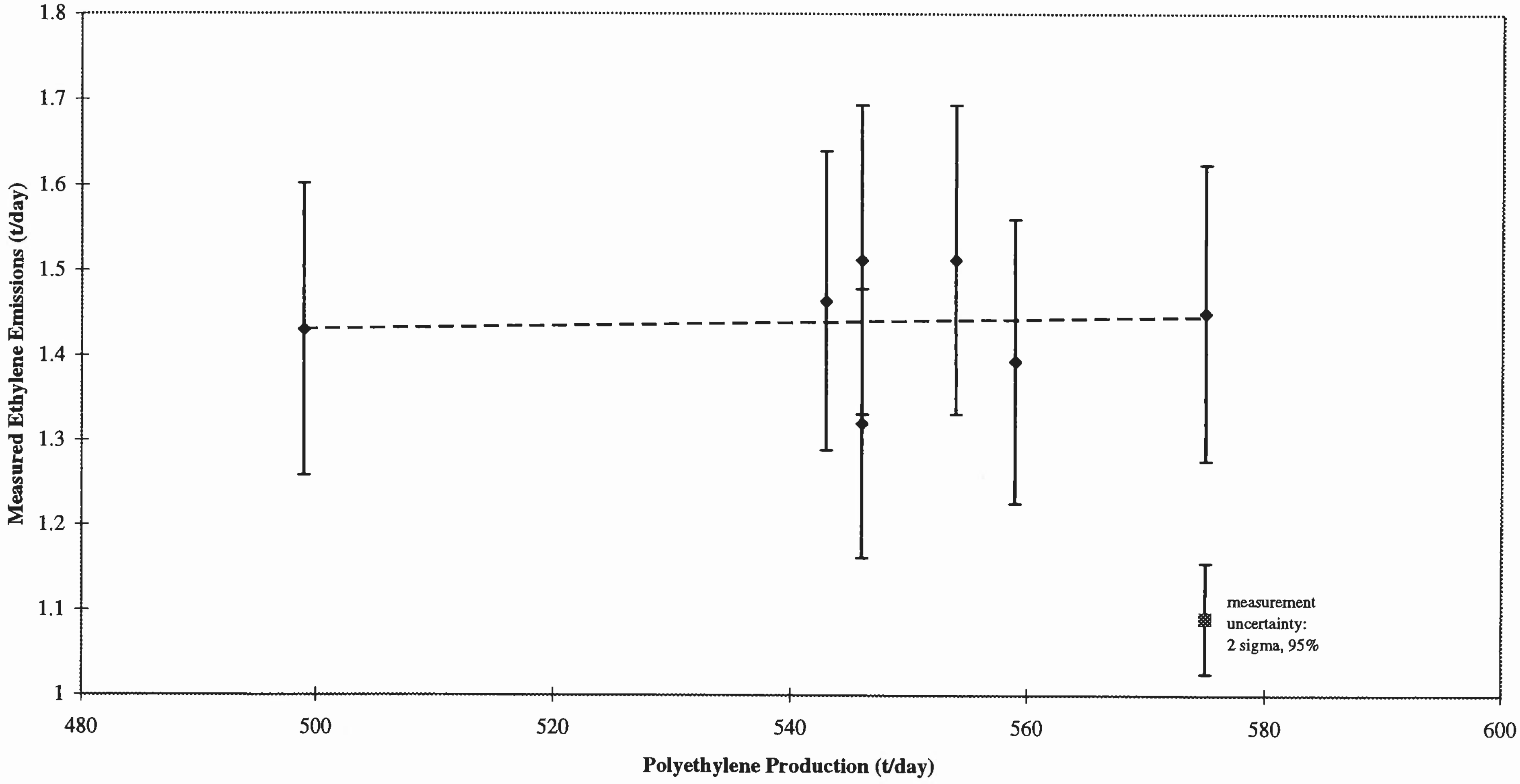
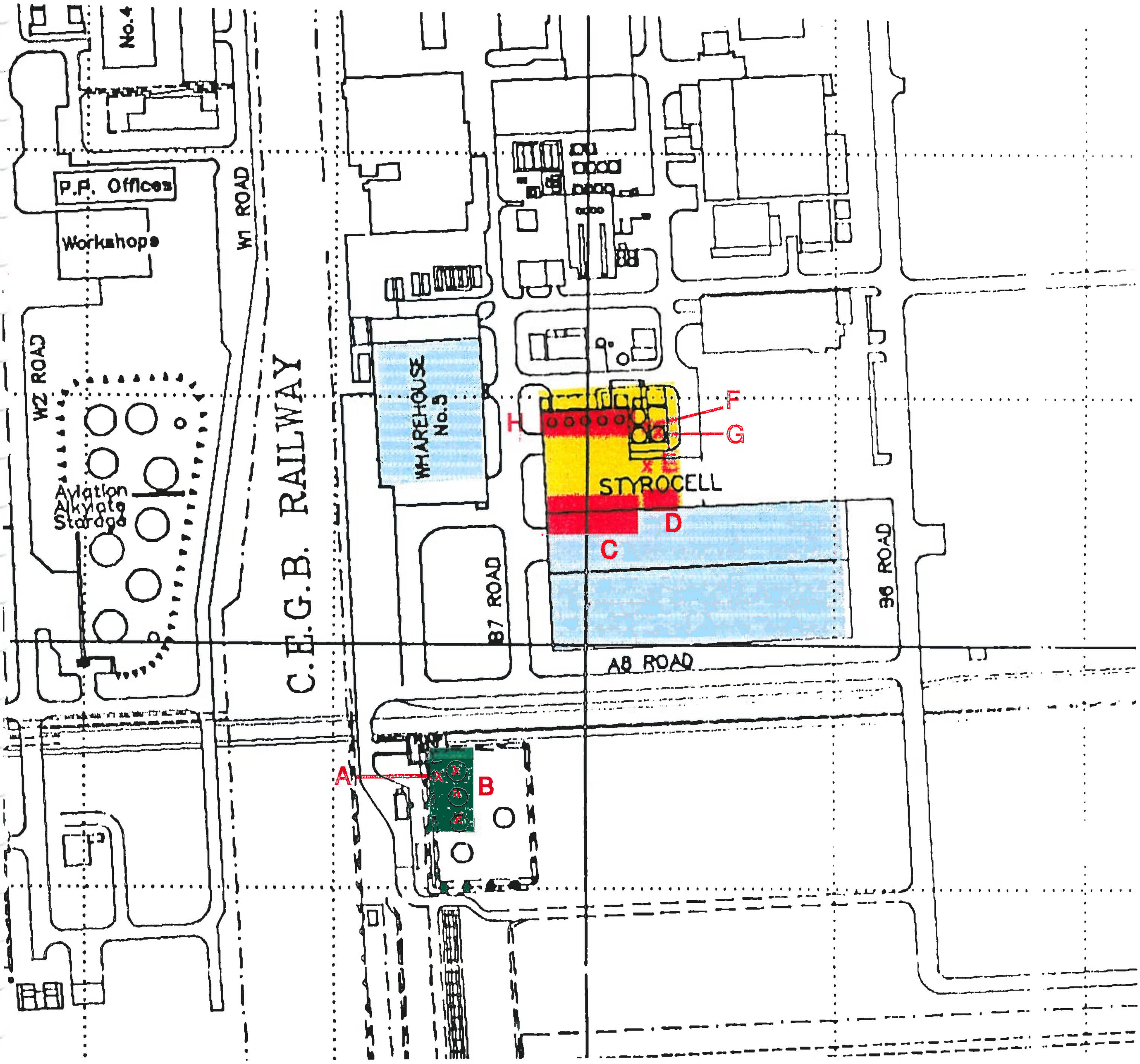


Figure 21: Summary of DIAL Measured Emissions from Polyethylene Plant as a function of Plant Throughput

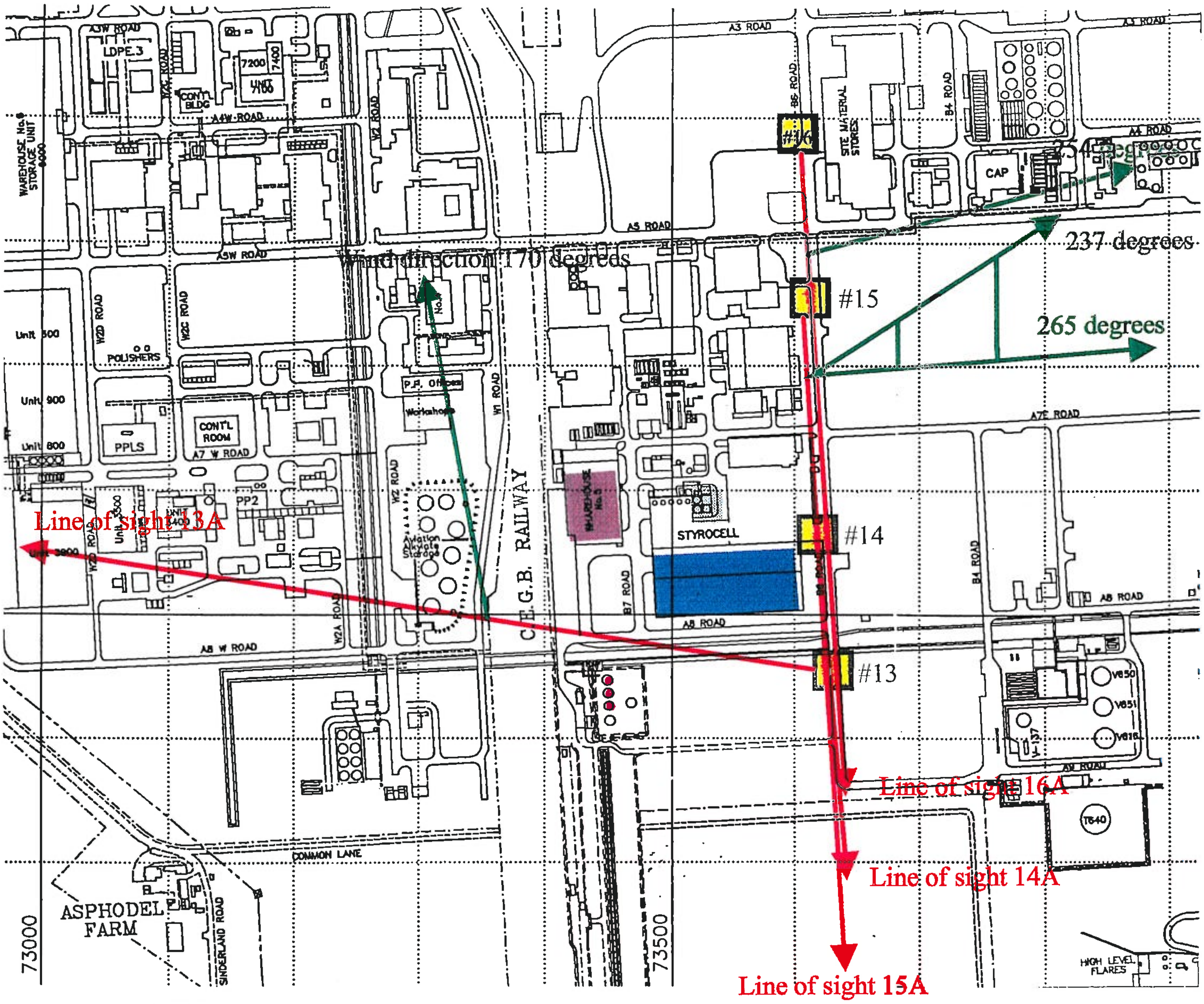
Figure 22 Location of pentane emission sources at Shell Carrington.



KEY:

A - Pentane pump vent (10m)	E - Hopper vent (30m)
B - Pentane tank vents (8m)	F - Vents (3 off)
C - Hopper vents (8 off) (12-31m)	G - Buffer vessels (18m)
D - Drier vents (3 off) (25m)	H - Reactor vents (20m)
- Styrene plant	- Pentane storage tanks
- Styrene warehouses	

Figure 23 Pentane emission measurements February 1st 1994.



KEY:-

= Warehouse 5

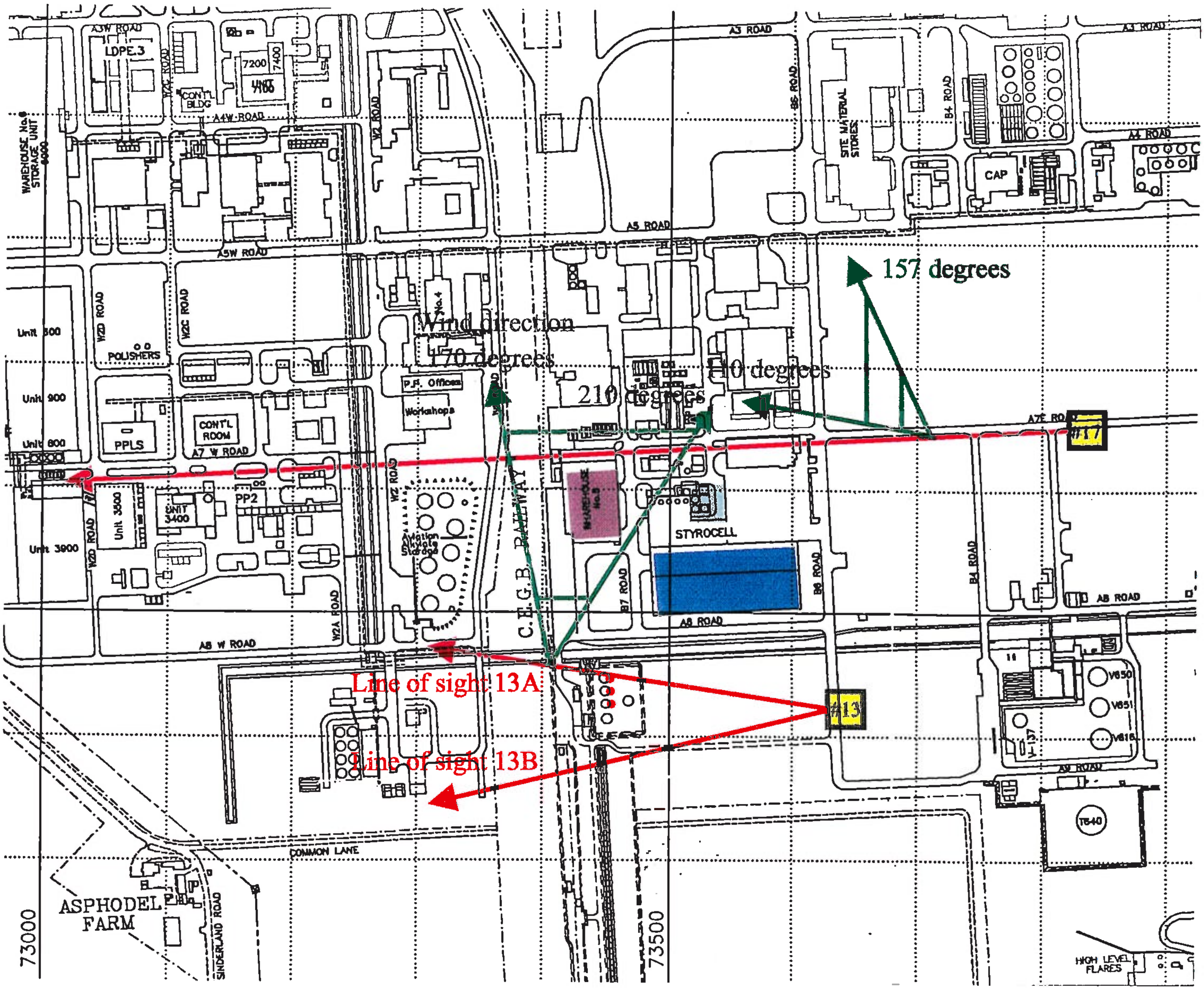
= Warehouse 11

= DIAL Van position

= Styrocell plant

= Pentane tanks

Figure 24 Pentane emission measurements February 2nd 1994.



KEY:-

= Warehouse 5

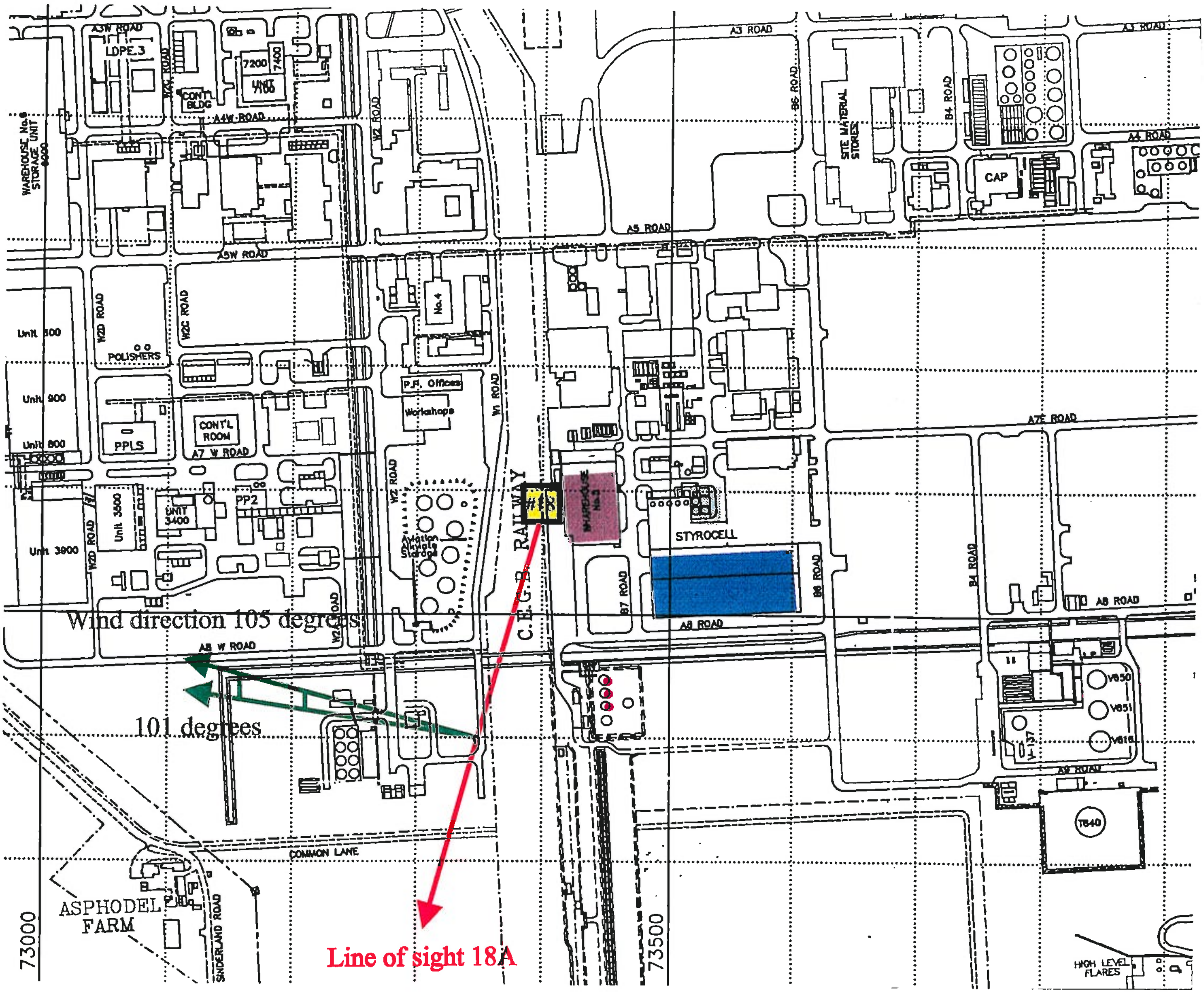
= Warehouse 11

= DIAL Van position

= Styrocell plant

= Pentane tanks

Figure 25 Pentane emission measurements February 3rd 1994.



KEY:-

= Warehouse 5

= Warehouse 11

= DIAL Van position

= Styrocell plant

= Pentane tanks

BAR

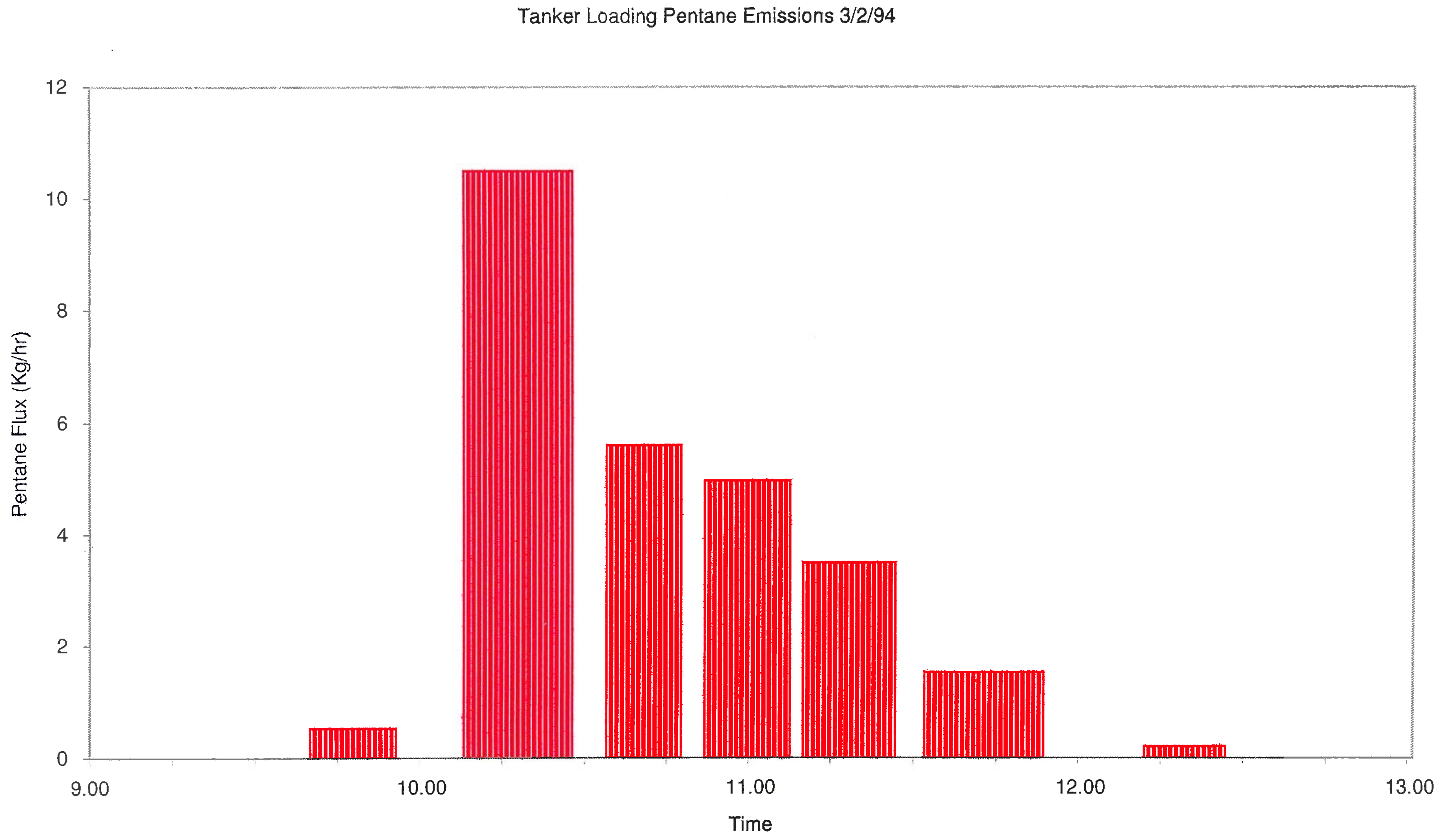


Figure 26 **Pentane emissions recorded whilst Road Tanker was unloading into Pentane Tanks on February 3rd 1994.**

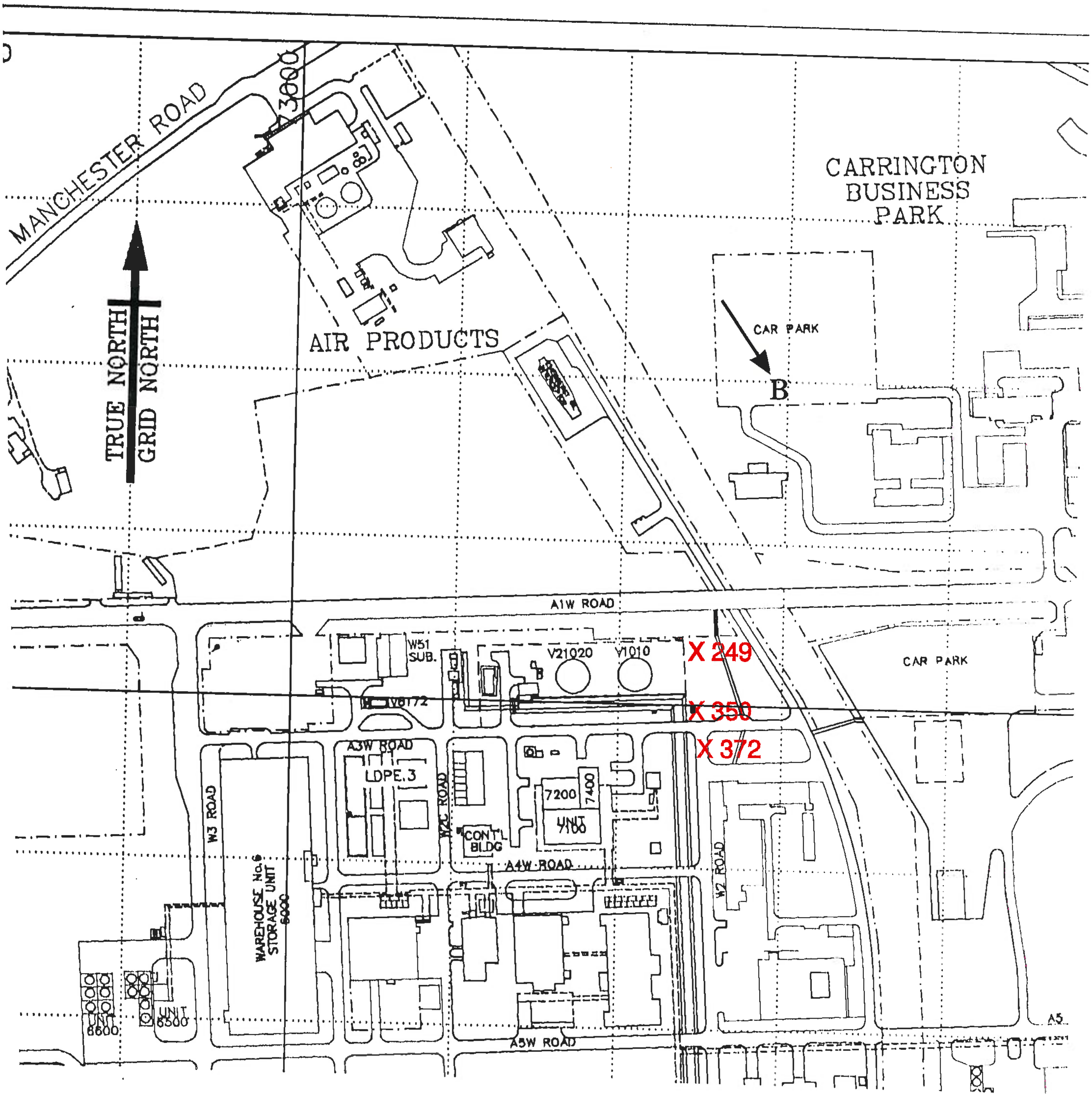


Figure 27 **Location of NPL Whole Air Samples taken between 13.51 and 14.05 hrs, 26/1/94.**

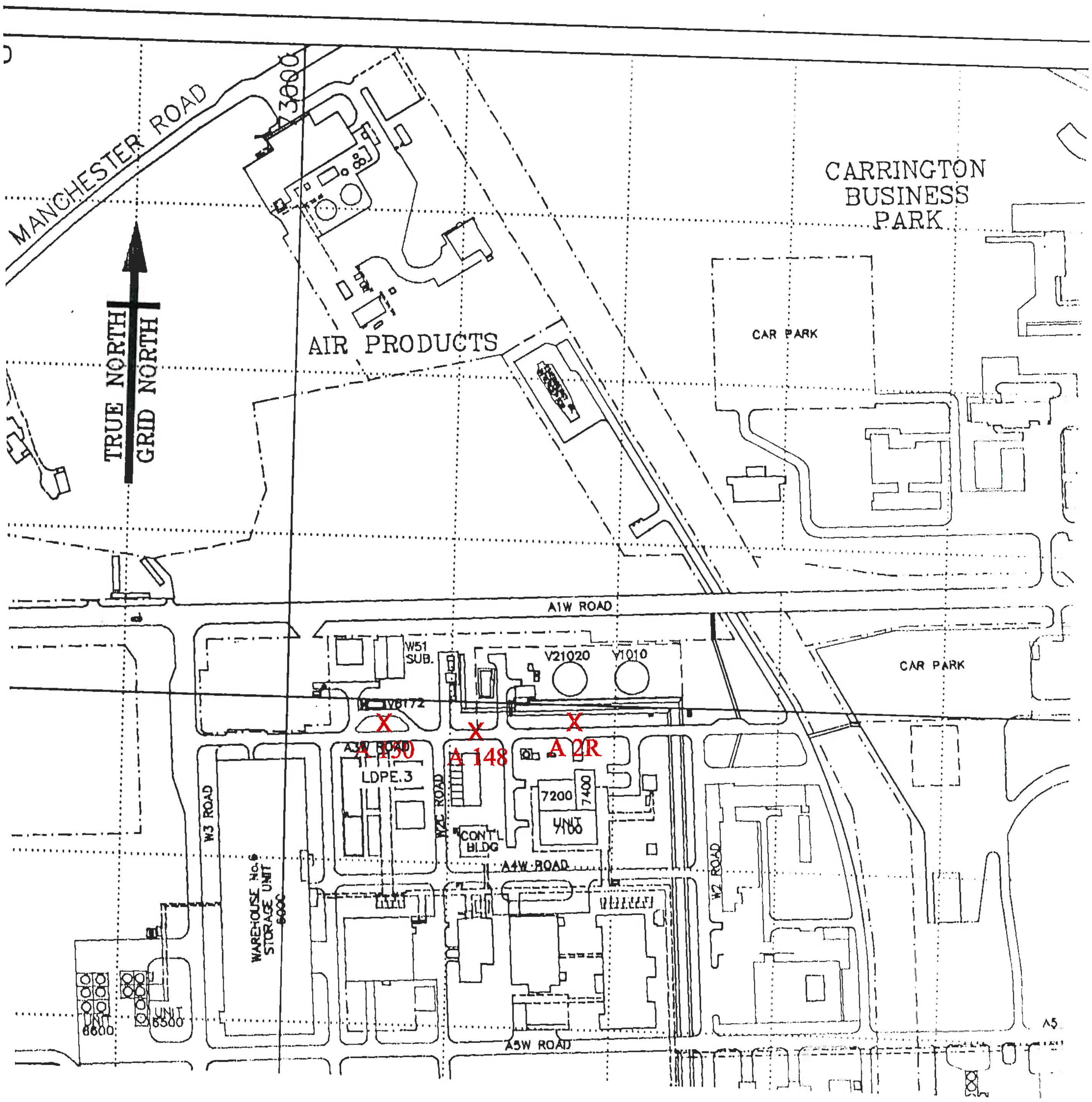
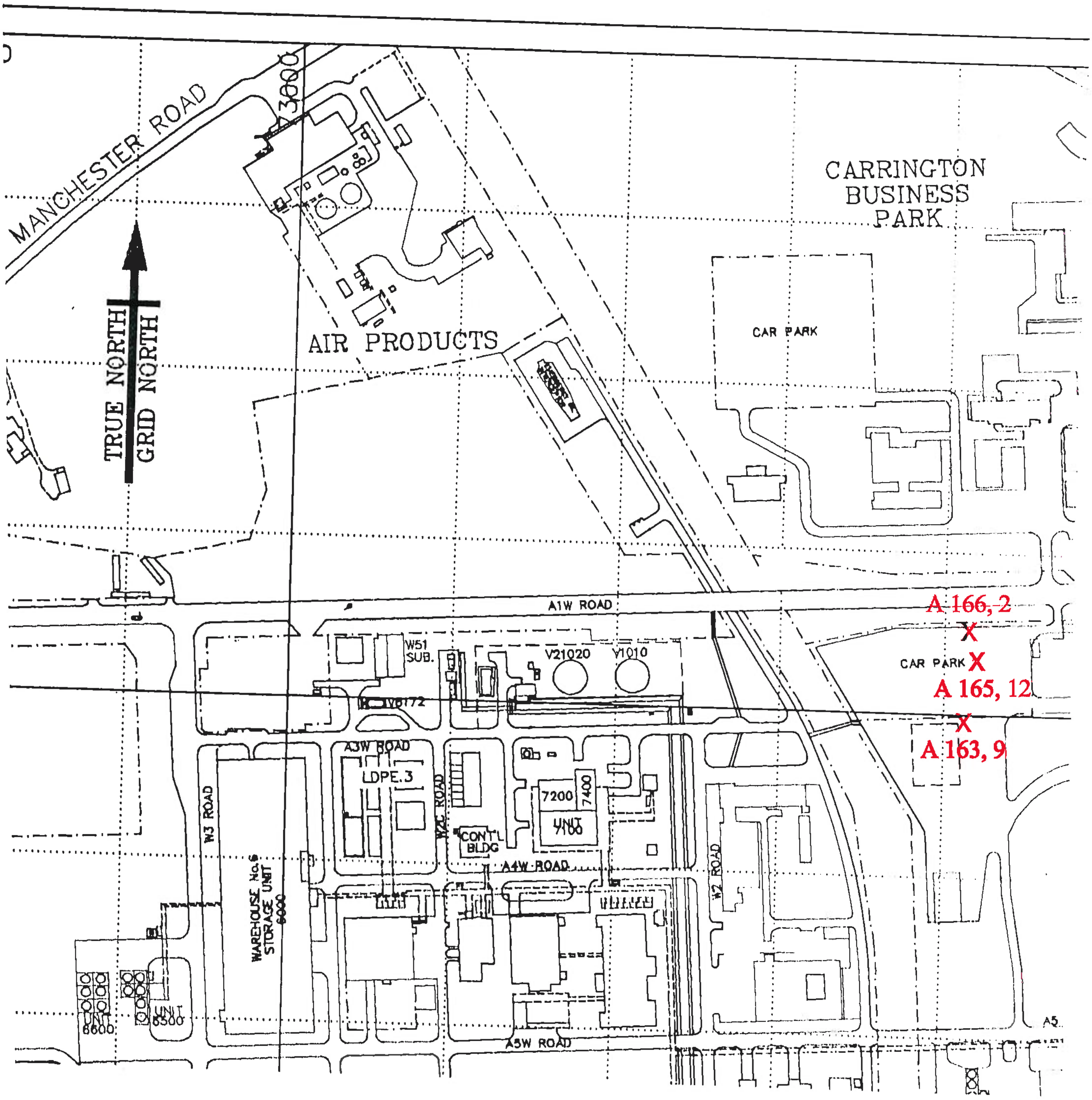


Figure 28 Location of NPL Whole Air Samples taken between 15.40 and 15.48 hrs, 26/1/94.



SAMPLES 9, 12, AND 2 ARE SHELL CARRINGTON SAMPLES

Figure 29 **Location of NPL Whole Air Samples taken between 15.34 and 15.44 hrs, 27/1/94.**

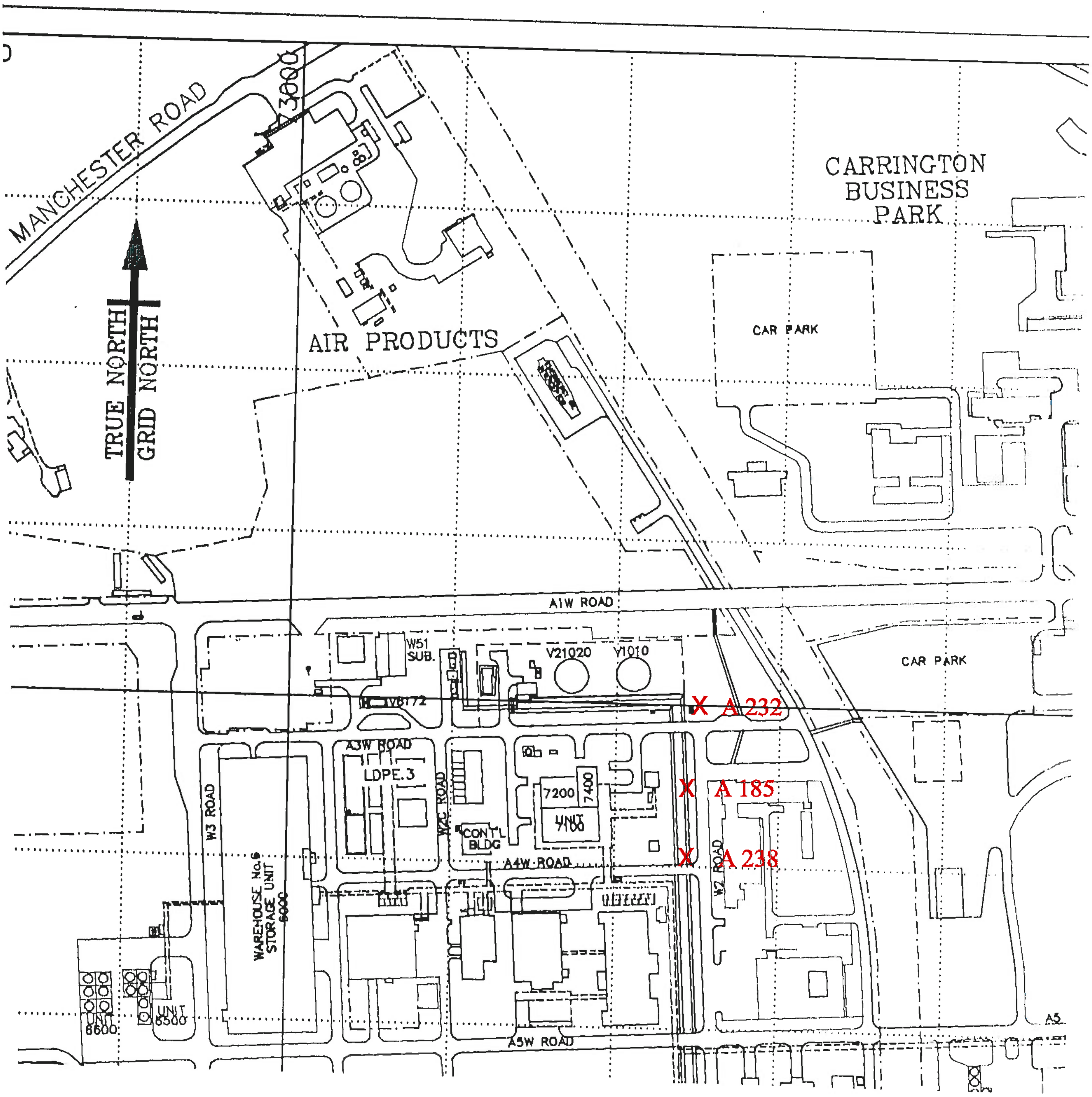


Figure 30 **Location of NPL Whole Air Samples taken between 16.45 and 16.55 hrs, 30/1/94.**

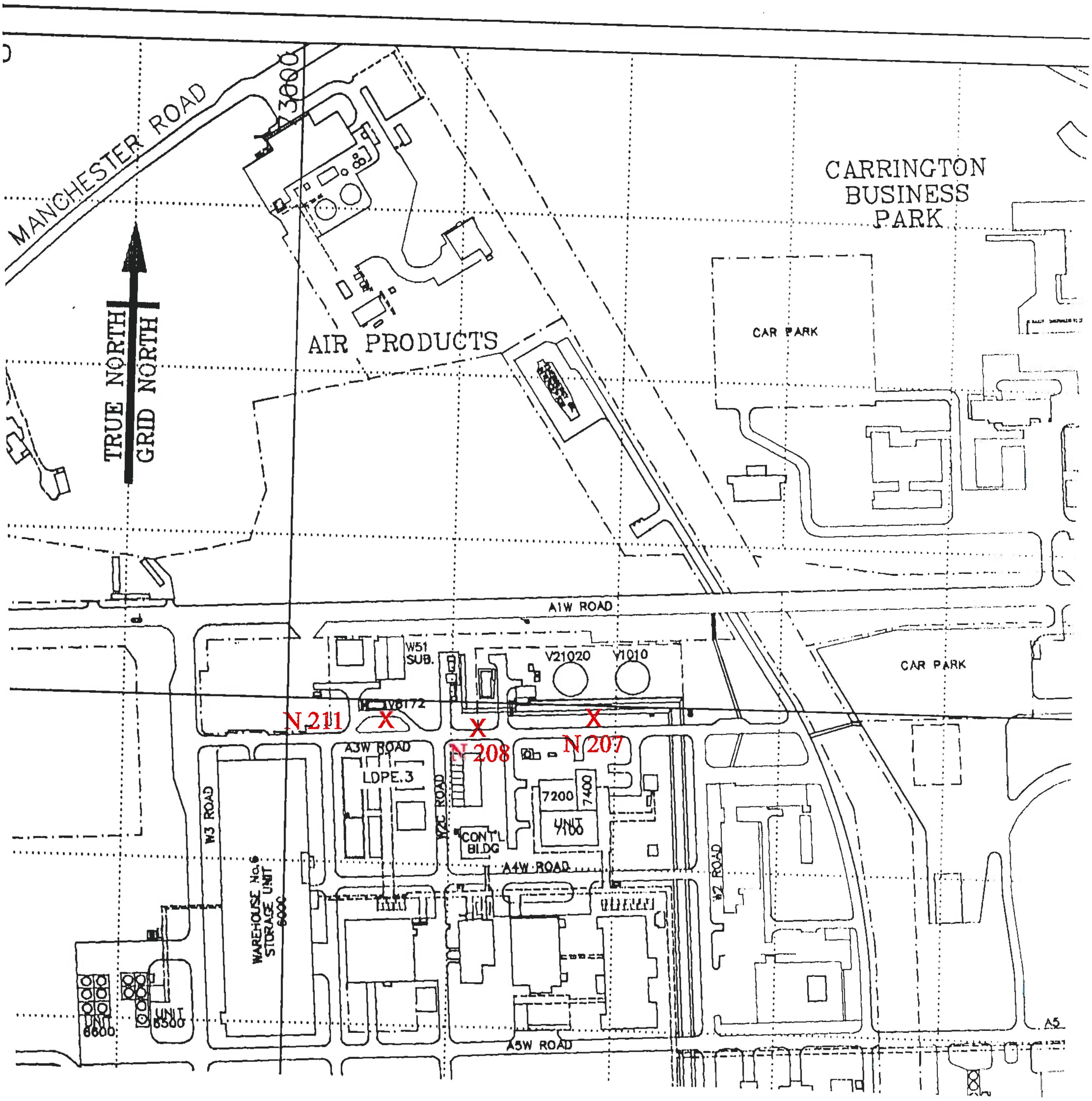


Figure 31 Location of NPL Whole Air Samples taken between 15.51 and 16.09 hrs, 31/1/94.

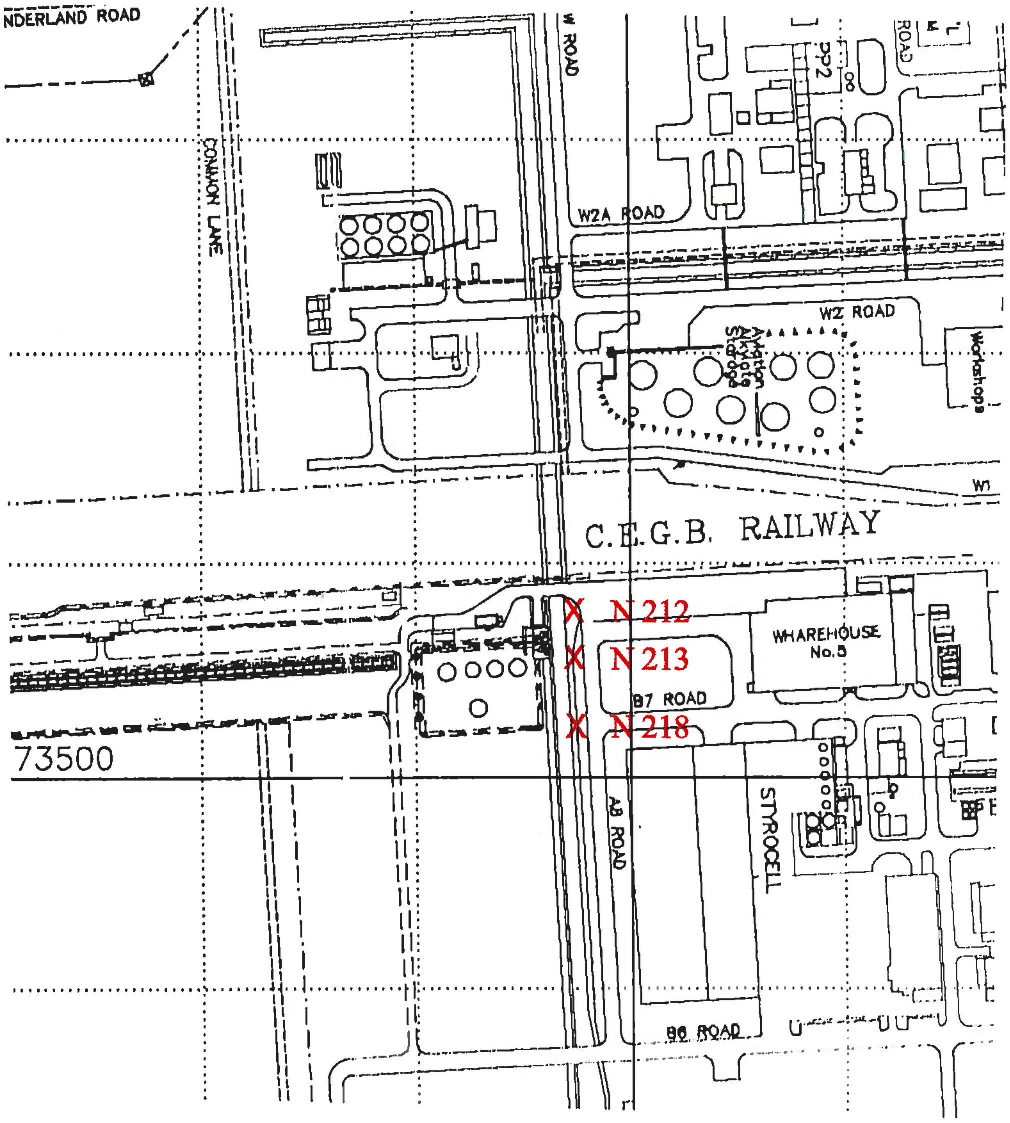


Figure 32 Location of NPL Whole Air Samples taken between 10.26 and 10.40 hrs, 2/2/94.

APPENDIX A

RESULTS OF IN-SITU VOC MEASUREMENTS USED TO SUPPORT INDUSTRY LOSS ESTIMATION PROCECURES

APPENDIX A

IN-SITU VOC MEASUREMENTS USED TO SUPPORT INDUSTRY LOSS ESTIMATION PROCEDURES

Table A1 **Summary of Flange VOC Screened-Concentration Values Obtained using OVA 128 Instrument**

		Total emission rate, kg/hr		
Ethylene concentration, ppmv	**No of Flanges**	**Leak/no leak**	**Stratified**	**Correlations**
<11 (default zero)	181	0.01086	0.00362	0.016833
>14085 (pegged source)	3	0.1125	0.1125	0.1125
70	1	0.00006	0.00002	0.00055
42	1	0.00006	0.00002	0.00036
281	1	0.00006	0.00002	0.00173

Table A2 **Summary of Flange VOC Screened-Concentration Values Obtained Using HVM 680 Instrument**

		Total emission rate, kg/hr		
Ethylene concentration, ppmv	**No of Flanges**	**Leak/no leak**	**Stratified**	**Correlations**
<11 (default zero)	97	0.00582	0.00194	0.00902
2820	1	0.00006	0.00875	0.01144
2358	1	0.00006	0.00875	0.00988
3142	1	0.00006	0.00875	0.01251

Table A3 Industrial Valve VOC Screened-Concentration Values Obtained using OVA 128 Instrument (18/1/94)

				Component leak rate, kg/hr		
ID	Press, barg	Material	Corrected screening value, ppmv	Leak/no leak	Stratified	Correlation
1	17	ethylene	282	0.00048	0.00014	0.00038
2	17	ethylene	28	0.00048	0.00014	0.00008
3	17	ethylene	14085	0.0451	0.0451	0.0451
4	17	ethylene	0	0.00048	0.00014	0.000033
5	17	ethylene	70	0.00048	0.00014	0.00015
6	17	ethylene	0	0.00048	0.00014	0.00003
7	17	ethylene	704	0.00048	0.00014	0.00072
8	17	ethylene	14085	0.0451	0.0451	0.0451
9	325	ethylene	0	0.00048	0.00014	0.00003
10	325	ethylene	0	0.00048	0.00014	0.00003
11	325	ethylene	0	0.00048	0.00014	0.00003
12	325	ethylene	0	0.00048	0.00014	0.00003
13	325	ethylene	282	0.00048	0.00014	0.00038
14	325	ethylene	282	0.00048	0.00014	0.00038
15	3200	ethylene	14085	0.0451	0.0451	0.0451
16	3200	ethylene	140	0.00048	0.00014	0.00023
17	200	NBA(LL)	0	0.00171	0.00028	0.00045
18	200	NBA(LL)	0	0.00171	0.00028	0.000451
19	0	NBA(LL)	0	0.00171	0.00028	0.00045
20	0.3	ethylene	28	0.00048	0.00014	0.00008
21	0.3	ethylene	0	0.00048	0.00014	0.00003
22	0.3	ethylene	0	0.00048	0.00014	0.00003
23	0.3	ethylene	113	0.00048	0.00014	0.00020
24	0.3	ethylene	0	0.00048	0.00014	0.00003
25	0.3	ethylene	0	0.00048	0.00014	0.00003
26	0.3	ethylene	0	0.00048	0.00014	0.00003
27	0.3	ethylene	0	0.00048	0.00014	0.00003
28	2.5	ethylene	0	0.00048	0.00014	0.00003
29	2.5	ethylene	0	0.00048	0.00014	0.00003
30	0.3	ethylene	0	0.00048	0.00014	0.00003
31	0.3	ethylene	0	0.00048	0.00014	0.00003

Table A4 Individual Valve VOC Screened Concentration Values Obtained using OVA 128 Instrument (25-27/1/94)

ID	Press, barg	Material	Corrected screening value, ppmv	Component leak rate, kg/hr		
				Leak/no leak	Stratified	Correlation kg/hr
1	17	ethylene	211	0.00048	0.00014	0.00031
2	17	ethylene	0	0.00048	0.00014	0.00003
3	17	ethylene	14085	0.0451	0.0451	0.0451
4	17	ethylene	70	0.00048	0.00014	0.00015
5	17	ethylene	2817	0.00048	0.00165	0.00188
6	17	ethylene	0	0.00048	0.00014	0.00003
7	17	ethylene	7042	0.00048	0.00165	0.00354
8	17	ethylene	14085	0.0451	0.0451	0.0451
9	325	ethylene	0	0.00048	0.00014	0.00003
10	325	ethylene	0	0.00048	0.00014	0.00003
11	325	ethylene	0	0.00048	0.00014	0.00003
12	325	ethylene	0	0.00048	0.00014	0.00003
13	325	ethylene	1127	0.00048	0.00165	0.00100
14	325	ethylene	423	0.00048	0.00014	0.00050
15	3200	ethylene	14085	0.0451	0.0451	0.0451
16	3200	ethylene	140	0.00048	0.00014	0.00023
17	200	NBA(LL)	0	0.00171	0.00028	0.00045
18	200	NBA(LL)	0	0.00171	0.00028	0.00045
19	0	NBA(LL)	0	0.00171	0.00028	0.00045
20	0.3	ethylene	0	0.00048	0.00014	0.00003
21	0.3	ethylene	0	0.00048	0.00014	0.00003
22	0.3	ethylene	0	0.00048	0.00014	0.00003
23	0.3	ethylene	0	0.00048	0.00014	0.00003
24	0.3	ethylene	0	0.00048	0.00014	0.00003
25	0.3	ethylene	14	0.00048	0.00014	0.00005
26	0.3	ethylene	0	0.00048	0.00014	0.00003
27	0.3	ethylene	0	0.00048	0.00014	0.00003
28	2.5	ethylene	0	0.00048	0.00014	0.00003
29	2.5	ethylene	0	0.00048	0.00014	0.00003
30	0.3	ethylene	0	0.00048	0.00014	0.00003
31	0.3	ethylene	0	0.00048	0.00014	0.00003
32	17	ethylene	14085	0.0451	0.0451	0.0451
33	0.3	ethylene	0	0.00048	0.00014	0.00003

ID	Press, barg	Material	Corrected screening value, ppmv	Component leak rate, kg/hr		
				Leak/no leak	Stratified	Correlation kg/hr
34	17	ethylene	0	0.00048	0.00014	0.00003
35	17	ethylene	0	0.00048	0.00014	0.00003
36	17	ethylene	0	0.00048	0.00014	0.00003
37	17	ethylene	0	0.00048	0.00014	0.00003
38	17	ethylene	0	0.00048	0.00014	0.00003
39	17	ethylene	0	0.00048	0.00014	0.00003
40	17	ethylene	0	0.00048	0.00014	0.00003
41	17	ethylene	14085	0.0451	0.0451	0.0451
42	17	ethylene	0	0.00048	0.00014	0.00003
43	17	ethylene	0	0.00048	0.00014	0.00003
44	17	ethylene	0	0.00048	0.00014	0.00003
45	17	ethylene	14	0.00048	0.00014	0.00005
46	17	ethylene	0	0.00048	0.00014	0.00003
47	17	ethylene	0	0.00048	0.00014	0.00003
48	17	ethylene	42	0.00048	0.00014	0.00010
49	0.3	ethylene	0	0.00048	0.00014	0.00003
50	0.3	ethylene	0	0.00048	0.00014	0.00003
51	5	ethylene	0	0.00048	0.00014	0.00003
52	10	ethylene	0	0.00048	0.00014	0.00003
53	17	ethylene	0	0.00048	0.00014	0.00003
54	17	ethylene	28	0.00048	0.00014	0.00008
55	0.1	ethylene	0	0.00048	0.00014	0.00003
56	5	ethylene	0	0.00048	0.00014	0.00003
57	0.1	ethylene	0	0.00048	0.00014	0.00003
58	10	ethylene	0	0.00048	0.00014	0.00003
59	0.1	ethylene	0	0.00048	0.00014	0.00003
60	325	ethylene	0	0.00048	0.00014	0.00003
61	0.1	ethylene	0	0.00048	0.00014	0.00003
62	0.1	ethylene	0	0.00048	0.00014	0.00003
63	0.1	ethylene	704	0.00048	0.00014	0.00072
64	0.1	ethylene	14085	0.0451	0.0451	0.0451
65	0.1	ethylene	0	0.00048	0.00048	0.00003
66	17	ethylene	0	0.00048	0.00014	0.00003
67	17	ethylene	0	0.00048	0.00014	0.00003
68	17	ethylene	0	0.00048	0.00014	0.00003

ID	Press, barg	Material	Corrected screening value, ppmv	Component leak rate, kg/hr Leak/no leak	Stratified	Correlation kg/hr
69	17	ethylene	0	0.00048	0.00014	0.00003
70	17	ethylene	0	0.00048	0.00014	0.00003
71	17	ethylene	0	0.00048	0.00014	0.00003
72	17	ethylene	0	0.00048	0.00014	0.00003
73	325	ethylene	28	0.00048	0.00014	0.00008
74	325	ethylene	42	0.00048	0.00014	0.00010
75	325	ethylene	0	0.00048	0.00014	0.00003
76	325	ethylene	0	0.00048	0.00014	0.00003
77	0.1	ethylene	0	0.00048	0.00014	0.00003
78	0.1	ethylene	0	0.00048	0.00014	0.00003
79	0.1	ethylene	0	0.00048	0.00014	0.00003
80	0.1	ethylene	0	0.00048	0.00014	0.00003
81	0.1	ethylene	0	0.00048	0.00014	0.00003
82	0.1	ethylene	0	0.00048	0.00014	0.00003
83	0.1	ethylene	0	0.00048	0.00014	0.00003
84	0.1	ethylene	0	0.00048	0.00014	0.00003
85	0.1	ethylene	0	0.00048	0.00014	0.00003
86	0.1	ethylene	0	0.00048	0.00014	0.00003
87	0.1	ethylene	0	0.00048	0.00014	0.00003
88	0.1	ethylene	0	0.00048	0.00014	0.00003
89	0.1	ethylene	0	0.00048	0.00014	0.00003
90	0.1	ethylene	14	0.00048	0.00014	0.00003
91	0.1	ethylene	42	0.00048	0.00014	0.00010
92	0.1	ethylene	282	0.00048	0.00014	0.00038
93	0.1	ethylene	423	0.00048	0.00014	0.00050
94	0.1	ethylene	14	0.00048	0.00014	0.00005
95	0.1	ethylene	704	0.00048	0.00014	0.00072
96	0.3	ethylene	14	0.00048	0.00014	0.00005
97	0.3	ethylene	0	0.00048	0.00014	0.00003
98	0.3	ethylene	0	0.00048	0.00014	0.00003
99	0.3	ethylene	0	0.00048	0.00014	0.00003
100	0.3	ethylene	0	0.00048	0.00014	0.00003
101	0.3	ethylene	0	0.00048	0.00014	0.00003
102	0.3	ethylene	0	0.00048	0.00014	0.00003
103	0.3	ethylene	0	0.00048	0.00014	0.00003

ID	Press, barg	Material	Corrected screening value, ppmv	Component leak rate, kg/hr		
				Leak/no leak	Stratified	Correlation kg/hr
104	0.3	ethylene	14	0.00048	0.00014	0.00005
105	0.3	ethylene	0	0.00048	0.00014	0.00003
106	0.3	ethylene	0	0.00048	0.00014	0.00003
107	0.3	ethylene	704	0.00048	0.00014	0.00072

Table A5 **Individual Valve VOC Screened Concentration Values Obtained using HVM 680 Instrument (31/5/94)**

ID	Press, barg	Material	Corrected Screening value ppmv	Leak/no leak kg/hr	Stratified kg/hr	Correlation kg/hr
1	17	ethylene	0	0.00048	0.00014	0.00003
2	17	ethylene	0	0.00048	0.00014	0.00003
3	17	ethylene	32	0.00048	0.00014	0.00008
4	17	ethylene	66	0.00048	0.00014	0.00014
5	17	ethylene	0	0.00048	0.00014	0.00003
6	17	ethylene	0	0.00048	0.00014	0.00003
7	17	ethylene	0	0.00048	0.00014	0.00003
8	17	ethylene	0	0.00048	0.00014	0.00003
9	325	ethylene	0	0.00048	0.00014	0.00003
10	325	ethylene	0	0.00048	0.00014	0.00003
11	325	ethylene	0	0.00048	0.00014	0.00003
12	325	ethylene	0	0.00048	0.00014	0.00003
13	325	ethylene	0	0.00048	0.00014	0.00003
14	325	ethylene				
15	3200	ethylene	4211	0.00048	0.00165	0.00248
16	3200	ethylene	197	0.00048	0.00014	0.000423
17	200	NBA(LL)	0	0.00171	0.00028	0.00045
18	200	NBA(LL)	0	0.00171	0.00028	0.00045
19	0	NBA(LL)	0	0.00171	0.00028	0.00045
20	0.3	ethylene	0	0.00048	0.00014	0.00003
21	0.3	ethylene	14	0.00048	0.00014	0.00005
22	0.3	ethylene	0	0.00048	0.00014	0.00003
23	0.3	ethylene	0	0.00048	0.00014	0.00003
24	0.3	ethylene	0	0.00048	0.00014	0.00003
25	0.3	ethylene	0	0.00048	0.00014	0.00003
26	0.3	ethylene	0	0.00048	0.00014	0.00003
27	0.3	ethylene	8	0.00048	0.00014	0.00003
28	2.5	ethylene				
29	2.5	ethylene				
30	0.3	ethylene	0	0.00048	0.00014	0.00003
31	0.3	ethylene	0	0.00048	0.00014	0.00003
32	17	ethylene	0	0.00048	0.00014	0.00003
33	0.3	ethylene	0	0.00048	0.00014	0.00003
34	17	ethylene	0	0.00048	0.00014	0.00003
35	17	ethylene	0	0.00048	0.00014	0.00003
36	17	ethylene	0	0.00048	0.00014	0.00003

ID	Press, barg	Material	Corrected Screening value ppmv	Leak/no leak kg/hr	Stratified kg/hr	Correlation kg/hr
37	17	ethylene	0	0.00048	0.00014	0.00003
38	17	ethylene	0	0.00048	0.00014	0.00003
39	17	ethylene	0	0.00048	0.00014	0.00003
40	17	ethylene	0	0.00048	0.00014	0.00003
41	17	ethylene	0	0.00048	0.00014	0.00003
42	17	ethylene	0	0.00048	0.00014	0.00003
43	17	ethylene	0	0.00048	0.00014	0.00003
44	17	ethylene	0	0.00048	0.00014	0.00003
45	17	ethylene	0	0.00048	0.00014	0.00003
46	17	ethylene	0	0.00048	0.00014	0.00003
47	17	ethylene	0	0.00048	0.00014	0.00003
48	17	ethylene				
49	0.3	ethylene	0	0.00048	0.00014	0.00003
50	0.3	ethylene	0	0.00048	0.00014	0.00003
51	5	ethylene	0	0.00048	0.00014	0.00003
52	10	ethylene	0	0.00048	0.00014	0.00003
53	17	ethylene	0	0.00048	0.00014	0.00003
54	17	ethylene	62	0.00048	0.00014	0.00003
55	0.1	ethylene	0	0.00048	0.00014	0.00003
56	5	ethylene	0	0.00048	0.00014	0.00003
57	0.1	ethylene	0	0.00048	0.00014	0.00003
58	10	ethylene	0	0.00048	0.00014	0.00003
59	0.1	ethylene	0	0.00048	0.00014	0.00003
60	325	ethylene	0	0.00048	0.00014	0.00003
61	0.1	ethylene				
62	0.1	ethylene				
63	0.1	ethylene	0	0.00048	0.00014	0.00003
64	0.1	ethylene	14	0.00048	0.00014	0.00005
65	0.1	ethylene	0	0.00048	0.00014	0.00003
66	0.1	ethylene				
67	17	ethylene	0	0.00048	0.00014	0.00003
68	17	ethylene	0	0.00048	0.00014	0.00003
69	17	ethylene	0	0.00048	0.00014	0.00003
70	17	ethylene	0	0.00048	0.00014	0.00003
71	17	ethylene	0	0.00048	0.00014	0.00003
72	17	ethylene	0	0.00048	0.00014	0.00003
73	325	ethylene	8	0.00048	0.00014	0.00003
74	325	ethylene	0	0.00048	0.00014	0.00003

ID	Press, barg	Material	Corrected Screening value ppmv	Leak/no leak kg/hr	Stratified kg/hr	Correlation kg/hr
75	325	ethylene				
76	325	ethylene				
77	0.1	ethylene	0	0.00048	0.00014	0.00003
78	0.1	ethylene	0	0.00048	0.00014	0.00003
79	0.1	ethylene	0	0.00048	0.00014	0.00003
80	0.1	ethylene	0	0.00048	0.00014	0.00003
81	0.1	ethylene	0	0.00048	0.00014	0.00003
82	0.1	ethylene	0	0.00048	0.00014	0.00003
83	0.1	ethylene	0	0.00048	0.00014	0.00003
84	0.1	ethylene	0	0.00048	0.00014	0.00003
85	0.1	ethylene	0	0.00048	0.00014	0.00003
86	0.1	ethylene				
87	0.1	ethylene				
88	0.1	ethylene				
89	0.1	ethylene				
90	0.1	ethylene				
91	0.1	ethylene				
92	0.1	ethylene	0	0.00048	0.00014	0.00003
93	0.1	ethylene	94	0.00048	0.00014	0.00018
94	0.1	ethylene	0	0.00048	0.00014	0.00003
95	0.1	ethylene	0	0.00048	0.00014	0.00003
96	0.3	ethylene	0	0.00048	0.00014	0.00003
97	0.3	ethylene	20	0.00048	0.00014	0.00005
98	0.3	ethylene	0	0.00048	0.00014	0.00003
99	0.3	ethylene	0	0.00048	0.00014	0.00003
100	0.3	ethylene	0	0.00048	0.00014	0.00003
101	0.3	ethylene	0	0.00048	0.00014	0.00003
102	0.3	ethylene	0	0.00048	0.00014	0.00003
103	0.3	ethylene	0	0.00048	0.00014	0.00003
104	0.3	ethylene				
105	0.3	ethylene				
106	0.3	ethylene				
107	0.3	ethylene				

APPENDIX B

ANNUAL EMISSION RATES DERIVED USING INDUSTRY LOSS-ESTIMATION PROCEDURES

APPENDIX B

ANNUAL EMISSION RATES DERIVED USING INDUSTRY ESTIMATION-LOSS PROCEDURES

It should be noted that all the annual emission rates determined in this Appendix are based on a 100% plant utilisation rate (8760 hrs per year). This is subsequently corrected to the near realistic 91% plant utilisation rate in the main text.

Table B1 Emission Estimates based on Component Count Procedure (LDPE-3 Plant)

a) Flanges

Total Flanges from all areas	=1566
x1.1 (add 10% for missed flanges)	=1723
x0.00083 (kg/hr/source)	=1.43 kg/hr

b) Valves (gas)

Total valves (gas) from all areas	=129
x1.1 (add 10% for missed valves)	=142
x0.0056 (kg/hr/source)	=0.80 kg/hr

c) Valves (light liquid)

Total valves (LL) from all areas	=76
x1.1 (add 10% for missed valves)	=84
x0.0071 (kg/hr/source)	=0.59 kg/hr

d) Relief Valves which go to Vent

Total Relief valves 12 + 3(possible)	=15
x0.104 (kg/hr/source)	=1.56 kg/hr

e) Compressor Seals =12

This is based on an estimate of:	single stream x 2 stages (primary compressor) = 2 seals
	2 streams x 3 stages (primary compressor) = 6 seals
	2 streams x 2 stages (hyper compressor) = 4 seals
x0.228	=2.74 kg/hr

f) Total emissions

Total annual fugitive (including vents) emissions based on component count

=(1.43+0.795+0.59+1.56+2.736) x 8760/1000 (tonnes/year)

= 62 tonnes/year

Table B2 **Estimated Emission Rates for Flanges and Valves using Leak/No Leak approach (LDPE-3 Plant)**

a) Flanges

Total for screened flanges	
(OVA)	= (0.01086+0.1125+[0.00006x4])x8760/1000
	= 1.083 tonnes/year
Scaled up for total number of flanges	= 1.083 x (1723/188)= 9.926 tonnes/year
(HVM)	= (0.00582+[0.00006x3])x8760/1000
	= 0.0067 tonnes/year
Scaled up for total number of flanges	= 0.0067x(1723/100) = 0.115 tonnes/year

b) Valves (gas)

Total for screened valves (gas)	
(OVA)	= ([98x0.00048]+[6x0.0451]x8760/1000
	= 2.78 tonnes/year
Scaled up for total number of valves	= 2.78x(141/104)= 3.77 tonnes/year
(HVM)	= ([84x0.00048]x8760/1000
	= 0.353 tonnes/year
Scaled up for total number of valves	= 0.045x(141/84)=0.593 tonnes/year

c) Valves (light liquid)

No light liquid valves measured leaked. Therefore for both OVA and HVM :
Emission for year = (84x0.00171)x8760/1000=1.26 tonnes/year

d) Total emissions

Total emissions of flange & valves (gas and LL) for:

OVA = 9.926+3.77+1.26 = 15 tonnes/year
HVM = 0.115+0.593+1.26 = 2 tonnes/year

Table B3 **Estimated Emission Rates for Valves and Flanges based on Stratified Approach (LDPE-3 Plant)**

a) Flanges

Rate for screened flanges (OVA)	= (0.00362+0.1125+[0.00002x4])x8760/1000
	= 1.018 tonnes/year
Scaled up for total number of flanges	= 1.018 x (1723/188)= 9.33 tonnes/year
Rate for screened flanges (HVM)	= (0.00194+[0.00875x3])x8760/1000
	= 0.247 tonnes/year
Scaled up for total number of flanges	= 0.0067x(1723/100) = 4.255 tonnes/year

b) Valves (gas)

Total for screened valves (gas)	
(OVA)	= ([98x0.00014]+[6x0.0451]x8760/1000
	= 2.49 tonnes/year
Scaled up for total number of valves	= 2.49x(141/104)= 3.37 tonnes/year
(HVM)	= ([83x0.00014+0.00165]x8760/1000
	= 0.116 tonnes/year
Scaled up for total number of valves	= 0.116x(141/84)=0.195 tonnes/year

c) Valves (light liquid)

No light liquid valves measured leaked. Therefore for both OVA and HVM :

Emission for year = (84x0.00028)x8760/1000=0.21 tonnes/year

d) Total emissions of flanges & valves

OVA= 9.33+3.37+0.21	= 12.9 tonnes/year
HVM= 4.255+0.195+0.21	= 4.66 tonnes/year

Table B4 Estimated Emissions for Valves and Flanges based on Correlation Approach (LDPE-3 Plant)

a) Flanges

Rate for screened flanges (OVA) = .01683+.1.19+.00055+.00036+.00173+.00367)x8760/1000
= 1.19 tonnes/year
Scaled up for total number of flanges = 1.19 x (1723/188)= 10.89 tonnes/year

Rate for screened flanges (HVM) = (0.00902+0.01144+0.00988+0.01251)x8760/1000
= 0.375 tonnes/year
Scaled up for total number of flanges = 0.375x(1723/100) = 6.468 tonnes/year

b) Valves (gas)

Rate for screened valves (gas) (OVA) =
(76x0.00003+6x0.0451+0.00031+0.00015+0.00188+0.00354+0.001+0.00023+
3x0.00072+5x0.00005+0.00038+3x0.0001+2x0.00008+2x0.0005)x [8760/1000]
= 2.49 tonnes/year
Scaled up for total number of valves = 2.49x(141/104)= 3.38 tonnes/year

Rate for screened valves (gas) (HVM) =
(75x0.00003+0.00008+2x0.00014+0.00248+0.00042+2x0.00005+0.00013+0.00018x [8760/1000]
= 0.052 tonnes/year
Scaled up for total number of valves = 0.052x(141/84)=0.088 tonnes/year

c) Valves (light liquid)

No light liquid valves which were measured leaked. Therefore for both OVA and HVM :
Emission for year = (84x0.00045)x8760/1000=0.33 tonnes/year

d) Total emissions of flange & valves

OVA= 10.89+3.4+0.33 = 14.6 tonnes/year
HVM= 6.468+0.088+0.33 = 6.9 tonnes/year

APPENDIX C

ESTIMATED UNCERTAINTIES IN THE EPA/SOCMI PROCEDURES AS APPLIED IN THE SHELL CARRINGTON EXERCISE

APPENDIX C

ESTIMATED UNCERTAINTIES IN THE EPA/SOCMI PROCEDURES AS APPLIED IN THE SHELL CARRINGTON EXERCISE

C1 Incomplete sampling

We first consider the uncertainty in the number of leaking components. It should be noted that not all valves and flanges were measured. The mean emission rates in Table 24 were obtained by scaling the results from the measured components proportionately to allow for the unmeasured components. This scaling gives the most probable overall emission rate, but the incomplete sampling introduces a spread of possible values.

We now derive expectation values and upper and lower 95% confidence limits for the numbers of major leakers (i.e. those screening over 10,000 ppmv) in the whole population of valves and flanges, and apply the mean emission rate factors to obtain the corresponding leak/no leak emission rate estimates. However, as the leak/no leak, stratified, and correlation analyses methods give essentially the same result for the measurements considered here, these leak/no leak confidence limits are approximately valid for all methods.

If there are m components of a given type (e.g valves, flanges etc.) on a site, the proportion of leakers is ν and measurements are made on n randomly chosen components, the probability of finding x leakers is given by the hypergeometric distribution (the measurement process equivalent to sampling without replacement). However, in most cases, the hypergeometric distribution can be approximated by the simpler binomial distribution which strictly applies only to sampling with replacement (this corresponds to measuring randomly selected valves and permitting each valve to be measured more than once). By inversion of the distributions it is possible to calculate the best estimate and upper and lower confidence limits for ν when the n measurements indicate c leakers (the best estimate is simply $\nu=c/n$). For the binomial distribution there are statistical tables which give the required results. We have used such a table to determine the expected and 95% upper and lower confidence limit values for the numbers of leaky valves and flanges in the total population and calculated the inversions directly by an iterative process. The calculations duplicate (and agree with) the tabulated data for 95% confidence levels given by EPA but have the advantage that they can be used for any desired confidence level. They also give results for the hypergeometric distribution. The results of the calculations are given in Table C1 and have been used with the leak/no leak emission factors to obtain the range of emission estimates as described in Section 8.5.

* *Some of the binomial lower limits in Table C1 are less than the measured number of leakers because the binomial distribution is not strictly appropriate to describe the measurement process. Where this happens the measured number of leakers is used as the lower limit in the table.*

C2 Uncertainties in Emission Factors

We now consider the uncertainties in the emission factors. The global factors are the averages determined from measurements of a large number of components. The actual average of finite sample of components will deviate from the average global factors. We now consider this deviation. The first assumption is that the components at the plant being measured are part of the same population that was investigated to derive the average factors. This is not necessarily the case and this could introduce further systematic errors. Figure C1, which is derived from EPA data, shows the distribution of the log of the emission rates from gas/vapour valves with screening values of 10,000 ppmv or more ("pegged sources"). The standard deviation of this distribution is 0.8. The equivalent distribution for flanges has a standard deviation of 0.73 (ignoring one obvious outlier). The corresponding width, σ_m, of the distribution of the mean log emission rate from n leakers is $\sigma_m=0.8/\sqrt{n}$. A width, σ_m, in the log distribution gives confidence limits of $\mu_m \times 10^{\pm w\sigma m}$ about the mean emission rate, μ_m, where w is the deviation from the logarithmic mean that corresponds to the desired confidence limit (μ_m includes the scale bias correction factor). For 95% confidence limits, w is approximately 2 whilst for 97.5% limits it is approximately 2.25.

C3 Combined Uncertainties Arising from Limited Sampling and Emission Factor Spread

C3.1 Separate errors limits for valves and flanges

Because the error in the emission factor depends on the number of leakers it is affected by the uncertainties introduced by the incomplete sampling. The upper confidence limit for the total emission rate is given, in principle, by the solution for y of:

$$\int_0^\infty \left[\int_0^{y/n} \Pr(f)df \right] \Pr(n)dn = 1 - \alpha/2 \tag{1}$$

where 1-α is the desired confidence level, Pr(f) is the probability of having an emission factor f and Pr(n) is the probability of having n leakers. The EPA have simplified this approach and combined errors assuming that the limits on the product of the two independent terms n and f, to a confidence level 1-α, are given by the product of the limits on the individual terms to the confidence level 1-α/2. That is the required result is taken as the product of y_1 and y_2 which are the solutions to:

$$\int_0^{y_1} \Pr(n)dn = 1 - \alpha/4 \text{ and } \int_0^{y_2} \Pr(f)df = 1 - \alpha/4 \tag{2}$$

Complementary expressions are used for the lower confidence limits. For simplicity we have used equations (2) in this work although the relationship between them and the more rigorous expression in equation (1) is not entirely clear. In order to estimate 95% confidence limits we take the solutions to equations (2) for α=0.05. The width of the distribution Pr(f) depends on the number of leakers, as outlined in Section C.2, so it is necessary to first derive the confidence limits for n then those for f. The distribution of emission factors in Figure C.1 is approximately lognormal and has a standard deviation of 0.8 on a $\log_{10}$ scale. For such a distribution the 97.5% confidence limits for the total emissions, $E\pm$, from n leakers are:

$$E_\pm = n\mu \times 10^{\pm 0.8w/\sqrt{n}} \tag{3}$$

where w=2.25. Figure C2 shows these limits as a function of n. It is possible in principle for the upper limit to be associated with the smallest number of leakers (because of the consequent uncertainty in the emission factor) but for our data the upper limit is generally associated with the maximum number of leakers and the lower limit with the minimum number.

The emission rate bounds derived from the leaker numbers in Table C1 and equation (3) are given in Table C2.

C3.2 Combined error limits for valves and flanges

The upper limits estimated for light liquid valve emissions are relatively large but this is because of poor statistics rather than genuinely likelihood of high emissions. The poor statistics arise because it was known at the outset that such emissions would form a small part of the total and therefore few measurements were done on these components. The light liquid emissions are therefore neglected in assessing the totals.

The remaining combination of gas/vapour valve and flange emissions is most easily estimated by assuming the distributions of pegged source emission factors for gas/vapour valves and flanges are identical (the means and standard deviations of the emission factor distributions are similar). We then assume the 97.5% confidence levels for the total numbers of valve and flange leakers can be obtained by adding the limits on the individual valve and flange numbers. Thus, to 97.5% confidence, from the hypergeometric distribution the maximum number of leaky components of both types at Carrington is 105 and the minimum is 10. With these values, the 95% confidence limits for the emission rate from the leakers is estimated from equation (3) with a mean emission factor of 0.0375 kg/hr** and a duty cycle of 8760 hours/year (100% plant utilisation). The contributions from the non-leakers are then estimated using the relevant no leak factors (0.00006 kg/hr for flanges and 0.00048 kg/hr for gas/vapour valves)and added. The final results are given in Table C3. It should be noted that these results have been modified for the more realistic plant annual utilisation rate of 91% in the main body of this Report.

** *The mean flange emission factor is used because the upper limit emission rate is dominated by the flange contribution. The valve emission factor (0.0451 kg/hr) is similar to the flange factor so the use of a weighted mean would not have a significant impact on the results.*

Table C1 **Confidence Limits for Numbers of Major (>10000 ppmv) Leaking Components Derived from Inversion of Binomial and Hypergeometric Distributions:**

(a) <u>95% Confidence levels</u>

	Binomial		Hypergeometric	
	Lower	**Upper**	**Lower**	**Upper**
Flanges	5	79	7	77
GV valves	6	17	6	10
LL valves	0	59	0	31

(b) <u>97.5% Confidence levels</u>

	Binomial		Hypergeometric	
	Lower	**Upper**	**Lower**	**Upper**
Flanges	4	87	5	84
GV valves	6	18	6	14
LL valves	0	67	0	64

Table C2 **Mean and Uupper and Lower 95% Confidence Limits for the Emission Rates from Individual Component Types (tonnes/yr)**

Carrington			
	Lower	Mean	Upper
Flanges	1.2	9.8	44
Gas/vapour valves	0.93	3.2	14
Light liquid valves	1.3	1.3	36

nb: based on 100% plant utilisation

Table C3 **Combined Emission Rates from Valves and Flanges**

Lower	Mean	Upper
2.8	13	55

nb: based on 100% plant utilisation

Figure C1, Distribution of "pegged" source emission rates for gas/vapour valves
(from Figure B2 - 3 4 of "Assessment of Atmospheric Emissions from Petroleum Refining" EPA-600/2 - 80 -075c, Wetherold, Provost and Smith)

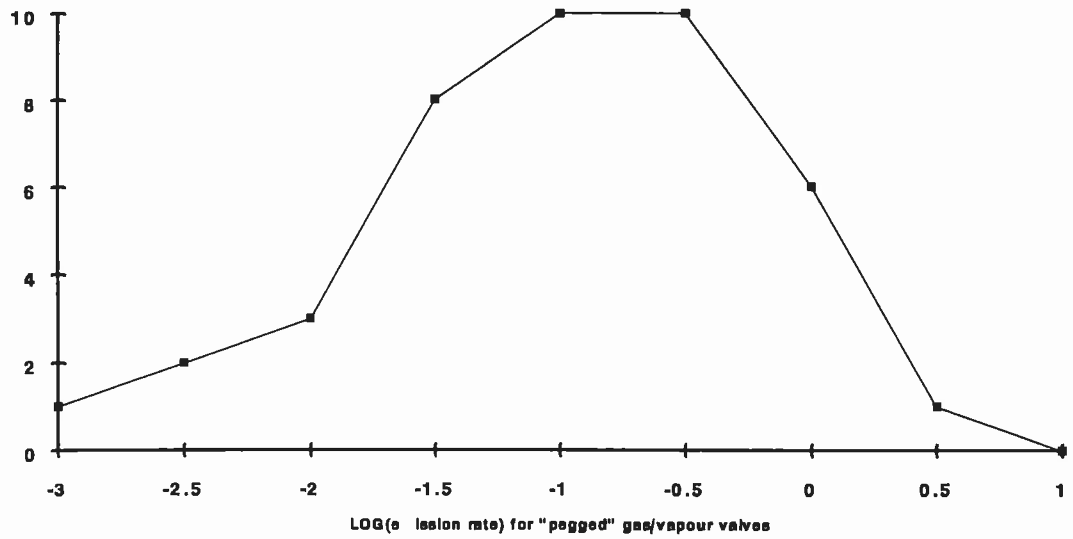


Figure C2, Upper and Lower 97.5% confidence limits for emission rate as a function of the no. of leakers