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Measurements of the Emissions of Volatile Organic Compounds Produced by a Retail Petrol-filling Station

by

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1 INTRODUCTION

This Report describes work carried out by the National Physical Laboratory, with support from the National Environmental Technology Centre, to measure the gaseous emissions to atmosphere produced by a typical UK service station which retails petroleum spirits. The aims of the project were to measure the total emissions of volatile organic compounds and of benzene to atmosphere arising from:

- retail vehicle-filling operations
- the restocking of the filling-station petrol storage tanks by road tankers.

2 BACKGROUND

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 ground level 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 been completed under the aegis of the United Nations Economic Commission for Europe's

Convention on Transboundary Air Pollution [3]. Within this Convention, twenty countries signed a Protocol in November 1991, 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 1989 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 the new national and 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.

AEA Technology provides technical policy support to the Department of Environment (DoE), Air Quality Division, on a range of issues relating to atmospheric emissions and air quality in the UK. One of the major areas of this programme is to provide valid estimates of the emissions of volatile organic compounds (VOCs) to atmosphere. These VOC emissions arise from a wide variety of industrial sectors, including motor vehicles [5]. Previous work has shown that the oil and petrochemical industries contribute significantly to the total UK emissions of VOCs, but the emission estimates for these industries were of low data quality. Recently, however, measurements have been made in the UK using a mobile remote-sensing differential-absorption lidar facility developed by the National Physical Laboratory (NPL). This has provided more accurate data on some of the sources of emissions within the oil refinery industry and petrochemical plant [6, 7]. However, the emissions from the industry involved with the distribution of refinery products, still has significant uncertainties and additional research is required.

There are about 18,500 retail filling stations within the UK, with total sales of approximately 25 million tonnes of petrol per year [8]. It is therefore important to estimate accurately the emissions from these filling stations in order to establish their contribution to the total VOC emission inventory within the UK. One aim of this project, therefore, was to carry out direct measurements of the emissions of VOCs to atmosphere from a representative petrol-filling station, so as to improve the estimates of VOC emissions from these UK sources.

In addition, an important requirement has arisen for accurate technical data on the

levels of emissions of benzene from the petroleum distribution system, particularly from petrol-filling stations. Benzene, itself a volatile organic compound, is also a carcinogen. This fact has led to the establishment in the UK of an ambient Air Quality Standard for benzene [9]. However, there is still considerable debate concerning public exposure to benzene in the atmosphere, through the use of petrol-driven motor vehicles, particularly regarding their short-term exposures in petrol station forecourts. A further aim of this Report, therefore, was to monitor the atmospheric concentrations and the emitted fluxes of benzene produced when vehicles are filled with fuel at vehicle filling stations, in addition to monitoring the total emissions of VOCs.

Methods have now become available, as noted above, for measuring directly the emissions of a range of gaseous species, including methane, benzene, and other VOCs, which are emitted fugitively by industrial processes, landfill etc [10]. These use remote, open-path, optical techniques which can be employed for direct measurements of the rates of emissions (ie the emitted fluxes) of the gases. Currently, the most versatile of these techniques for determining the emitted fluxes of gaseous species is known as differential-absorption lidar (DIAL). An outline of the operating principles of the DIAL technique is given in Section 5.2, and the methodology for using the technique to measure the fluxes of gaseous pollutants emitted by industrial sites is summarised in Section 5.4. In addition, a simpler technique, which uses an open-path monitor, has also been developed. This allows the total concentrations of VOCs to be monitored along one or more open paths in the atmosphere. The principles of this technique are described in Section 5.6, and the methodology whereby flux measurements are made is outlined in Section 5.7.

This Report discusses the measurement exercise carried out at a retail petrol-filling station using the two optical remote sensing technologies outlined above - the DIAL facility and the open-path monitor. As noted above, the main aims of this exercise were to measure directly the total emissions of non-methane VOCs and the benzene emissions specifically, which were emitted during normal operations of the filling station. However, additional measurements were made to determine the emissions produced whilst a road tanker was re-stocking the petrol storage tanks at the filling station. *In-situ* measurements were also made of the individual concentrations of a wide range of hydrocarbon species present in the atmosphere around the filling station. The methodologies for carrying out these different measurements, together with the results obtained, are presented in this Report.

3 OBJECTIVES OF THE PROJECT

Specific objectives of the project were to:

1. Define criteria for the selection of a representative retail filling station, and to choose a filling station satisfying these criteria;

2. Measure the total mass emissions to atmosphere of volatile organic compounds produced by filling station during:

    - normal vehicle filling operations;
    - re-stocking of the filling-station storage tanks from a road tanker;

3. Measure the concentrations of benzene and the total VOCs in the atmosphere within the filling-station forecourt during normal vehicle-filling operations, and to monitor their spatial and temporal variations.

4. Provide detailed data on the individual hydrocarbon species emitted from the site, by short-term atmospheric sampling.

5. Monitor the longer-term average concentrations of certain VOCs within the filling station forecourt, and in the surrounding area.

6. Produce estimates of the annual emissions of total volatile organic compounds which would occur during the normal operations of the filling station.

7. Estimate the long-term exposure of vehicle users to benzene which arises from vehicle filling operations.

8. To continue technical discussions, in collaboration with AEA Technology, with representative bodies of the oil and petrochemical industries, in order to promote improvements to the accuracy of the UK Emissions Inventory, and to secure more widespread acceptance of the UK methodology.

4 SELECTION AND DESCRIPTION OF THE SITE

The following selection criteria were used to chose a suitable location at which to perform the measurements.

- Total retail sales (throughput) of petrol and diesel to exceed 500,000 gallons

per year;

- Minimum interference from other potentially-interfering sources of hydrocarbon emissions, including roads;

- Access to locations near the filling station for NPL monitoring equipment, with suitable unobstructed optical measurement paths in the atmosphere;

- Access to detailed information on the amounts of petrol and diesel retailed during the measurement period;

The filling station selected for this exercise was the Retreat Garage at Polhill, near Sevenoaks, Kent (see Figure 1). This filling station fulfilled the necessary requirements, having a throughput of 600,000 gallons per year, with available space for the monitoring equipment. It is located on the A224, four miles to the north of Sevenoaks. It is also in a semi-rural location with no significant interfering VOC sources nearby. It is bypassed approximately one mile to the east by the M25. It therefore has mainly local patronage with peak periods of operation in the mornings, evenings, and at lunchtimes, usually from business traffic. Its location is on top of a hill, and its emissions are blown towards the M25 with prevailing (south-westerly) winds.

The forecourt has seven pumps on two islands (see Figure 2). One of these vends only diesel, a further two vend only unleaded or leaded petrol, and the others vend both unleaded and leaded petrol. There was no vapour recovery associated with the vehicle-filling pumps. Figure 3 shows the detailed arrangement of these pumps, and Table 1 gives the type of fuel dispensed from each. Figure 4 shows, as an example, the statistical distribution of all the vehicle filling operations which occurred, together with the amount of fuel delivered, on 15th February. The average volume of petrol delivered to a vehicle during this measurement exercise was 21 litres. The filling station's underground storage tanks and their associated vents to atmosphere are also shown in Figure 2. No vapour recovery system was present when these tanks were being filled.

The Polhill filling station was open between approximately 0700 hrs and 2100 hrs, and thus any 24-hourly averaged measurements will produce biased results (Section 7.3.2), when compared with those obtained for a continuously operating filling-station.

There is a car park to the north of the filling station from which measurements could

be made using the mobile DIAL facility. A second measurement location was identified for the DIAL facility in a lorry park to the south of the filling station. The NPL open-path monitor was deployed at a number of locations within the filling-station forecourt area.

5 REMOTE MONITORING TECHNIQUES DEVELOPED AT THE NATIONAL PHYSICAL LABORATORY FOR DIRECT MEASUREMENTS OF INDUSTRIAL EMISSIONS

5.1 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 absorption spectrum, and that the wavelength of the source can be chosen so that it coincides with one feature of this spectrum. Then, tuning the source wavelength on and off the spectral absorption feature and measuring the absorption that occurs, allows the concentration of the selected species to be determined. The performance of these remote techniques have been extended continually at NPL, particularly in terms of the number of gaseous species that are detectable, their detection sensitivities, and the measurement range. Field trials have been carried out regularly to demonstrate the extending capabilities of these new measurement techniques.

5.2 PRINCIPLES OF THE DIFFERENTIAL-ABSORPTION LIDAR TECHNIQUE

One of these remote monitoring facilities uses a principle similar to optical radar, known as differential-absorption lidar (DIAL). Figure 5 illustrates the principle of the technique. 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. This 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, as noted above, 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.

5.3 THE NPL DIAL FACILITY

The NPL DIAL technique operates using these principles in the infrared, visible, and ultraviolet spectral regions. This enables a wide range of gases including SO_2, NO, NO_2, CO, HCl, N_2O, CH_4, C_2H_4, C_2H_6, higher molecular weight alkanes and alkenes, and aromatics such as toluene and benzene, to be monitored specifically and sensitively [11]. Table 2 lists examples of these.

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 6. Figure 7 shows in more detail the scanning mirror, the receiving telescope and the detection system of this mobile laboratory.

5.4 METHOD FOR MEASURING GAS FLUX USING THE DIAL TECHNIQUE

As noted above, the DIAL technique measures directly the concentrations of the selected gas(es) as a function of range along any selected direction up to the maximum range. By scanning the direction in which the transmitted laser beam and the receiving telescope are pointed the spatial profile of the gas is obtained. The total amount of gas between any two points in the measurement direction can also be determined. If the direction in which the laser beam and the telescope are pointed is then scanned in a plane downwind of an industrial plant, in a manner similar to that shown in Figure 8, the total amount of the selected gas(es) passing through the plane can be measured. If similar measurements are carried out upwind, the total flux of gas emitted by the site can be determined, provided there are no large changes in wind velocity between the downwind and upwind measurements. Measurements of wind speed and direction are also required. The range of facilities available at NPL for making these meteorological measurements is shown in Figure 9. The methodology for determining the emitted fluxes from these measurements has been presented [7, 11].

5.5 VALIDATION OF THE NPL DIAL MEASUREMENTS

The accuracy of the DIAL technique depends critically on the wavelengths selected for a given measurement application. These wavelengths are chosen to avoid interferences due to gaseous atmospheric species which may potentially have overlapping spectra and to avoid spectral interferences from other gaseous pollutants which may be present.

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

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

- to monitor specifically the atmospheric concentrations of benzene;

- to avoid spectral interferences due to atmospheric water vapour, methane, sulphur dioxide, nitrogen oxides, carbon monoxide, carbon dioxide etc which may be present.

These wavelengths were monitored on-line using diagnostic facilities. The detailed methodology for ensuring the accuracy of the measurements has already been presented [7]. In addition, a number of exercises have been carried out to demonstrate the validity of the NPL DIAL measurements [7].

5.6 PRINCIPLES OF THE OPEN-PATH MONITORING TECHNIQUE

In the open-path monitoring technique a low energy optical source and mirror system launch a collimated infrared beam into the atmosphere, directed towards a mirror set at a suitable distance away (typically 10 to 300 m). The mirror returns a large proportion of the beam to the monitor unit for measurement. The wavelength of the infrared beam is selected by a filter to be in the absorption region of the gas that is to be monitored. The amount of that target gas present along the beam is obtained from the degree to which the beam is absorbed by the gas.

The monitor used in these trials was developed by NPL. It uses a wavelength-modulation technique to measure the target gas concentration. It operates by ratioing the wavelength-modulation signal against a total returned power signal. This gives an output which is proportional to gas concentration but independent of any attenuation due to, for example, rain or mist. A general diagram of the monitor is shown in Figure 10.

The open-path monitor because of its "double-ended" mode of operation, measures the integral amount or average gas concentration along the optical beam. Therefore unlike the DIAL technique, it gives no information of the spatial distribution of the gas.

5.7 METHOD FOR MONITORING GAS FLUX USING THE OPEN-PATH TECHNIQUE

Gas fluxes are measured with the open-path monitor in a manner similar to that for DIAL (Section 5.4). The monitor automatically integrates the amount of gas along the beam which is in an approximately horizontal direction. The use of several beams at different heights then enables the gas concentration between the monitor and the retroreflector (mirror) to be integrated in a vertical direction. If this method for area integration of the concentration is combined with the local wind speed, the gas flux across the measurement plane can be determined. The methodology for doing this is shown schematically in Figure 11.

5.8 SHORT-TERM MEASUREMENTS OF THE CONCENTRATIONS OF INDIVIDUAL SPECIES

Ambient air samples were drawn into previously-evacuated gas cylinders which have specially-passivated internal walls to ensure that there interiors were inert to the VOCs being sampled. The sampling procedure entailed opening the valve of the cylinder so that the flow rate into the 10 litre capacity cylinder was about 0.5 to 1 l/minute. The sampling time for a particular cylinder was therefore usually 10-15 minutes. (This, however, can be modified to suit the application). The cylinder valve was then closed and the contents were analysed at NPL using sensitive gas chromatography (detection sensitivity achievable ~2 parts in 10^{11} by volume). Calibration was carried out using internationally-validated gravimetric multicomponent VOC standards held at NPL [12]. This method thus provides short-term snapshots of the concentrations of a very wide range of hydrocarbon species present in the filling station. The results obtained during this exercise are discussed in Section 8.6.

5.9 METHOD FOR MEASURING VOC CONCENTRATIONS USING DIFFUSION TUBES

Diffusion tubes, containing tenax, were used for longer-term measurements of certain VOCs. These were subsequently analysed for benzene, toluene, ethyl benzene and the (meta, para, and ortho) xylenes. The analyses were carried out using thermal desorption of the VOCs into a gas chromatograph, which was fitted with a flame ionisation detector. This chromatograph was calibrated by using similar diffusion tubes, which contained known concentrations of benzene, toluene, ethyl benzene, and the xylene isomers. The results obtained are presented in Section 8.7.

6. OUTLINE WORK PROGRAMME

The work programme, carried out by the National Physical Laboratory, and the National Environmental Technology Centre, to achieve the objectives given in Section 3, is summarised below:

(i) Preliminary visits were made to a short-list of twenty petrol stations pre-selected according to the criteria listed in Section 4. The Polhill garage was chosen as the measurement site.

(ii) A measurement exercise was carried out at the Polhill site in which:

- The DIAL and the open-path facilities were used to monitor the VOC fluxes emitted during normal forecourt vehicle-filling operations at the filling station.

- The DIAL technique was used to monitor the ambient concentrations of benzene which were present in the atmosphere within the filling station forecourt area during vehicle filling operations.

- The open-path technique was used to measure the concentrations of VOC's within the forecourt area during vehicle-filling operations.

- The DIAL and open-path techniques were used to monitor the emitted fluxes of VOC's which occurred during the period when a road tanker was unloading into the station's storage tanks.

(ii) A detailed record was prepared of all the vehicle-filling operations which occurred during this period. The garage till receipts were also used to

determine the delivered volume of each filling operation.

(iv) The required meteorological parameters, including wind speed and direction, were monitored simultaneously with the concentration measurements, as outlined in Section 5.

(v) Whole-air samples were taken at various locations in and around the filling station for subsequent analyses by gas chromatographic techniques.

v) Diffusion tubes were mounted adjacent to each of the fuel pumps. These were subsequently analysed be gas chromatography to determine the average concentrations of VOCs which were present over a two week period in the filling station.

7 MEASUREMENTS CARRIED OUT AT POLHILL FILLING STATION

This Section describes the measurements which were carried out in order to meet the objectives of the project of determining:

- the atmospheric benzene concentrations
- the total atmospheric VOC concentrations
- the emitted fluxes of VOCs

7.1 RANGE-RESOLVED ATMOSPHERIC MEASUREMENTS OF VOC'S AND BENZENE USING THE DIAL TECHNIQUE

Two types of measurement were carried out using the DIAL facility:

i) Vertical scans were carried out downwind of the filling station which, when combined with meteorological measurements, enabled the emitted fluxes to be determined.

ii) Range-resolved measurements were made by directing the optical beam along fixed directions across the petrol pumps at approximately head heights as close to the customer's head as practical during vehicle-filling operations. The measured concentrations were therefore representative of those which the customer would be likely to breath whilst filling a vehicle petrol tank.

Table 3 lists the data sets obtained with the DIAL facility during the measurement exercise, using the two measurement strategies outlined above.

7.2 OPEN-PATH HYDROCARBON MEASUREMENTS

One of the objectives of operating the open-path monitoring system during the Polhill exercise was to demonstrate the validity of using this technique in future as a complementary method to the well-validated DIAL technique, since this latter technique had been validated for such measurements, and in addition it can be employed effectively on larger-scale industrial installations.

The open-path monitor measures the total hydrocarbon concentrations present in the atmosphere along any path between the monitor and a retro-reflector. Two monitors were employed during this exercise using one of the two following measurement strategies :

i) Both monitors measured across the downwind edge of the forecourt, in the configuration shown in Figure 10.

ii) One monitor measured along a line-of-sight across the filling-station forecourt, at head height, passing directly across one set of petrol pumps.

7.3 IN-SITU AIR SAMPLE MEASUREMENTS

7.3.1 Short-term Whole-air Samples

Twelve whole-air samples were taken during this measurement exercise in special-passivated cylinders. They were sampled at various locations within the filling-station forecourt. Figures 12 and 13 show the locations where the whole-air samples were taken, on the 15th and 16th February respectively. Table 4 lists the exact locations and times at which these were taken.

7.3.2 Long-term Diffusion-tube Measurements

Four tenax diffusion tubes were attached to vertical metal posts adjacent to each filling station pump, using adhesive tape, approximately 1.5 m from the ground. They were mounted away from the surface of these posts using 50 mm wooden spacers. A further tube was mounted adjacent to the road 0.5 km upwind of the filling station, and another was retained as a blank. Table 5 gives the location of each tube, and Figure 14 shows the location of one of these tubes relative to one of the petrol pumps. The sampling time for these diffusion-tube measurements was approximately two weeks.

7.4 METEOROLOGICAL MEASUREMENTS

Wind speed and direction were logged during the measurement exercise on four sets of equipment, as shown schematically in Figure 9. These were located on :

i) A 15-metre mast attached to the DIAL facility.

ii) A two-metre high tripod, which was located in open ground to the south of the garage. (anemometer B)

iii) A two-metre high tripod, which was located at the southern edge of the car park to the north of the filling station. (anemometer D)

iv) A ten-metre mast, which was also used to mount the retro-reflectors for the open-path monitors. This was generally located at the north-west corner of the garage forecourt. (anemometer C)

The meteorological data obtained during this exercise were vector-averaged to provide the wind directions and speeds required to calculate the emitted fluxes of VOCs.

8 RESULTS

8.1 BENZENE : SHORT-TERM CONCENTRATIONS

The short-term concentrations of benzene were monitored, as outlined above, when customers were filling vehicles with petrol and diesel, and were thus representative of the short-term exposure which they would be likely to receive whilst filling their vehicle petrol tanks.

Figures 15 and 16 show examples of typical time series of the range-resolved, concentrations of benzene which were measured next to petrol pumps 7 and 6 respectively, whilst a vehicle was being filled at that pump. Any operations which were occurring at other petrol pumps on the forecourt at the same time are also indicated on these Figures.

Figure 17 gives an example of a longer measured time-series of atmospheric benzene concentrations. This example should be compared with the time-series shown in Figure 18, which gives the amounts of petrol dispensed from the pumps during the

same period, and the times that these occurred. It can be seen that the degree of correlation is reasonable. Figure 19 displays the same data, presented in a sequential order rather than as a time series, so as to show the variability in the measured concentrations of benzene which were present in the atmosphere during individual vehicle-filling operations only.

The benzene concentrations measured in the atmosphere at these locations over periods when vehicle filling was taking place during this measurement exercise, were generally between 1 and 10 ppm by volume

8.2 BENZENE: LONGER-TERM EXPOSURE

The results obtained from the fourteen-day-average diffusion tube measurements of benzene toluene, ethyl benzene and xylene concentrations are shown in Table 5. It can be seen that the average benzene concentration, close to the pumps was 3.2 ppb. However, as noted previously, these diffusion tubes were exposed during periods at night when the filling station was closed. The average benzene concentration during the period when the filling station was operational was thus ~5 ppb. The average concentration measured adjacent to the road 0.5 km north of the filling station was 0.4 ppb.

8.3 SHORT-TERM VOC CONCENTRATIONS

The total concentrations of VOCs in the atmosphere on the forecourt were monitored continuously, and with good time resolution, using an open-path monitor. This probed the atmosphere at similar locations to those where the DIAL benzene measurements were being made.

An example of the time-series of VOC concentration measurements obtained with this monitor is shown in Figure 20. This may be compared with Figure 21 which shows the time-series of amounts of fuel dispensed by the adjacent pumps. (Small differences in the times in the two graphs are associated with time differences between the NPL and the filling station clocks). It should be noted that, as expected, the diesel filling operations produced considerably less emissions than those associated with petrol filling.

The range of VOC concentrations measured during petrol vehicle-filling operations was generally between 100-1000 ppm by volume adjacent to the filling pumps.

8.4 TOTAL FLUXES OF VOCs EMITTED DURING VEHICLE FILLING OPERATIONS

Both the open-path monitor and the DIAL facility were used to measure the total fluxes of VOCs emitted by the filling station during vehicle-filling operations, as outlined in Section 7. The wind speed and direction were measured using anemometers as outlined in Section 7.4. Examples of the results obtained from the four anemometers are shown in Figure 22.

It was practical to use the open-path monitor to monitor individual vehicle-filling operations, and the temporal fluctuations which occurred within these. The fluxes from these individual operations were then determined. These emitted fluxes were then compared against the volumes of fuel delivered in each filling operation. Figure 23 shows the results obtained - the emissions measured by the open-path technique are plotted against the volume of petrol delivered to each vehicle during the short measurement periods.

The DIAL technique, however, required 4-10 mins to complete a vertical scan, in order to produce a flux measurement of the required accuracy. During this period several vehicles may have been filled with petroleum product. Therefore, in this case, all the vehicle-filling operations which occurred during the period of the DIAL flux measurements were added together in order to provide the total delivered volume of fuel transferred during that period. Figure 24 shows the results obtained - the emissions measured by the DIAL technique are plotted against the total volume of petrol delivered during the measurement periods.

Figures 23 and 24 also give the optimum fitted straight-line correlations between the total VOCs emitted to atmosphere (by mass) and the amount of petrol (by mass) delivered to the vehicles. (The density of petrol was taken as 738 $kg.m^{-3}$ [13]). It can be seen that the measured emissions obtained by the two techniques are consistent. The measured emissions to atmosphere correspond to 0.3% by mass of the petrol delivered to the vehicles.

8.5 THE FLUXES OF VOCs EMITTED DURING ROAD-TANKER RE-STOCKING OF THE FILLING-STATION STORAGE TANKS

The DIAL facility and the open-path monitor both made independent measurements of the emissions produced during a road-tanker delivery of petrol to the filling station. Figure 3 shows the road-tanker storage-tank filling points and the vent stacks of these filling station tanks. The road tanker delivered 30,000 litres of petrol (15,000

litres unleaded plus 15,000 litres four-star).

The results obtained by the DIAL facility provided the more accurate results on this occasion. The DIAL facility made two flux measurements whilst the filling station storage tanks were being refilled. Table 6 gives the results.

The measured loss of VOCs to atmosphere corresponded to 0.17%, by mass, of the total delivery. It was not possible, to differentiate between the emissions which arose from leaded and unleaded petrol transfers during these measurements.

8.6 SPECIATION OF VOC EMISSIONS

8.6.1 Short-term Whole-air Sample Results

The complete set of analyses of all the speciated hydrocarbons contained in the whole-air samples are given in Table 7. The locations where these samples were taken have already been discussed (Table 3). Table 8 summarises the results obtained for the individual hydrocarbon species in the atmospheric samples which were related to vehicle filling-operations, expressed with respect to:

(i) the relative carbon-number contributions to the total emissions;

(ii) the relative amounts of benzene present in the total VOC emissions.

Figure 25 illustrates these same results. It can be seen that the majority of the VOC emissions arise from hydrocarbons with carbon numbers four and five, and that the average amount of benzene which was present in the atmosphere due to vehicle-filling operations is 0.7 percent of the total emissions by volume, or 0.83% by mass.

Table 9 and Figure 26 summarises, in a similar manner, the results which were associated with road-tanker re-stocking operations. Table 10 and Figure 27 show the results related to background concentrations away from the filling station. It can be seen that the concentration profile of hydrocarbons is significantly different away from the filling station. It should also be noted that the actual concentrations away from the filling station are considerably lower (Table 7).

8.6.2 Diffusion-tube Results

The results obtained from the diffusion-tube measurements, outlined in Section 7.3, are shown in Table 5. Figure 28 shows some results obtained by CONCAWE [13] for

comparison.

9 SUMMARY AND DISCUSSION OF THE RESULTS

9.1 MEASURED BENZENE EMISSIONS

The short-term benzene concentrations measured close to the locations in the atmosphere where vehicle drivers were breathing petrol vapour during vehicle filling operations were generally in the range 1 to 10 ppm by volume.

Benzene emissions constituted: 0.7 percent by volume of the VOC total emissions.
0.83 percent by mass of the VOC total emissions.

The longer-term diffusion-tube results obtained during this exercise showed that average benzene concentrations of ~3 ppb were present adjacent to the petrol filling pumps. If this result is scaled to allow for the periods when the filling station was closed (Section 8.3), the average concentration which would be present during operating hours is ~5 ppb. This result is not inconsistent with a set of results obtained by CONCAWE using diffusion tubes on twenty-four filling stations [14], shown for comparison in Figure 28.

9.2 ANNUAL EXPOSURE OF VEHICLE DRIVER TO BENZENE ON GARAGE FORECOURTS

The measured short-term benzene concentrations given in this Report can also be used to derive an estimate of the potential yearly exposure of an average car driver to benzene, on garage forecourts.

The average UK vehicle driver travels approximately 20,000 km per year. Thus, if the fuel consumption of the average vehicle is 11.1 litres per 100 km driven, the vehicle uses 2220 litres annually. It is also assumed that the average fill of petrol is 30 litres. The driver is therefore exposed to 74 vehicle filling operations per year. The measurements carried out during this exercise showed that the average exposure to benzene in the atmosphere during vehicle filling corresponded to 9 ppm-minutes, and that the average period for the filling operation was 1.5 minutes. This leads to a potential exposure of this average vehicle driver to 650 ppm-minutes of benzene per year. This corresponds to an exposure for this average vehicle driver of 1.2 ppb of benzene over the whole year, from petrol filling operations on garage forecourts.

This should be compared with the Air Quality Standard for public exposure to

benzene in the atmosphere [9], which is 5 ppb over any one-year period.

9.3 MEASURED VOC CONCENTRATIONS

The total VOC concentrations measured close to the locations in the atmosphere where vehicle drivers were breathing petrol vapour during vehicle filling operations, were generally in the range 100-1000 ppm by volume. Atmospheric whole air samples, which were taken during this exercise to provide speciated hydrocarbon data were consistent with these remote-monitoring results. The dominant species present were C_4 and C_5 hydrocarbons (see Table 8 and Figure 25).

9.4 MEASURED TOTAL VOC EMISSIONS

The measured total VOC emissions to atmosphere which arose from the filling station during this exercise were:

Vehicle filling operations: (no vapour recovery)	0.3 percent by mass of delivered petrol.
Road-tanker re-stocking operation: (no vapour recovery)	0.17 percent by mass of delivered petrol.

The emissions to atmosphere from diesel filling operations were considerably smaller (< 5% by mass of the petrol emissions).

The annual emissions of VOCs to atmosphere from this retail filling station may therefore be estimated as 5.7 tonnes per year from retail filling operations and a further 3.8 tonnes per year due to road-tanker re-stocking of the stations storage tanks (with no vapour recovery).

9.5 CONTRIBUTIONS TO THE UK VOC EMISSION INVENTORY

The total retail petrol sales in the UK correspond to about 25 million tonnes [8]. The VOC emissions to atmosphere produced by retail vehicle-filling operations measured during this exercise were 0.3%, by mass, of throughput. (These operations did not have a vapour recovery system in place). An estimate can therefore be made of the total emissions from all UK petrol-vehicle retail-filling operations. This corresponds to 75 ktonnes per year.

The VOC emissions to atmosphere produced by road tanker re-stocking of the filling station's storage tanks were measured during this exercise to be 0.17% by mass of the total petrol transferred. No vapour recovery system was in place at this filling station

to cover these operations (in common with most UK retail petrol-filling stations). An estimate can therefore be made of the total emissions from road-tanker re-stocking operations at all retail filling stations in the UK. This corresponds to 40 ktonnes per year.

The total VOC emissions from retail filling stations can thus be obtained by summing together the vehicle-filling and road-tanker restocking estimates. The total emissions then correspond to about 115 ktonnes per year. Clearly this estimate is subject to a large uncertainty due to the fact that the measurement exercise was of a very limited duration and only one filling station was monitored. However, the estimate may be compared with the estimate of VOC emissions from all UK oil refineries. This was estimated to be 180 ktonnes per year in 1993 [15], but a more recent estimate, provided by the petroleum industry, corresponded to 100 ktonnes per year in 1993 [16].

The above results do not include the VOC emissions which arise from road-tanker loading terminals. Some of these use a bottom-loading process with vapour recovery, and others use a top-loading (splash filling) process with no vapour recovery. It is therefore not valid to utilise the results obtained during this exercise to infer the emissions to atmosphere from these terminals.

10 ACKNOWLEDGEMENTS

The authors of this Report would like to acknowledge the Department of Environment, Air Quality Division, for their sponsorship of this important research activity. We would also like to thank Mr M Woodfield at the National Environmental Technology Centre for his continued interest and enthusiasm throughout the project. We would also like to thank the owners of the Polshill Service Station for their cooperation.

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TABLE 1: **Types of Fuel Dispensed at Each Pump at Polhill Retail Service Station**

'Side' No	Fuel
1	diesel only
2	leaded and unleaded petrol
3	leaded and unleaded petrol
4	leaded petrol only
5	leaded petrol only
6	unleaded petrol only
7	unleaded petrol only

TABLE 2: Examples of Detection Sensitivities Attainable with the 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	30 ppb
NO_2	20 ppb			N_2O	40 ppb
COS	0.5 ppb				
HCl	1 ppb				
HCHO	1 ppb				
HNO_3	1 ppb				

Table 3: Summary of Measurements made using DIAL Facility during the Polhill Exercise

Date	Type of Measurement
13 February	Benzene : 4 vertical scans : concentration measurements adjacent to petrol pumps
14 February	Gasoline: a) 8 vertical scans b) Repeated concentration measurements adjacent to the petrol pumps at human head level during vehicle filling operations
15 February	Gasoline: a) 2 vertical scans with road tanker unloading b) 20 vertical scans during vehicle filling Benzene: 4 vertical scans
16 February	Benzene: Repeated concentration measurements adjacent to the petrol pumps at human head level during vehicle filling

Table 4 : Locations of NPL Whole-Air Samples

Date	Cylinder name	Start time	End time	Location	Notes
14.2.95	AND 944	11.50	11.55	Middle of Forecourt edge, next to public footpath	Upwind
	AND 943	11.50	11.51	Behind Petrol Station	About 70 m downwind
15.2.95	SCOTT 7960	10.02	10.07	Adj. public footpath and sign	Upwind of tanker delivery; downwind of filling station
	RAS 180	10.02	10.06	On ground between NPL van and car	Downwind of road tanker
	SCOTT 7585	10.02	10.06	On wall, 1m off ground, adjacent to station storage tank vents and vent pipes	Downwind of tanker, midway between open-path monitor and retro.
	RAS 117	10.08	10.10	Replaced above cylinder	As above
16.2.95	SCOTT 7977	10.51	10.52	Near FID nozzle (shop entrance), at ground level	Simultaneous either side of vehicle filling with 30 l.
	SCOTT 7609	10.51	10.52	On island between pumps 5 and 7	
	SCOTT 7577	12.25	12.26	On island between pumps 1 and 2	Simultaneous, either side of vehicle filling with 30 l of unleaded.
	SCOTT 7954	12.25	12.26	Outside edge of forecourt, opposite SCOTT 7577.	
	RAS 187	12.54	12.55	Adj. operator of pump 2, approx 1 m height	Filling with 30 l unleaded
	RAS 202	13.03	13.04	Adj. operator of pump 2, approx 1 m height	Filling with 30 l unleaded

Table 5: Results of Diffusion-tube Measurements

Tube No.	Location	Benzene ppbv	Toluene ppbv	Ethylbenzene ppbv	m&p-xylene ppbv	o-xylene ppb
1	Adjacent to side 1 (diesel only)	1.98	3.71	0.44	1.22	0.71
2	Adjacent to sides 2 & 3 (leaded and unleaded)	3.25	6.52	0.72	2.04	0.95
3	Adjacent to sides 4 & 5 (leaded only)	3.22	6.03	0.64	1.8	0.83
4	Adjacent to sides 6 & 7 (unleaded only)	3.13	6.45	0.71	2.17	0.91
	Average of tubes 2, 3 & 4	3.2	6.33	0.69	2.00	0.90
5	On lamp post by the side of the road 0.5 km north of filling station	0.36	0.6	0.09	0.24	0.17
6	Blank	0.04	0.09	0.02	0.04	0.06

Table 6: VOC Emissions from Road-tanker Re-stocking of Storage Tanks

Amount of petrol delivered	21 x 10^3kg
Delivery time	34 minutes
Average VOC loss estimate (measured by DIAL)	62.5 kg.hr^{-1}
Total VOCs emitted to atmosphere	35 kg
VOC loss of fuel delivered	0.17%
Estimated benzene emissions	0.22 kg

Table 7: Locations of NPL Whole-Air Samples

Sample location and details:	Car filling gnd level, shop	Car filling nr pump	Car filling nr pumps	Car filling gnd level road	Car filling nr operator	Car filling nr operator	Tanker delivery upwind	Tanker delivery downwind	Tanker delivery downwind nr vent	Tanker delivery downwind nr vent	Upwind of station nr road	Downwind behind station
Cylinder No:	SCOTT 7977	SCOTT 7609	SCOTT 7577	SCOTT 7954	RAS 187	RAS 202	SCOTT 7960	RAS 180	SCOTT 7585	RAS 117	AND 944	AND 943
Date sampled:	16/02/95	16/02/95	16/02/95	16/02/95	16/02/95	16/02/95	15/02/95	15/02/95	15/02/95	15/02/95	14/02/95	14/02/95
Sample No.	1	2	3	4	5	6	1	2	3	4	1	2
Concentration:	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
Methane	1.8	2.01	1.91	1.91	2.01	1.83	2.08	2.5	2.05	1.74	1.83	1.9
Ethane	0.004	0.082	0.004	0.005	0.235	0.047	0.008	0.275	0.156	0.007	0.011	0.007
Ethene	0.002	0.004	0.004	0.005	0.013	0.006	0.006	0.	0.003	0.003	0.002	0.003
Ethyne	0.002	0.	0.	0.003	0.	0.	0.008	0.	0.	0.002	0.055	0.004
Propane	0.01	1.106	0.031	0.026	3.276	2.244	0.021	2.111	1.185	0.033	0.005	0.005
Cyclopropane	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
Propene	0.001	0.01	0.001	0.002	0.022	0.	0.	0.015	0.009	0.002	0.001	0.001
2-Methyl propane	0.104	11.163	0.385	0.359	48.65	29.78	0.102	11.38	6.46	0.17	0.	0.002
n-Butane	0.217	29.747	0.71	0.453	97.67	75.86	0.376	59.86	33.3	0.741	0.017	0.002
Cyclobutane	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.002	0.
Trans 2-butene	0.001	0.129	0.005	0.003	0.294	1.255	0.004	0.132	0.073	0.002	0.002	0.
1-Butene	0.001	0.041	0.004	0.002	0.081	0.827	0.004	0.043	0.023	0.001	0.001	0.
2-Methyl propene	0.002	0.076	0.004	0.003	0.255	1.104	0.007	0.153	0.086	0.004	0.001	0.011
Cis 2-Butene	0.002	0.286	0.009	0.006	0.507	0.999	0.003	0.147	0.082	0.003	0.002	0.
1,3-Butadiene	0.	0.	0.	0.	0.	0.033	0.	0.	0.	0.	0.	0.
2,2-Dimethyl propane	0.	0.013	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
Cyclopentane	0.002	0.173	0.005	0.004	0.	0.	0.002	0.	0.	0.005	0.001	0.
2-Methyl butane	0.102	12.308	0.325	0.216	54.49	20.4	0.156	28.23	15.12	0.324	0.033	0.003
n-Pentane	0.012	1.347	0.025	0.02	5.003	4.234	0.015	1.323	0.746	0.02	0.004	0.001
Trans 2-pentene	0.004	0.577	0.016	0.01	1.679	1.049	0.008	0.969	0.542	0.015	0.002	0.
Pentenes	0.013	0.937	0.049	0.028	4.907	3.472	0.025	2.82	1.575	0.038	0.007	0.
Cis 2-Pentene	0.002	0.322	0.009	0.005	0.942	0.581	0.005	0.546	0.305	0.008	0.001	0.
Isoprene	0.	0.099	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
Sat C6	0.011	1.35	0.034	0.176	4.512	1.166	0.018	2.308	1.282	0.038	0.004	0.003
2-Methyl pentane	0.01	1.039	0.026	0.019	5.585	1.489	0.012	1.285	0.712	0.022	0.003	0.001
3-Methyl pentane	0.004	0.525	0.012	0.009	0.	1.044	0.007	0.765	0.44	0.013	0.002	0.
n-Hexane	0.	0.167	0.	0.002	0.486	0.572	0.003	0.176	0.101	0.	0.001	0.
unsat. C6s	0.	0.501	0.022	0.016	1.513	0.868	0.002	0.908	0.451	0.	0.002	0.
Benzene	0.006	0.474	0.007	0.006	1.475	1.117	0.008	0.672	0.385	0.01	0.	0.002
sat. C7s	0.	0.48	0.009	0.004	1.234	0.711	0.006	0.625	0.509	0.006	0.004	0.
2&3-Methyl Hexane	0.	0.	0.	0.	0.309	0.309	0.	0.12	0.	0.	0.	0.
n-Heptane	0.	0.024	0.001	0.001	0.	0.	0.	0.	0.	0.	0.	0.
Methyl Benzene	0.012	0.245	0.007	0.007	1.289	0.826	0.009	0.416	0.237	0.013	0.004	0.004
sat. C8s	0.	0.194	0.013	0.006	0.678	0.53	0.003	0.801	0.433	0.009	0.003	0.
n-Octane	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
Ethyl Benzene	0.001	0.009	0.001	0.001	0.059	0.038	0.002	0.029	0.016	0.	0.001	0.001
1,4&1,3-Dimethyl Ben	0.003	0.023	0.002	0.002	0.153	0.119	0.006	0.076	0.044	0.006	0.002	0.002
1,2-Dimethyl Benzene	0.001	0.012	0.001	0.001	0.05	0.035	0.003	0.027	0.016	0.	0.001	0.001
n-Nonane	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
C9	0.	0.	0.	0.	0.	0.	0.	0.	0.007	0.	0.	0.
1,3,5-Trimethyl Benzer	0.	0.	0.	0.005	0.	0.	0.	0.	0.	0.	0.	0.
1,2,4-Trimethyl Benzer	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.

Table 8

Sample location	Car filling	Car filling	Car filling	Car filling	Car filling	Car filling	
	gnd level, shop	nr pump	nr pumps	gnd level road	nr operator	nr operator	
Cylinder No:	SCOTT 7977	SCOTT 7609	SCOTT 7577	SCOTT 7954	RAS 187	RAS202	
Date sampled:	16/02/95	16/02/95	16/02/95	16/02/95	16/02/95	16/02/95	average %
c2	0.7	0.1	0.2	0.4	0.0	0.0	0.2
c3	1.5	1.2	1.3	1.3	1.0	1.1	1.2
c4	55.9	59.4	58.9	51.6	56.6	67.6	58.3
c5	29.0	28.2	28.3	22.1	32.2	22.9	27.1
c6	8.0	8.6	8.0	21.4	7.7	5.7	9.9
c7	3.2	1.8	1.5	1.3	1.8	1.9	1.9
c8	1.7	0.7	1.7	1.3	0.7	0.9	1.2
c9	0.0	0.0	0.0	0.7	0.0	0.0	0.1
benzene	1.4	0.9	0.5	0.5	0.8	0.9	0.8

Table 9

Sample location	Tanker delivery	Tanker delivery	Tanker delivery	Tanker delivery	
	downwind	downwind nr vent	downwind nr vent	upwind	
Cylinder No:	RAS 180	RAS 117	SCOTT 7585	SCOTT 7960	
Date sampled:	15/02/95	15/02/95	17/02/95	17/02/95	average %
c2	0.1	0.4	0.1	1.2	0.4
c3	1.3	1.6	1.3	1.8	1.5
c4	55.8	56.0	56.4	54.6	55.7
c5	32.8	31.0	32.0	28.9	31.2
c6	7.0	7.5	7.0	7.9	7.3
c7	1.5	1.8	1.8	2.7	2.0
c8	1.4	1.7	1.4	2.9	1.9
c9	0.0	0.0	0.0	0.0	0.0
benzene	0.7	0.8	0.7	1.2	0.9

Table 10

Sample location	Downwind	Upwind of station
	behind station	nr road
Cylinder No:	AND 943	AND 944
Date sampled:	16/02/95	16/02/95
c2	12.6	19.1
c3	7.2	2.6
c4	28.7	15.0
c5	10.3	36.6
c6	15.7	11.4
c7	12.0	8.3
c8	12.8	7.0
c9	0.8	0.0
benzene	3.6	0.3

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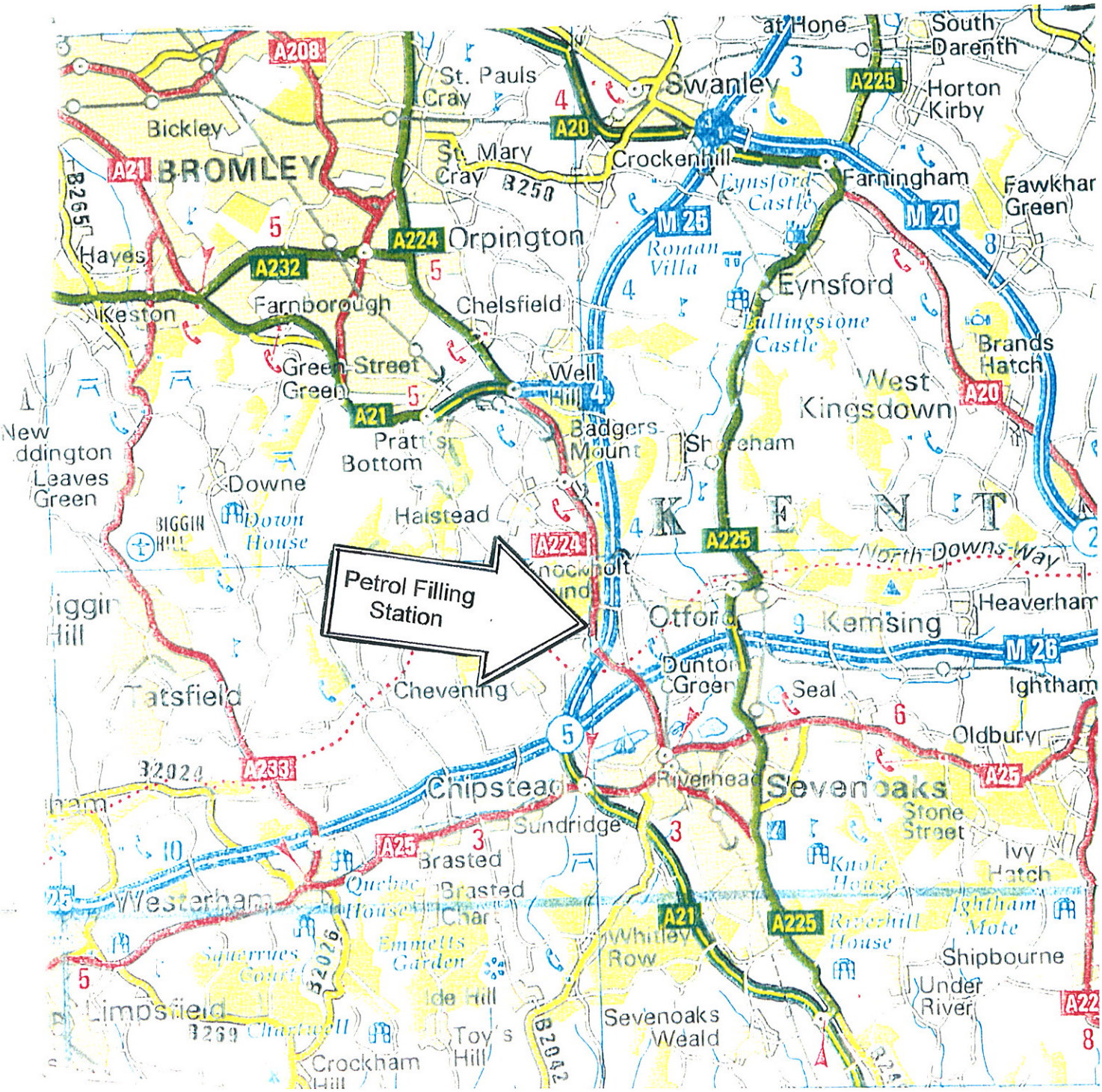

Figure 1: Location of selected retail petrol Filling station

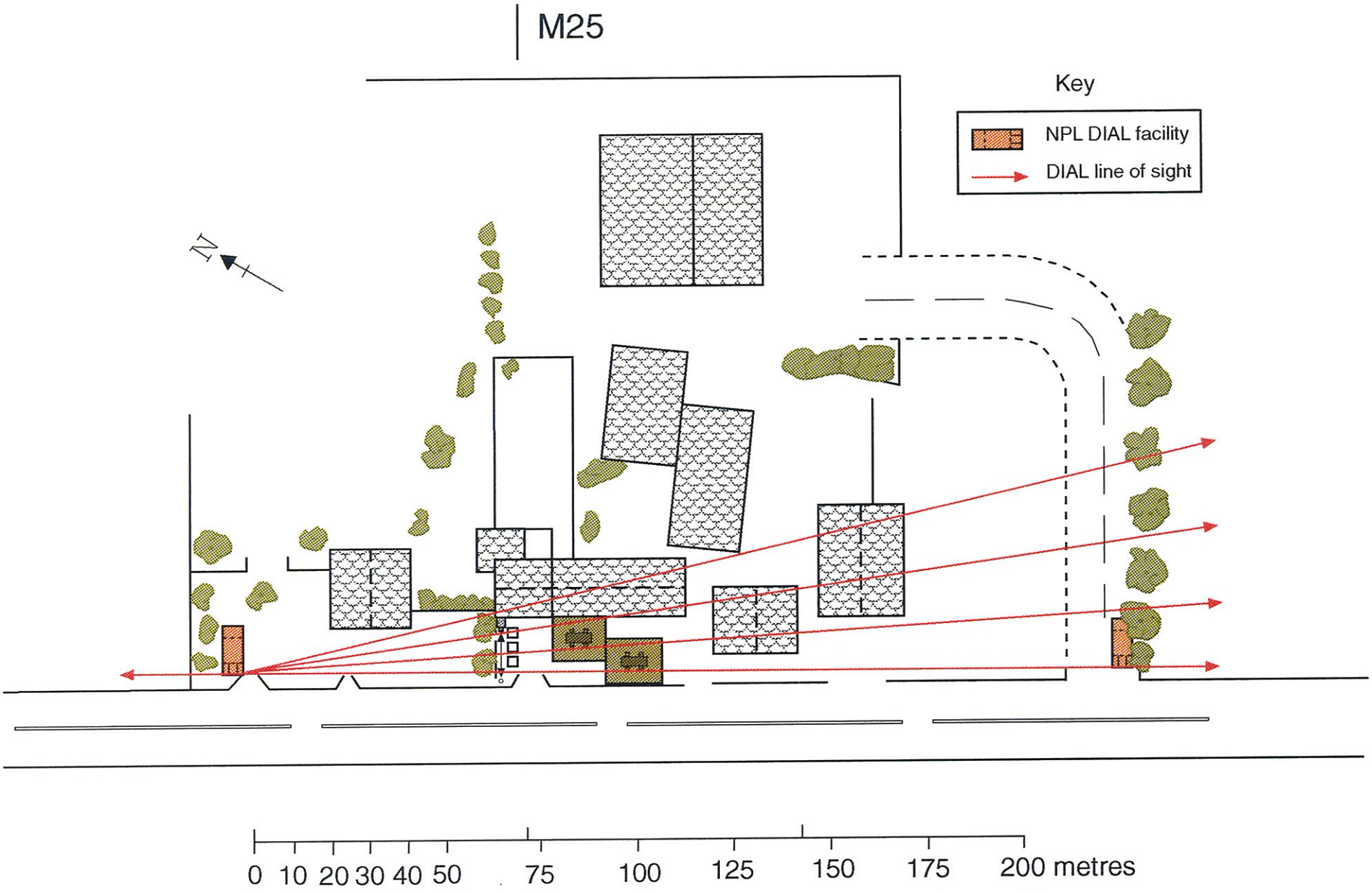

Figure 2: Layout of Filling station site

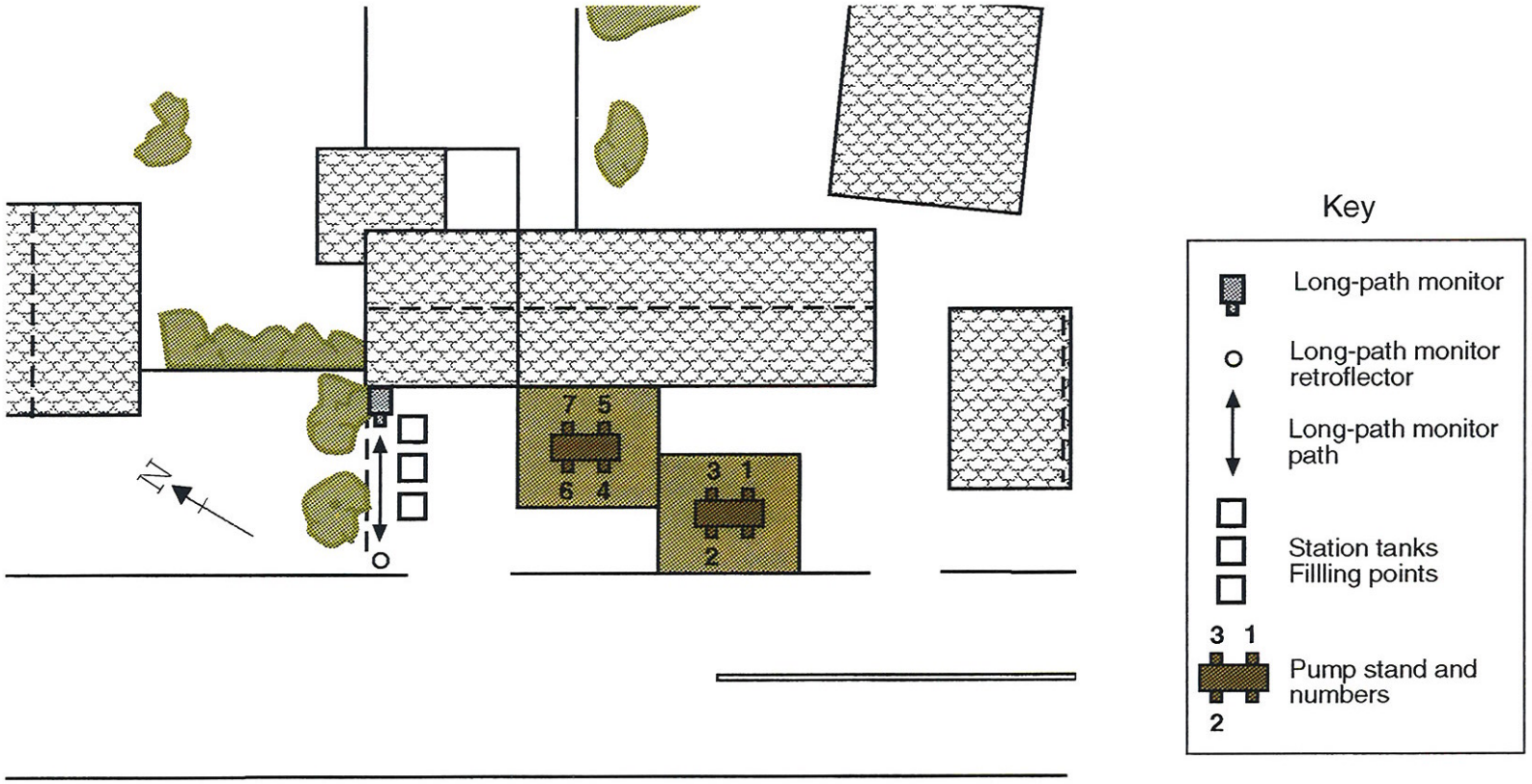

Figure 3: Detailed arrangement of Filling station site

Figure 4: Statistical distribution of volumes of petrol dispensed 15.2.95.

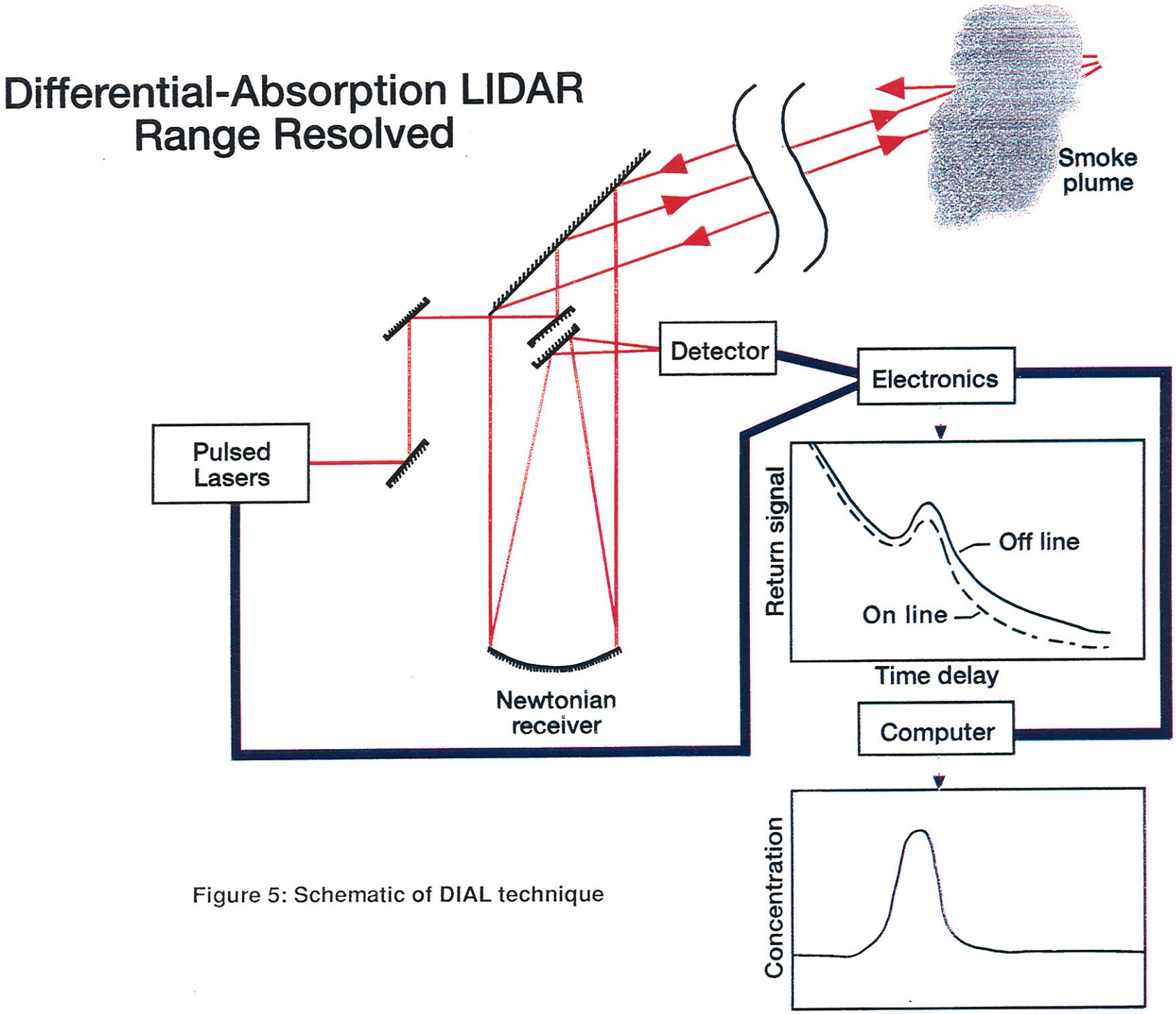

Figure 5: Schematic of DIAL technique

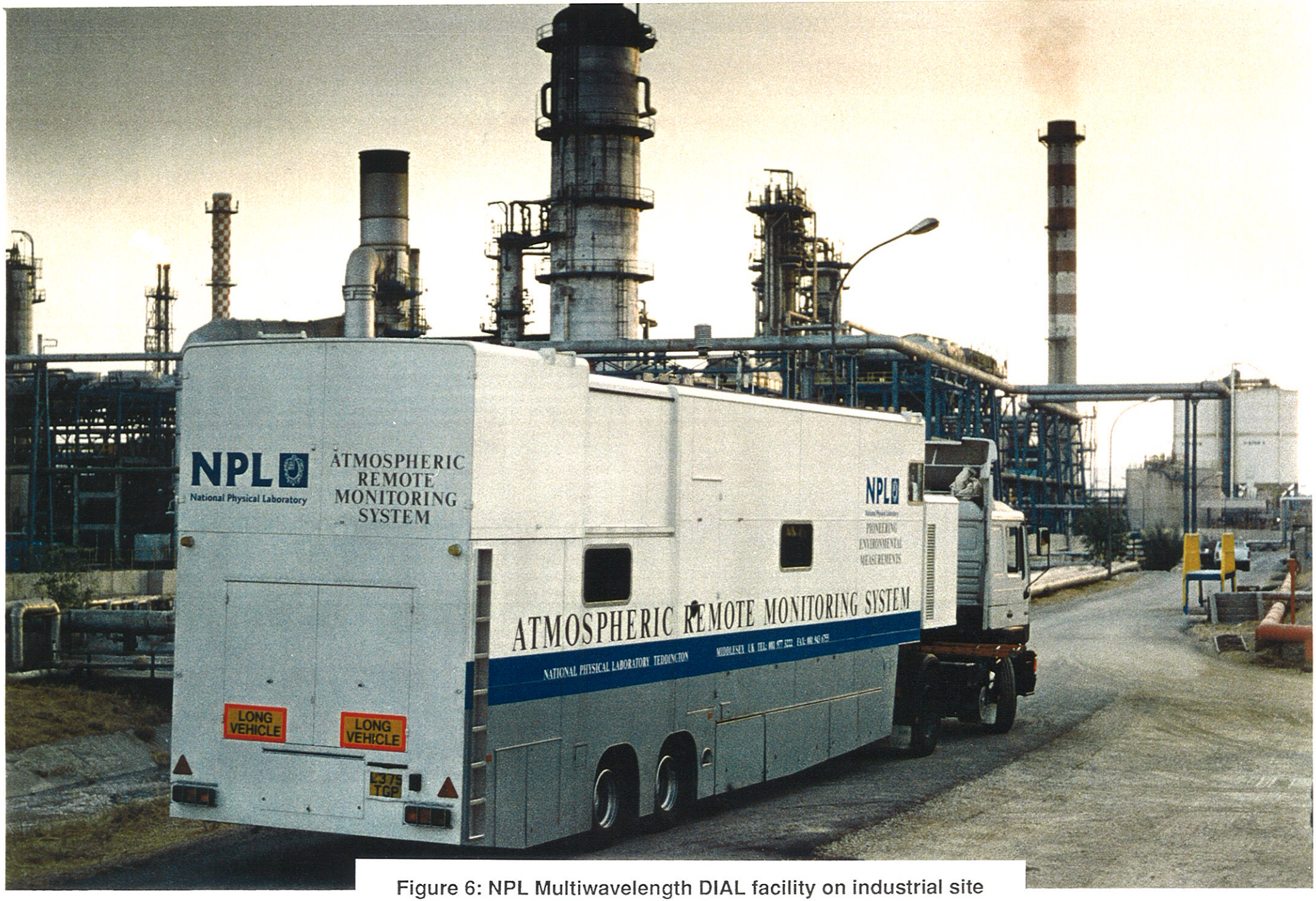

Figure 6: NPL Multiwavelength DIAL facility on industrial site

Figure 7: NPL DIAL facility transmitting and receiving telescope, and associated scanning system

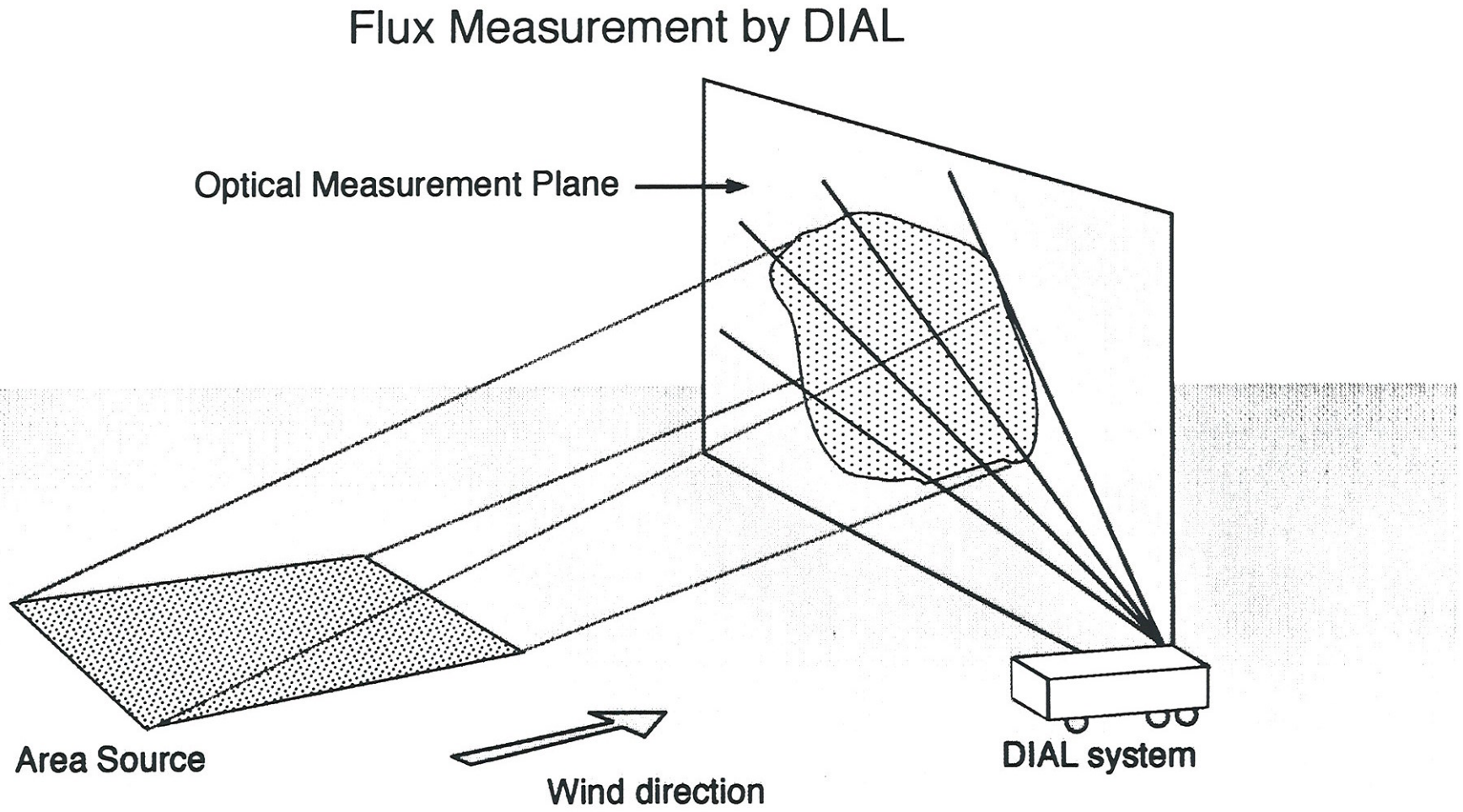

Figure 8: Arrangement for flux measurement using DIAL technique

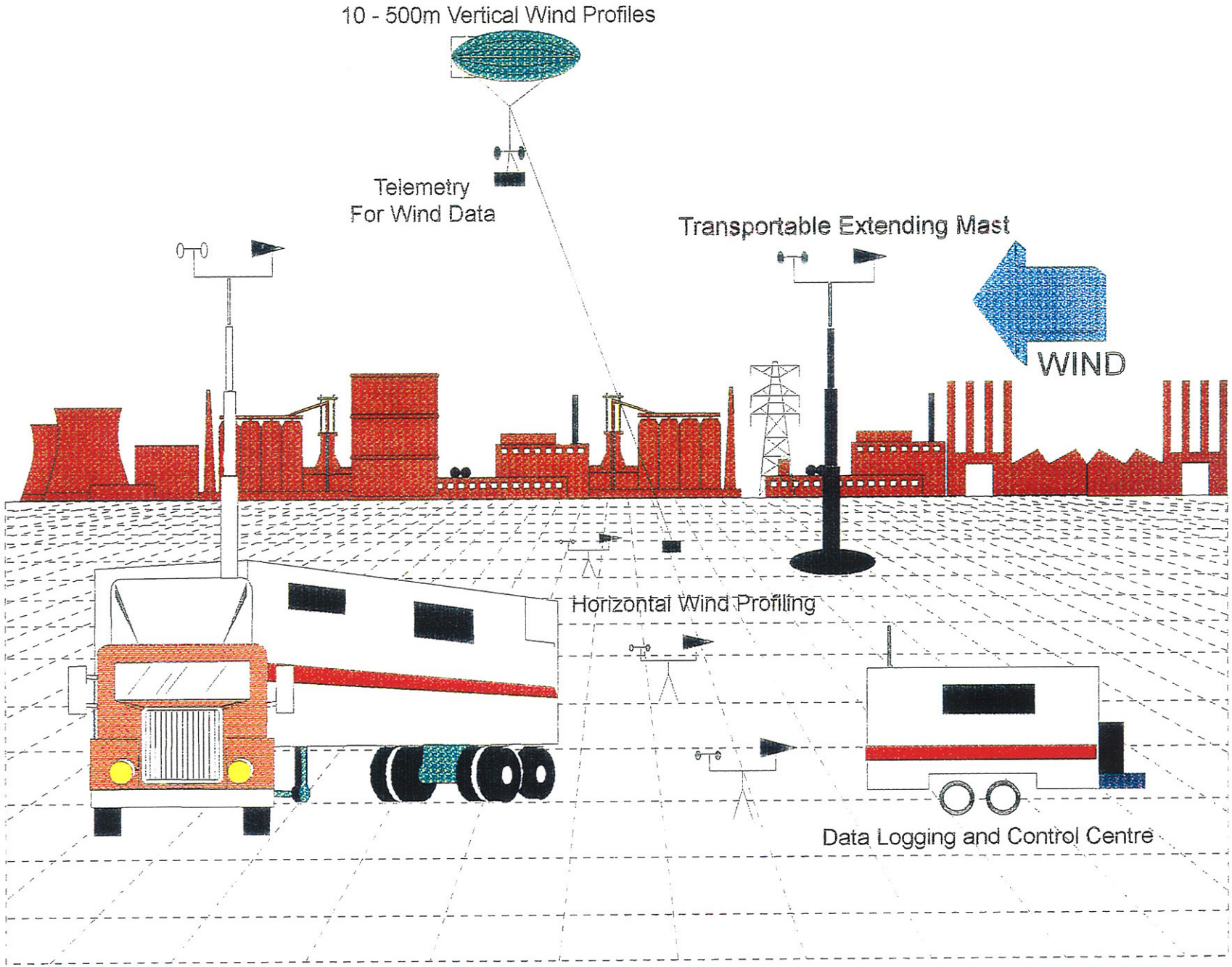

Figure 9: Meteorological equipment used in conjunction with NPL DIAL facility to measure emitted fluxes

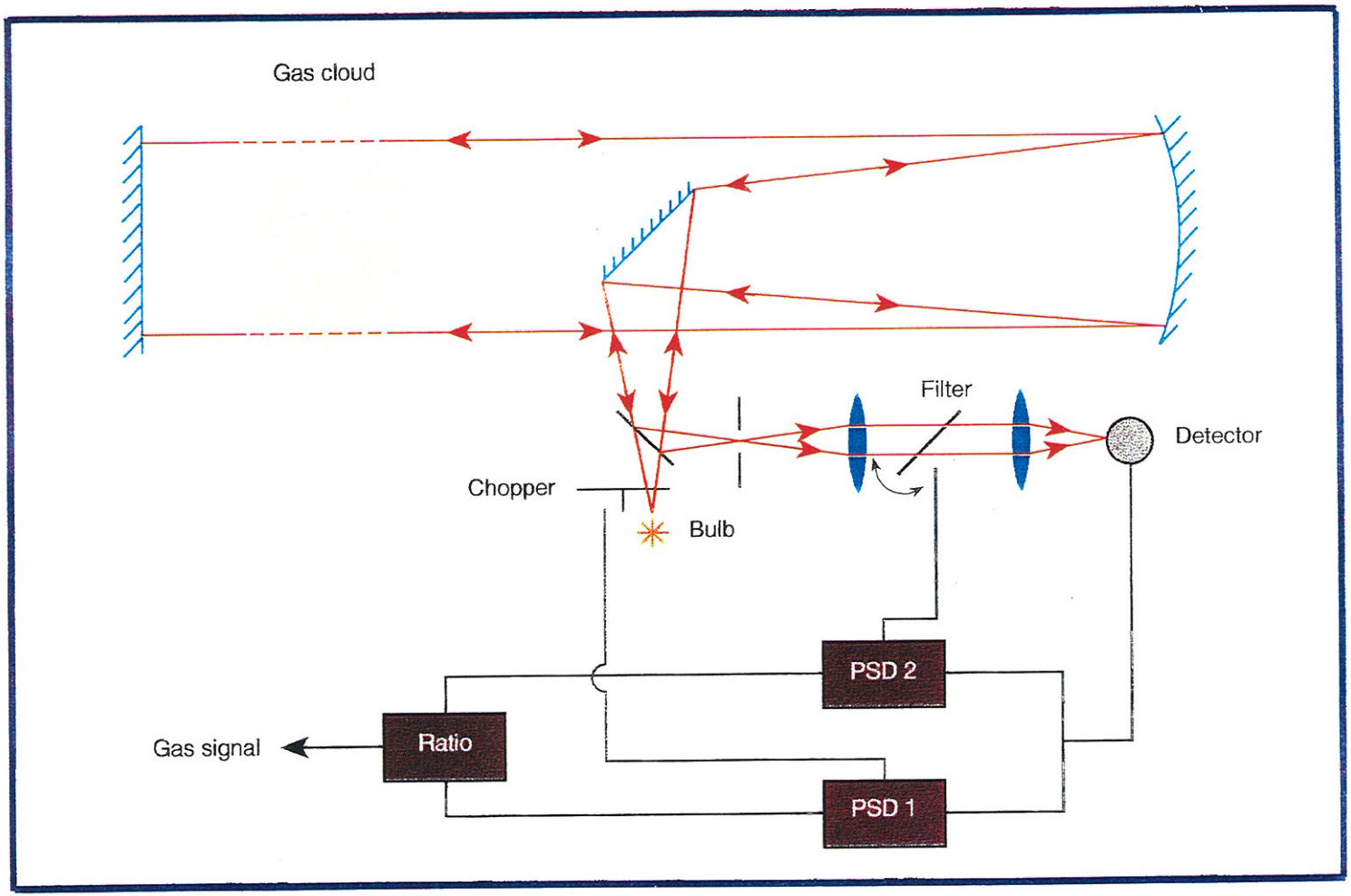

Figure 10: Schematic of the Open-path Monitor principle

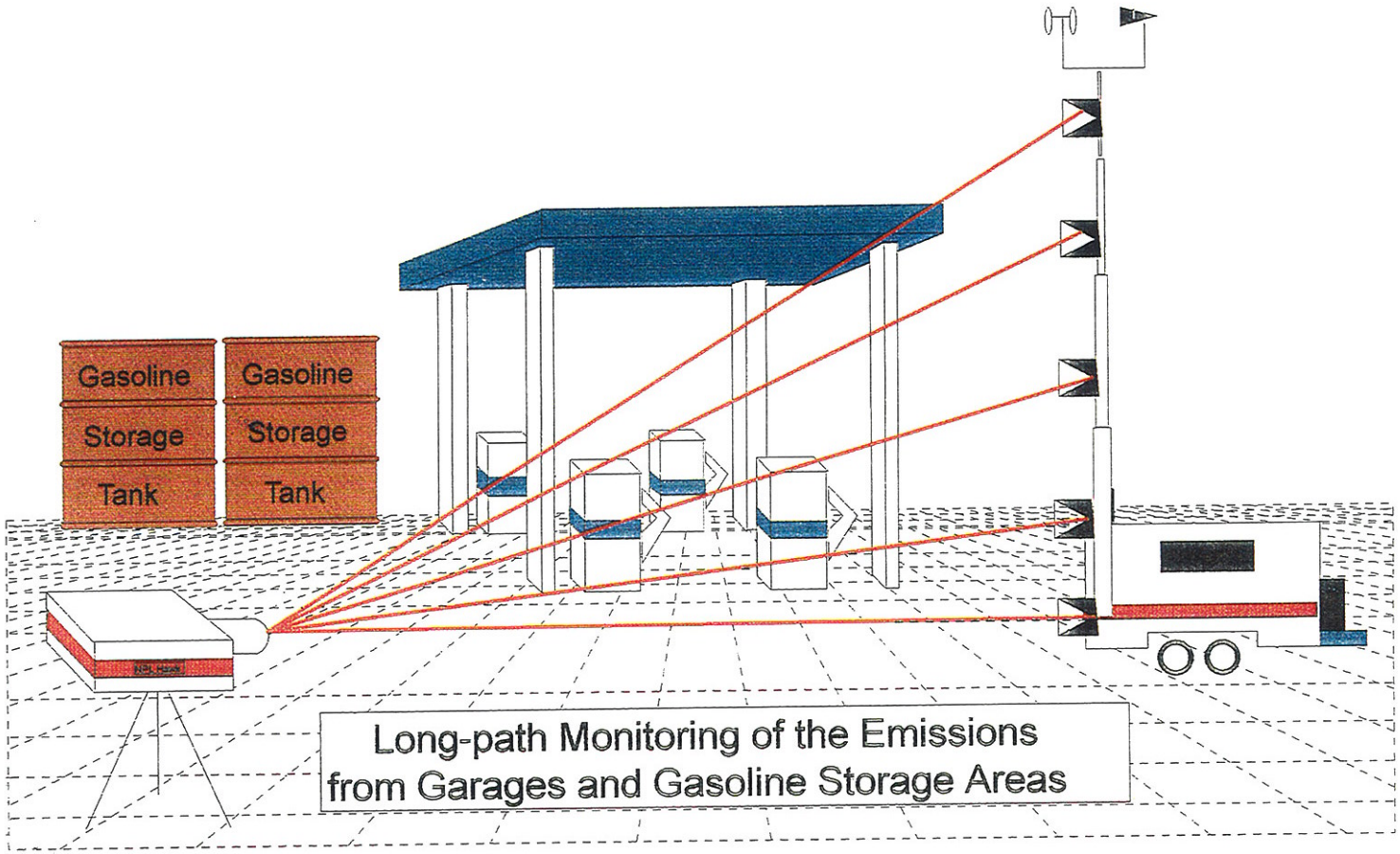

Figure 11: Methodology for measuring the fluxes of emitted gases when using the Open-path technique

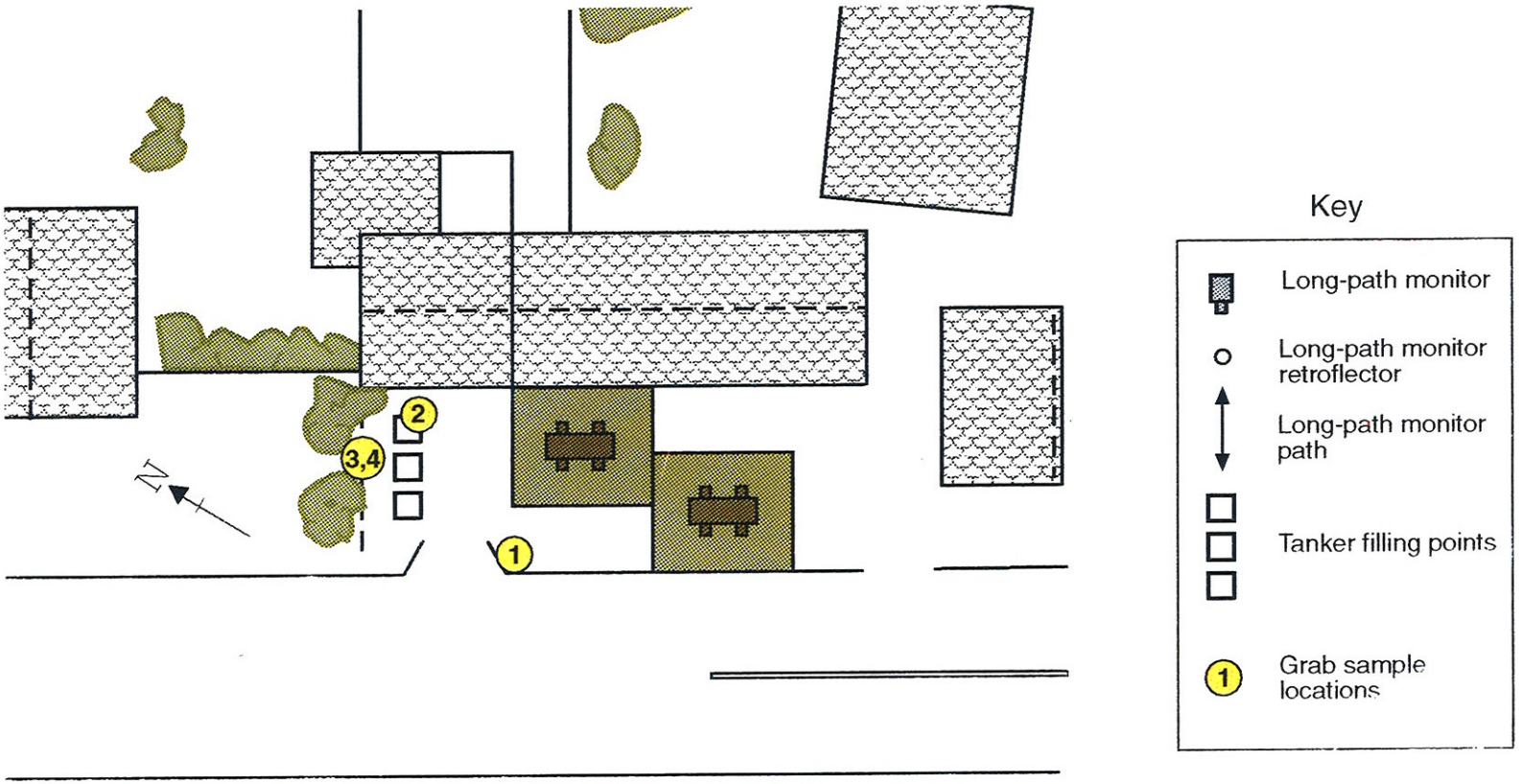

Figure 12: Location of Whole-air Samplers (15.2.95)

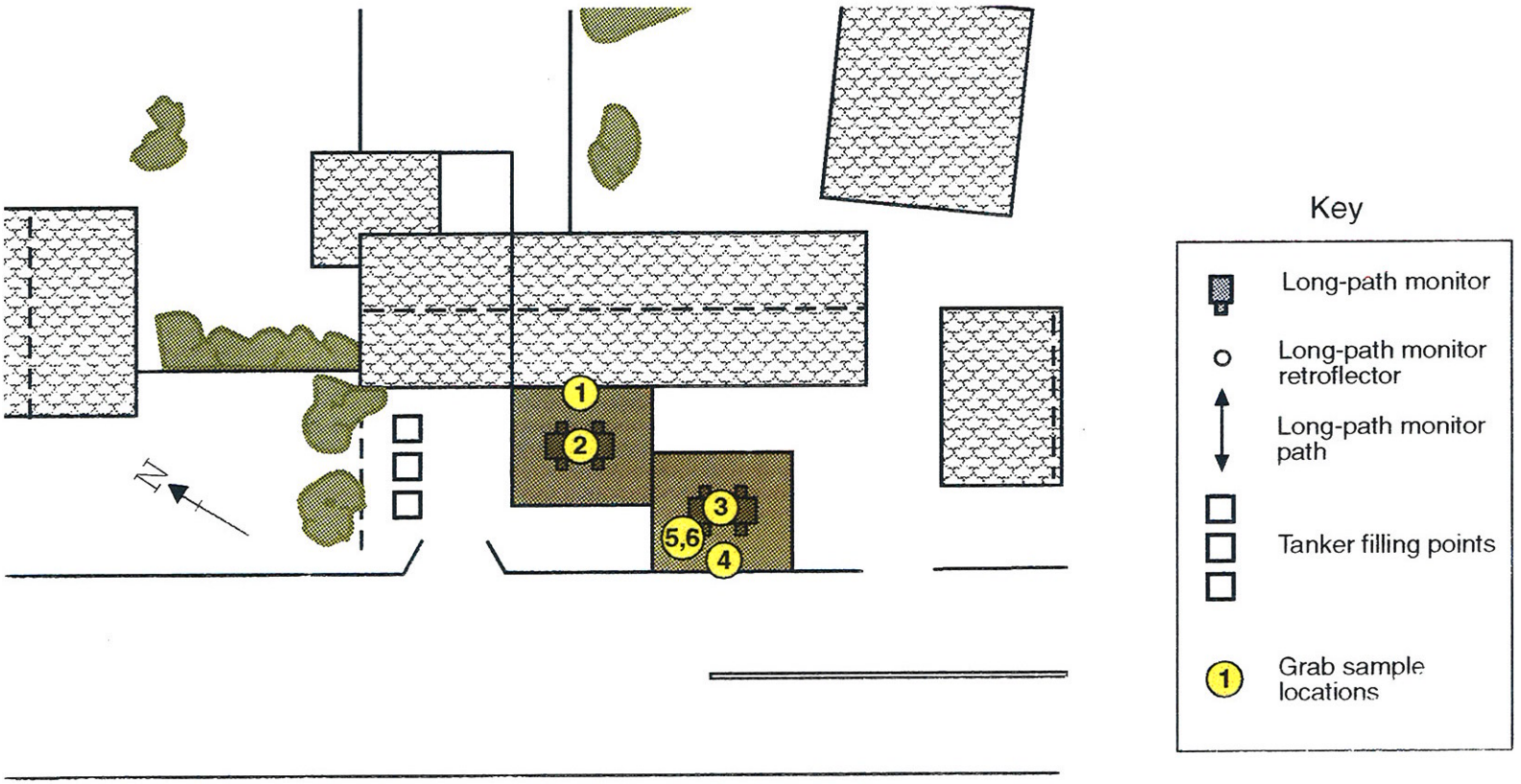

Figure 13: Location of Whole-air Samplers (16.2.95)

Figure 14: Method of Mounting Diffusion-tube Samples

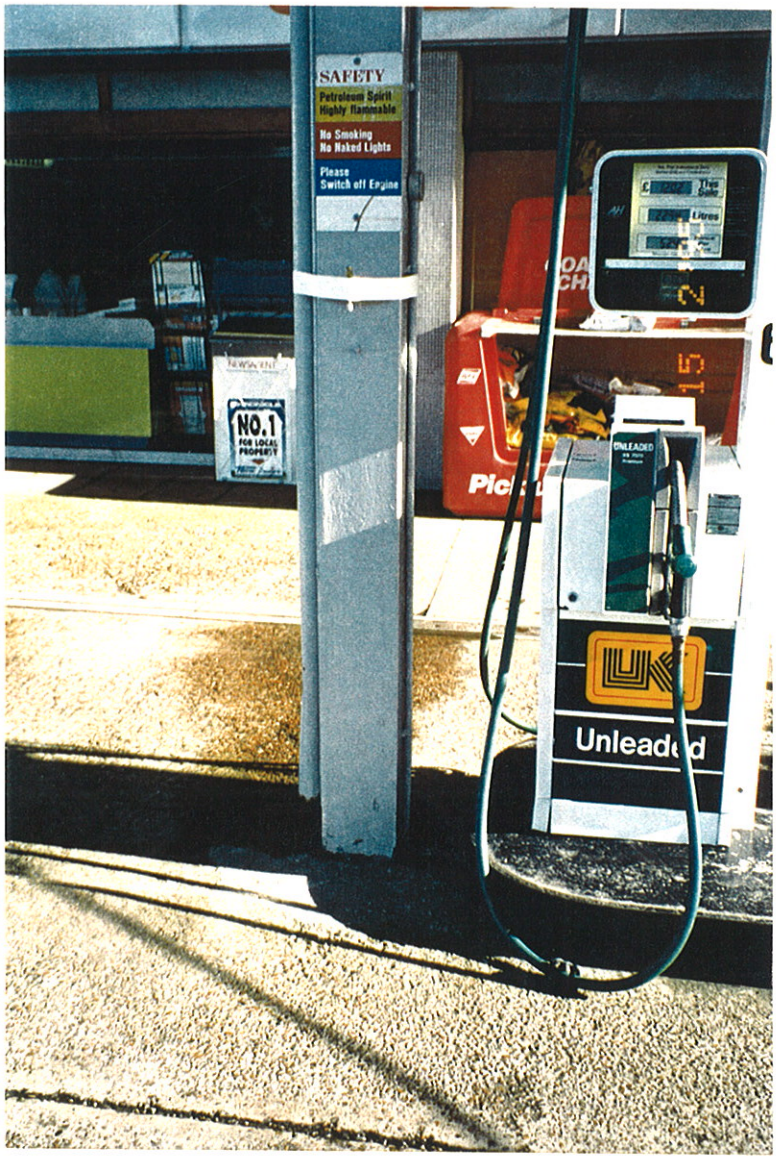

Figure 15: Variations in Benzene atmospheric concentrations during an individual filling (petrol pump 7)

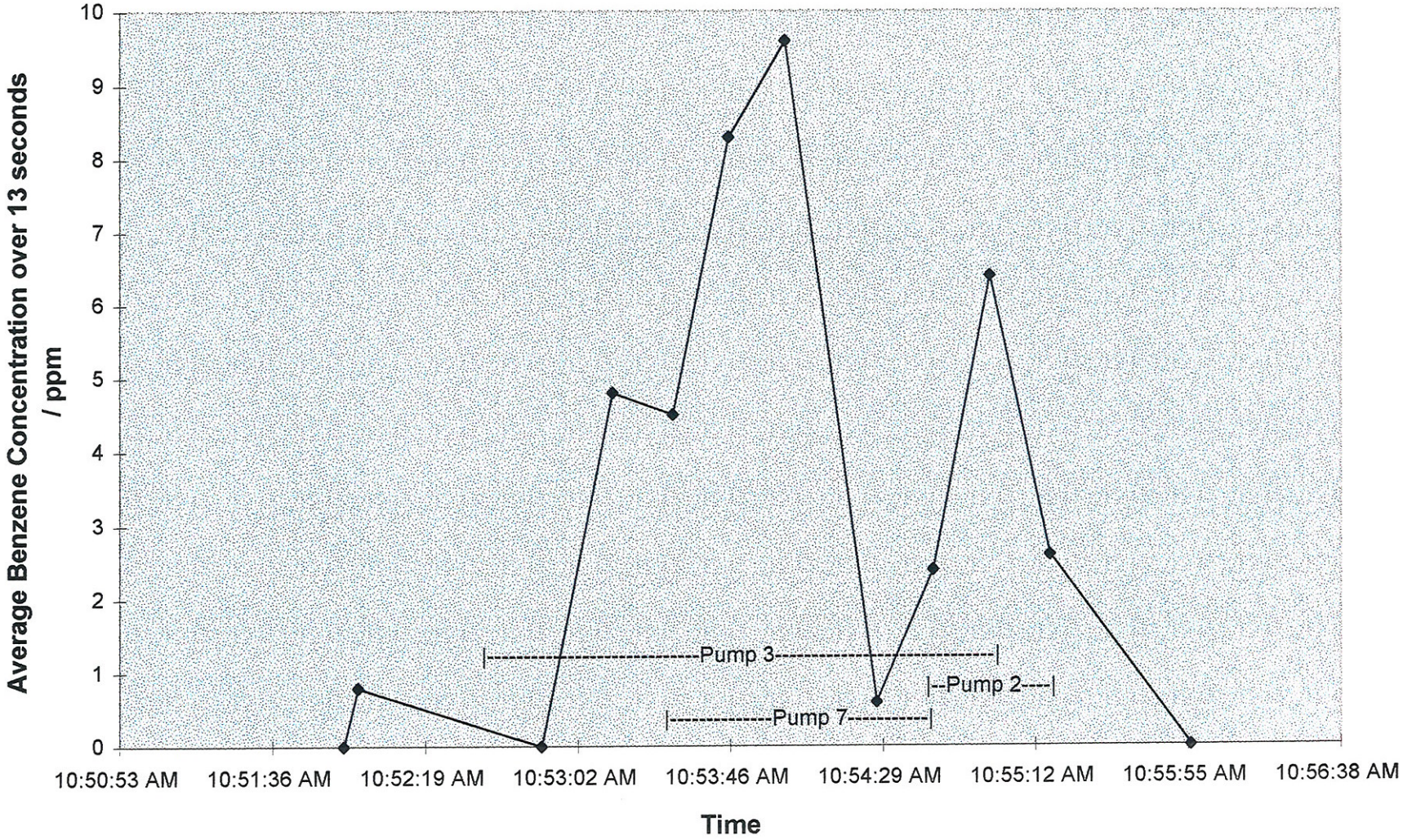

Figure 16: Variations in Benzene atmospheric concentrations during an individual vehicle filling (petrol pump 6)

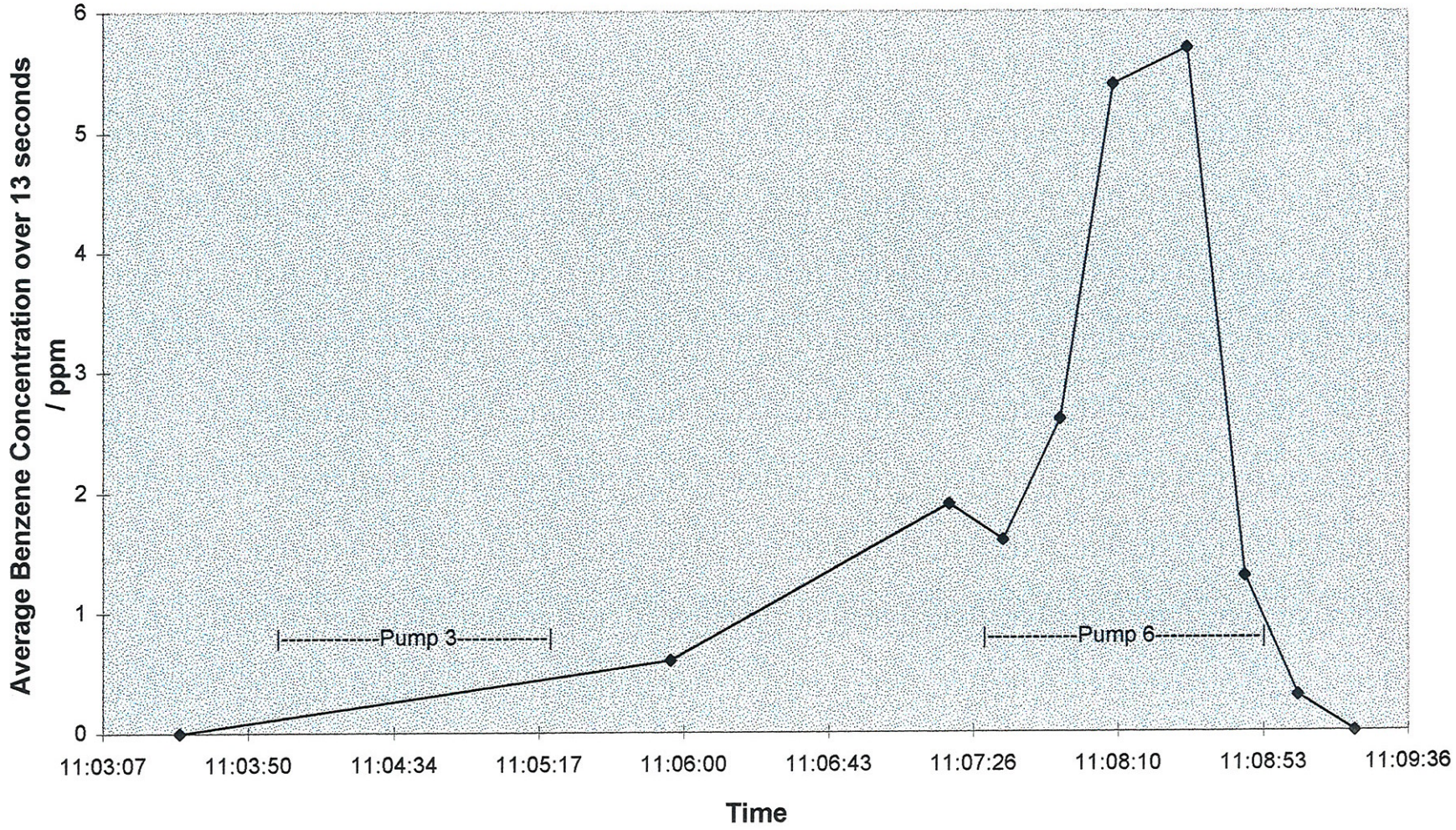

Figure 17: Time-series of the concentrations of Benzene during vehicle filling operations (13.2.95)

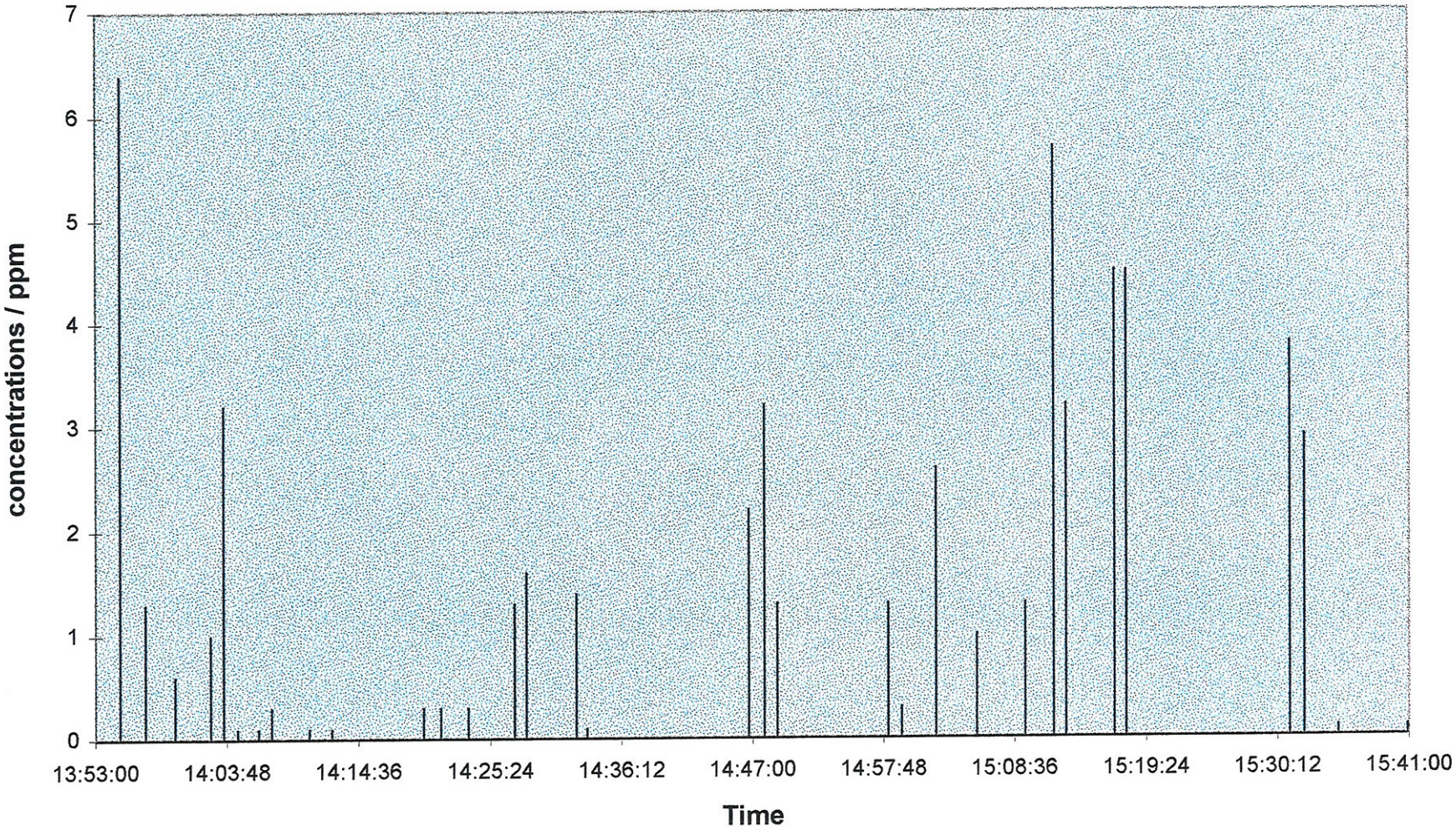

Figure 18: Time-series showing amounts of petrol dispensed during the same period as figure 17 (13.2.95)

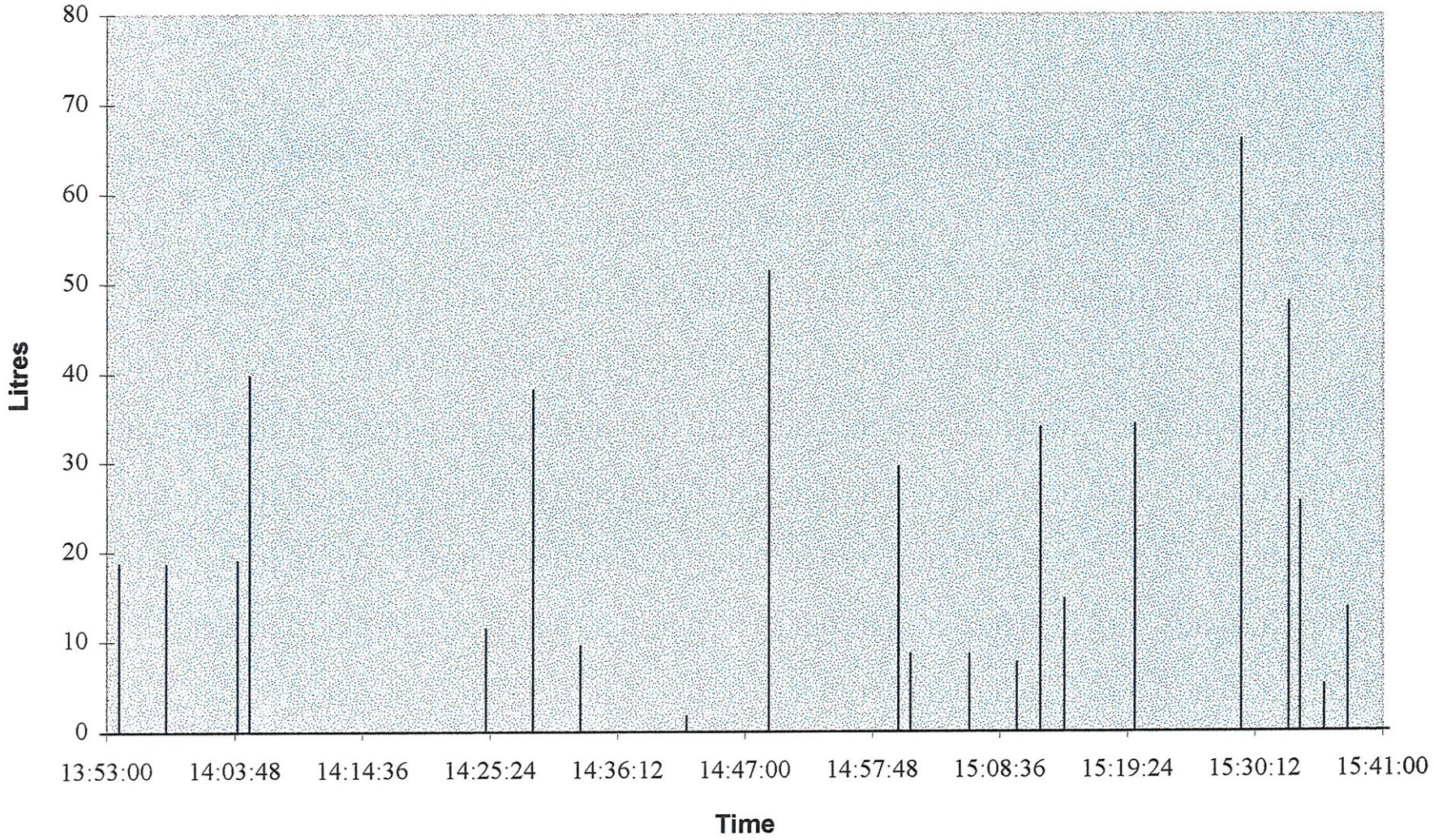

Figure 19: Variability in the average atmospheric Benzene concentrations during individual filling operations(13.2.95)

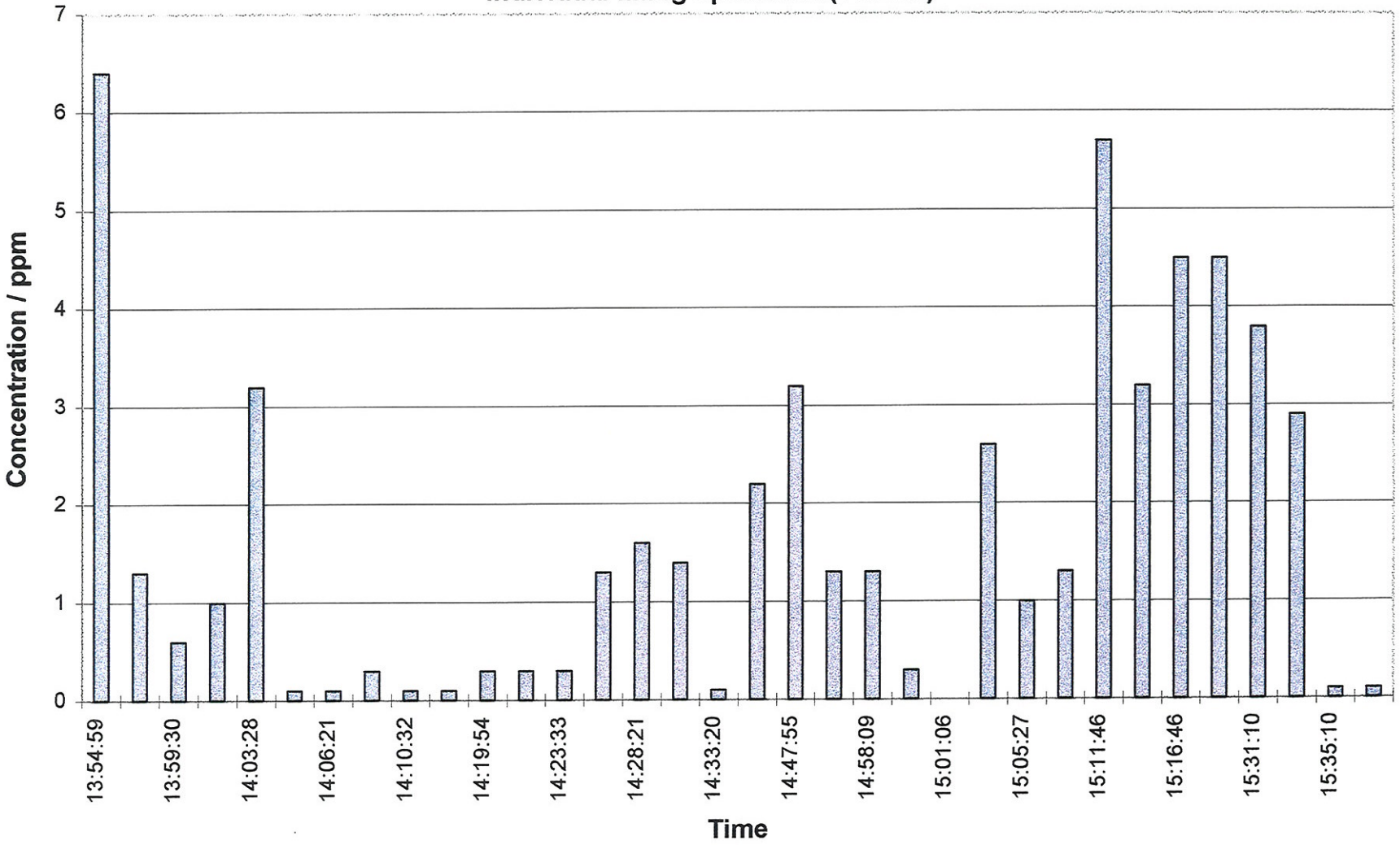

Figure 20: Time-series of VOC concentrations measured using the Open-path Monitor (15.2.95)

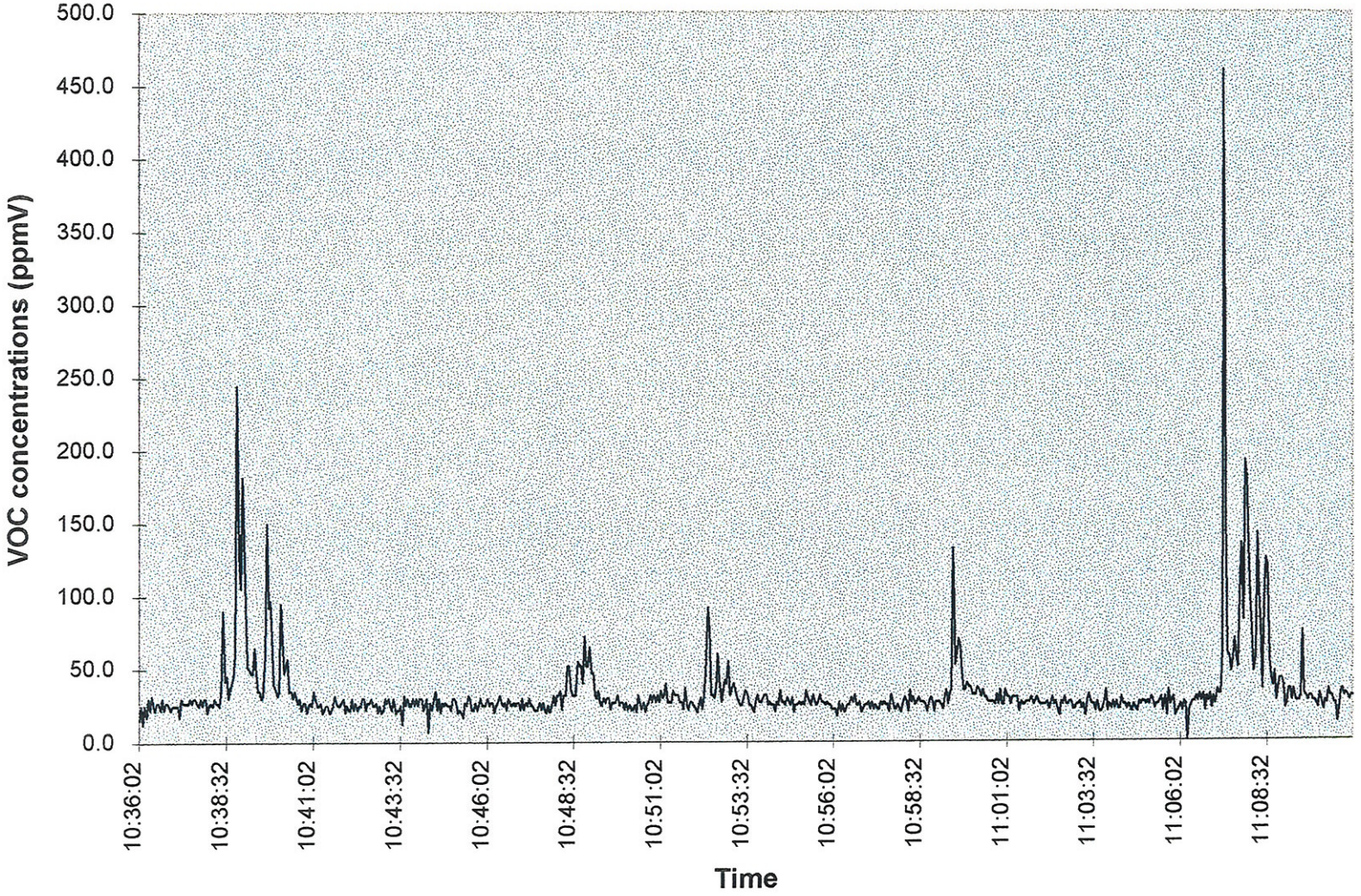

Figure 21: Time-series showing amounts of fuel dispensed during same period as figure 20

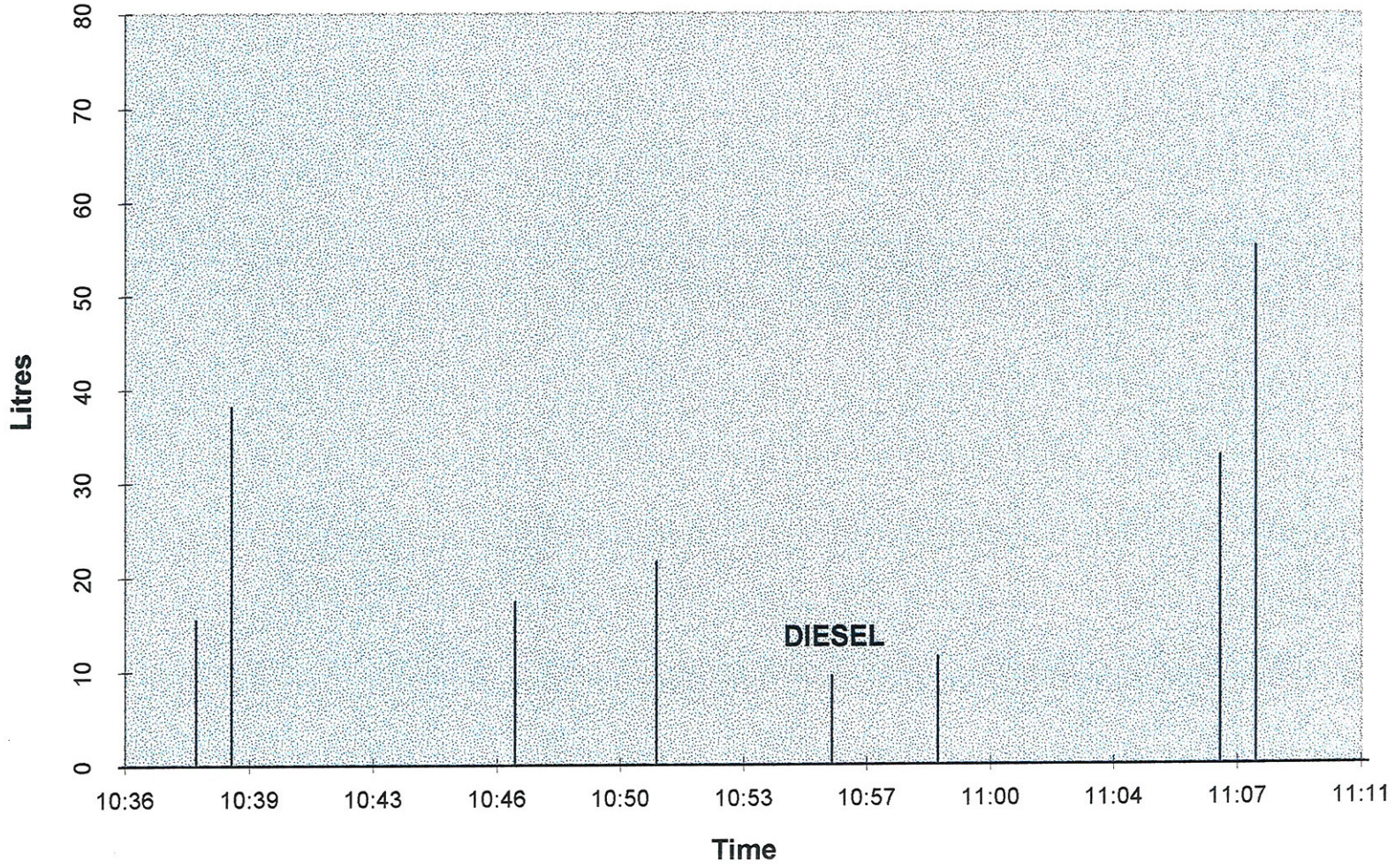

Figure 22: Example of wind-speed results obtained during the measurement exersize 15.2.95

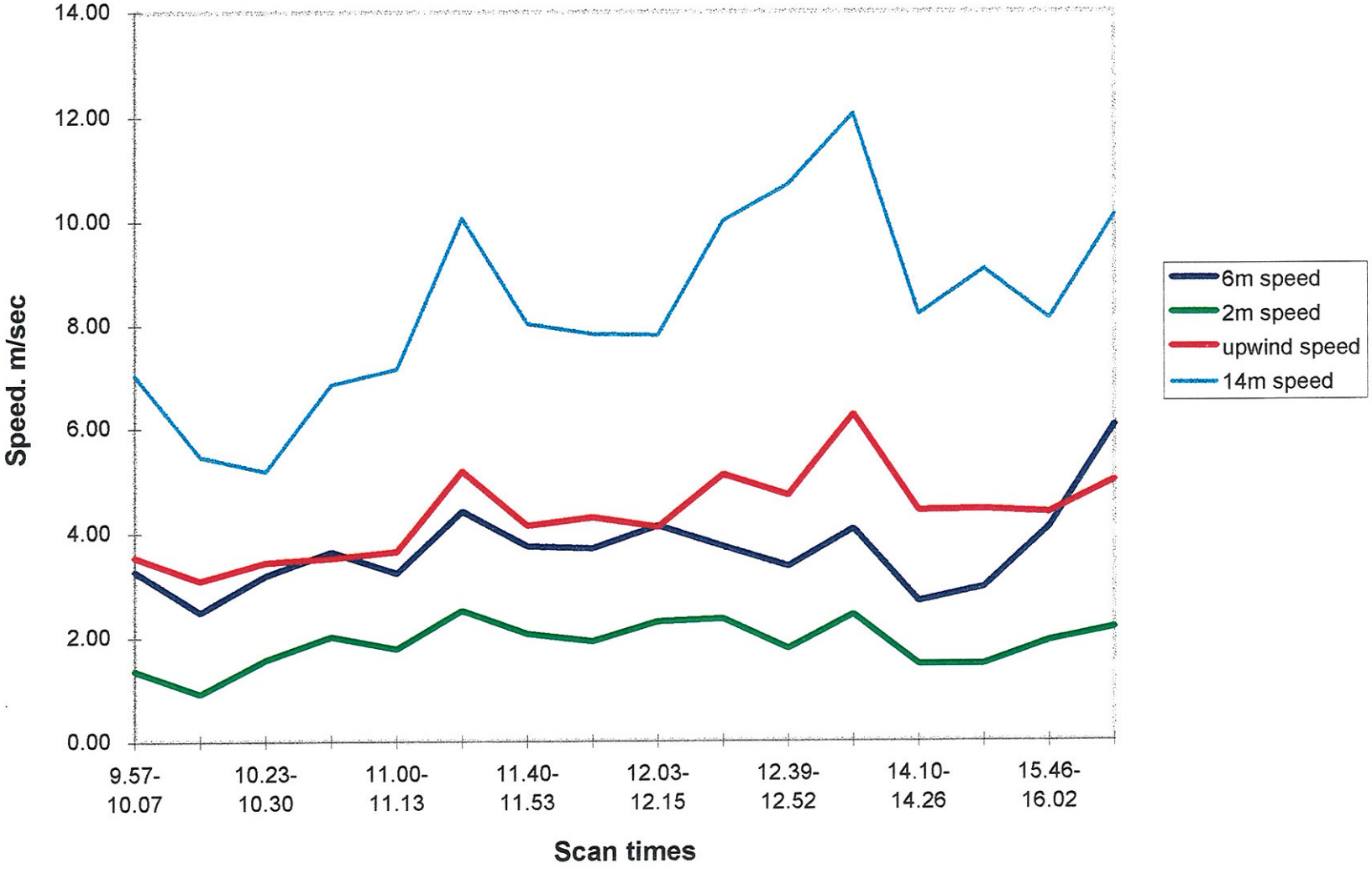

Figure 23: Filling station Open-path data (15.2.95)
Mass Emission vs Mass Delivered

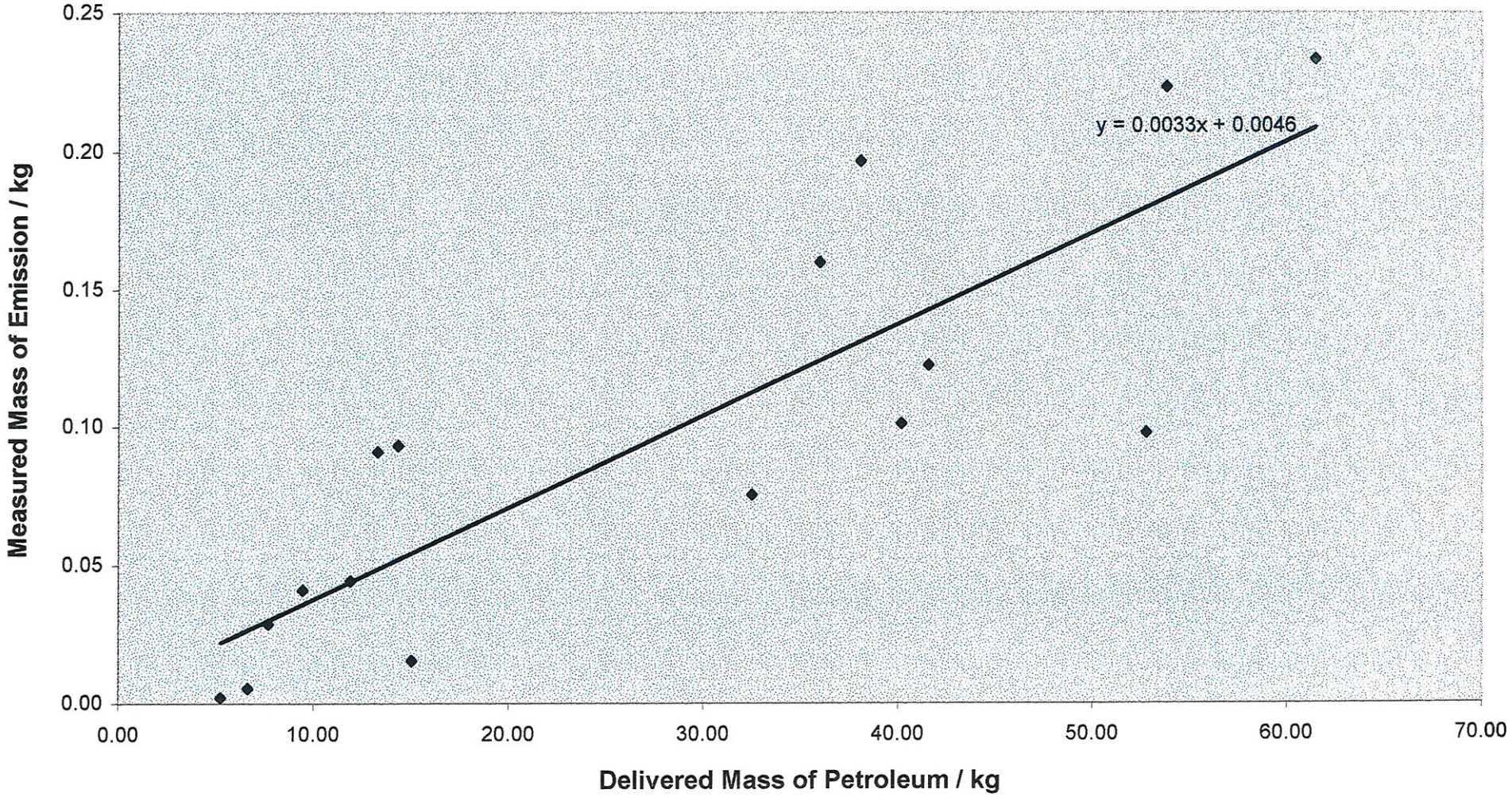

Figure 24: VOC emissions measured by DIAL facility versus Volume of petrol delivered to vehicles (16.2.95)

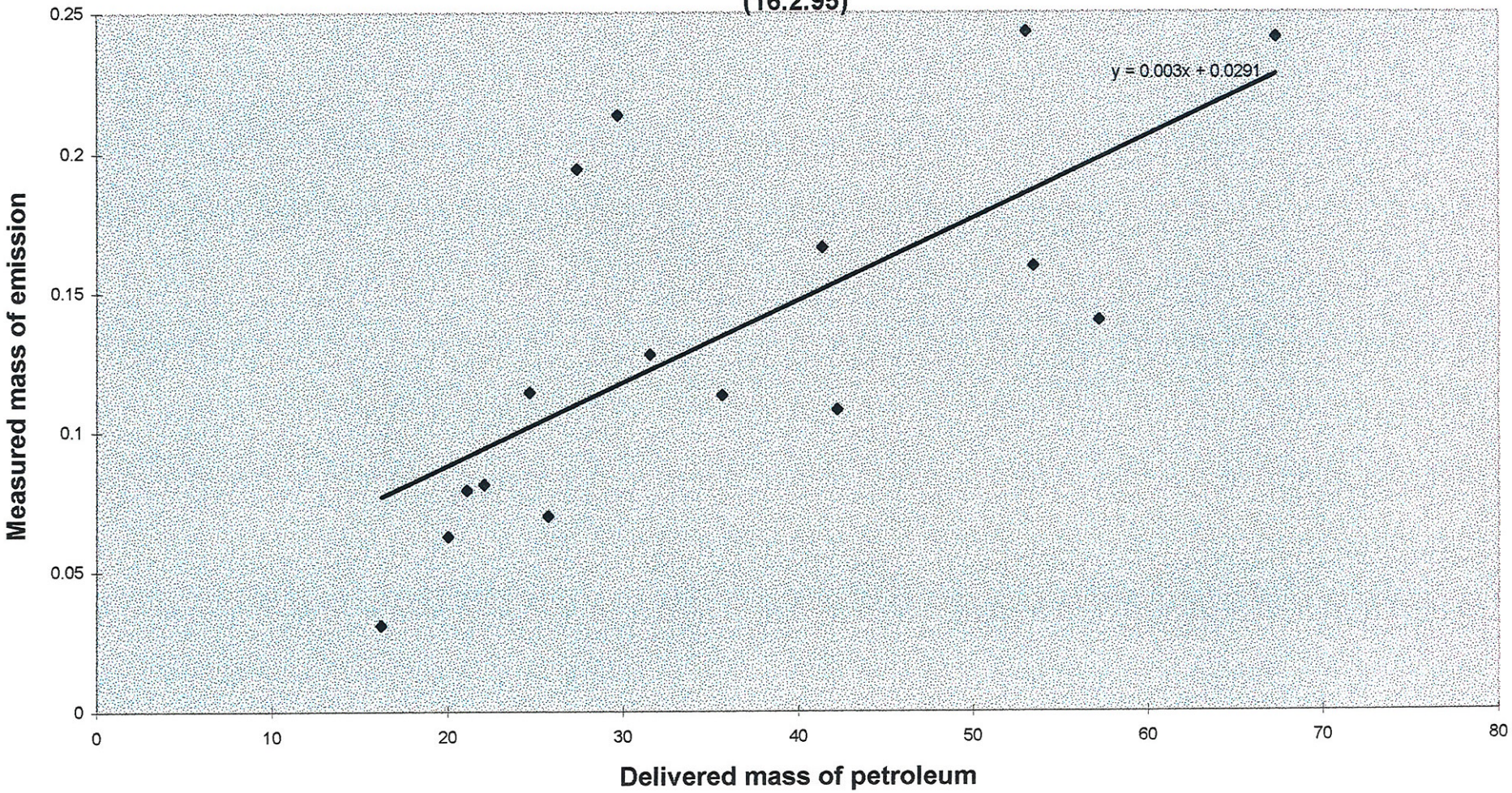

Figure 25: Hydrocarbon Samples Percentage Contributions by Mass Vehicle Filling

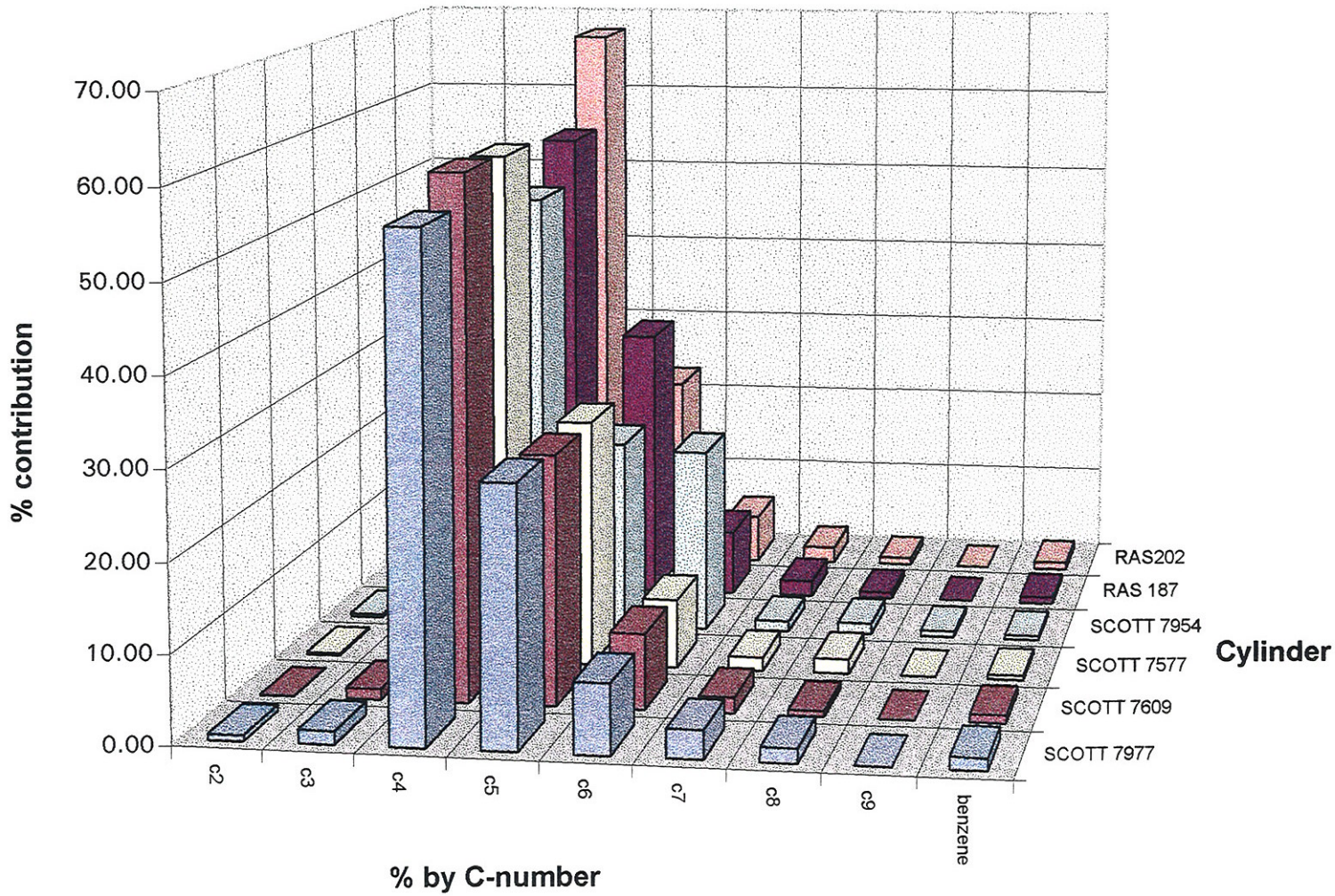

Figure 26: Hydrocarbon Samples Percentage Contributions by Mass Road Tanker Delivery

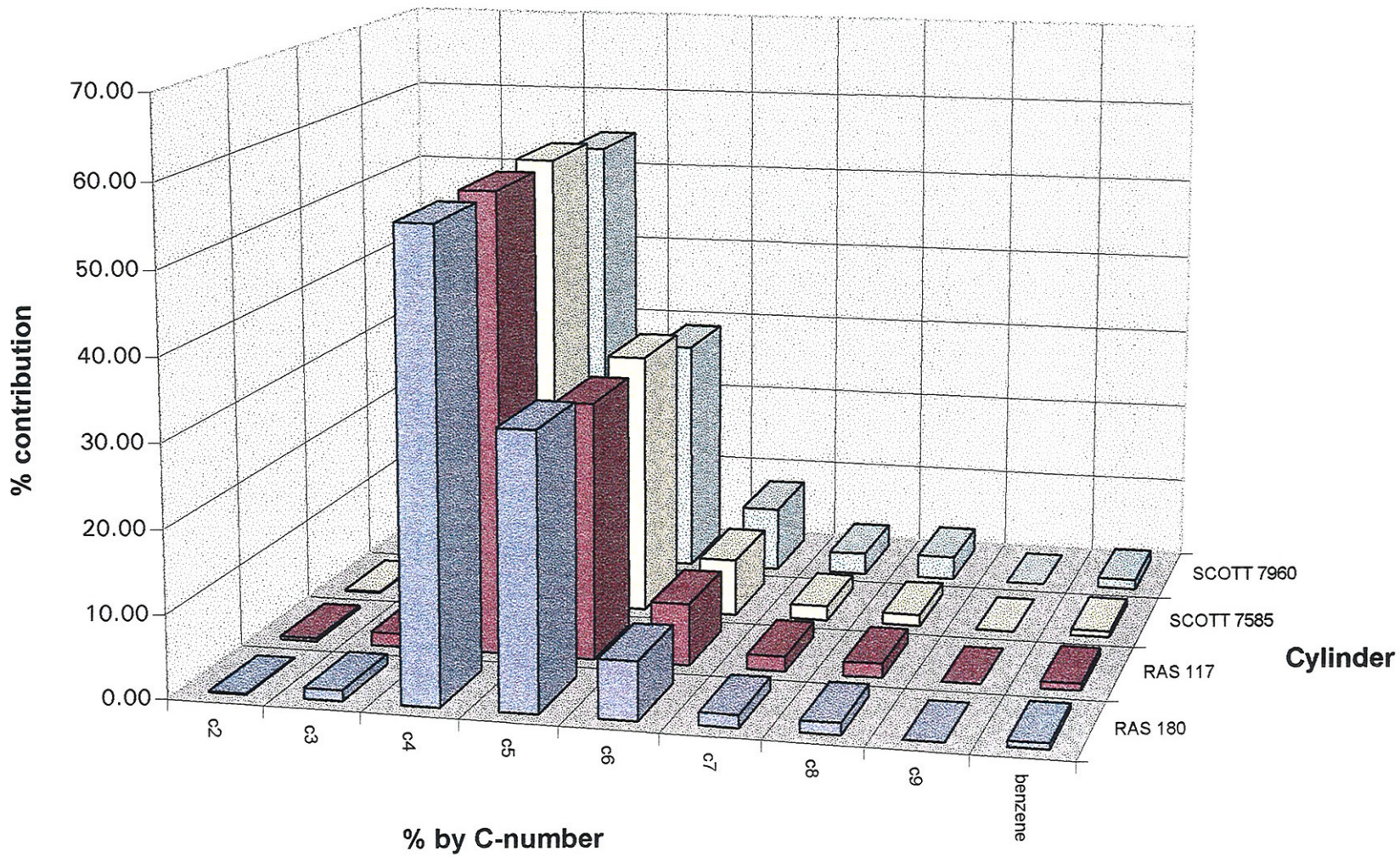

Figure 27: Hydrocarbon Samples Percentage Contributions by Mass Upwind & Downwind of Station

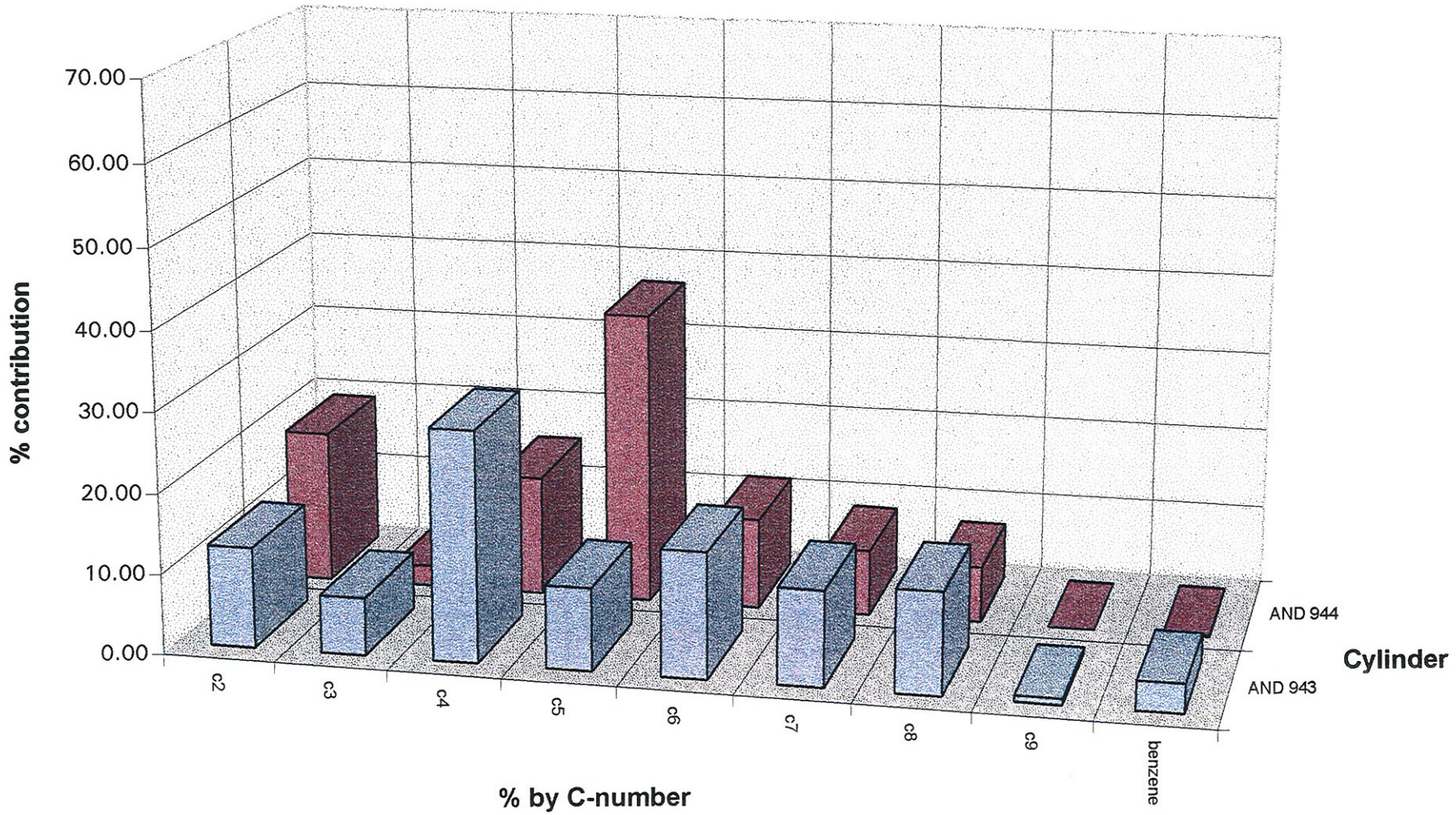

Figure 28: Results obtained by CONCAWE of long-term Benzene concentrations on petrol-station forecourts