a preliminary study of ambient air concentrations of benzene around service stations and distribution terminals in europe

Prepared for CONCAWE's Health Management Group by:

K. Bates
N. Cordingley
F. Christian
S. Lewis
D. Stanton
P. Tindle
N. Western

B.J. Simpson (Technical Coordinator)

Brussels
August 1994

ABSTRACT

CONCAWE initiated a programme to measure the ambient air concentrations of benzene in the vicinity of a number of gasoline stations and distribution terminals in Europe. The steps in the programme were: review previous studies/measurement methodologies; establish sampling and analytical procedures; perform a pilot study to establish a protocol and validate techniques; conduct the main study. The results showed benzene-in-air levels at the service station boundaries ranging from 1.6 to 119 $\mu g/m^3$, with the highest results generally recorded downwind of the service station. In general, the results obtained during the study were similar to previously reported levels for urban air. For distribution terminals the results indicated benzene-in-air levels of a similar magnitude.

KEYWORDS

Air quality, ambient air, analytical method, atmospheric emissions, benzene, distribution terminal, sampling technique, service station.

ACKNOWLEDGEMENT

The survey described in this report would not have been possible without the full cooperation of the personnel at those sites at which air sampling was undertaken. CONCAWE therefore wishes to thank the following companies who took part in the survey:

BP
Burmah Castrol
Esso
Kuwait Petroleum
Norsk Hydro
Shell
Statoil
Texaco

CONTENTS

APPENDICES

SUMMARY

One aspect of the current interest in the health aspects of benzene is the promulgation, in some European countries, of Air Quality Criteria based on health considerations. In view of this CONCAWE initiated a programme to measure the ambient air concentrations of benzene in the vicinity of a number of gasoline service stations and distribution terminals in Europe.

The programme consisted of the following steps:

- Review previous studies and measurement methodologies.
- Establish suitable sampling and analytical procedures.
- Perform a pilot study to establish an appropriate protocol and to validate the sampling and analytical techniques.
- Conduct the main study to determine ambient air levels of benzene in the vicinity of gasoline service stations and distribution terminals.

The study commenced in September 1990, was completed in March 1992 and covered Northern and Southern European countries. Twelve service stations in 9 countries and 4 distribution terminals in 3 countries were included and a "pilot study" was undertaken at a service station in the United Kingdom. The results of the pilot study were used to develop the protocol for the main study, for which sampling was conducted over two consecutive 12 hour periods at each location during both the summer and winter periods.

The benzene-in-air levels at the service station boundaries ranged from 1.6 to 119 $\mu g/m^3$ (0.5 ppb to 37.2 ppb) with the highest results generally recorded downwind (mean 20.6 $\mu g/m^3$). In general, the results obtained during the study were similar to the benzene levels for urban air reported for Italy, several North American States and by the OECD.

On average, daytime benzene-in-air levels were higher than those recorded at night. With the exception of levels measured downwind of the service stations, winter values were generally higher than summer values.

Since the data for distribution terminals was limited, no firm conclusions can be drawn except to note that the overall contribution of benzene to the ambient air from terminals was greater than from service stations.

Whilst the 24 hour data obtained in this preliminary study cannot be compared directly to any Air Quality Standard that is based on an annual average concentration, they are thought to be indicative of the daily average concentrations that can occur. Moreover, the mean values recorded at the boundary fence were of a similar order to the air quality standards proposed for benzene in some European countries.

A further study is in progress to assess the variability of ambient benzene levels around one service station over a period of 12 months.

1. INTRODUCTION

In 1989 CONCAWE recognized [1] that there was little information about benzene-in-air levels at the boundaries of service stations and distribution terminals. Because of this and in anticipation of the wider introduction of air quality standards in Europe, a programme was initiated to undertake a preliminary study with the objective of obtaining a general indication of the ambient levels of benzene in the vicinity of service stations and distribution terminals. Whilst it was not intended to generate data that would be directly compared with long term ambient air quality standards, nevertheless it was anticipated that it could provide a good general indication of prevailing ambient benzene levels. The studies were conducted to cover various northern and southern European countries in summer and winter.

The data and experience gained from the study would be used to plan further more comprehensive studies to examine annual average concentrations of benzene around service stations.

2. OUTLINE OF PROGRAMME

The programme was conducted in 2 phases:

Phase 1. Reviewed the methods available for sampling and analysis of ambient benzene-in-air and select the most appropriate technique.

Conducted a pilot study at a single service station to evaluate the selected methods for sampling and analysis. The pilot study also allowed logistical problems to be identified and resolved before commencing the second phase of the programme.

Phase 2. Conducted the main study at 12 service stations and 4 distribution terminals located throughout Europe.

Both phases are described in this report.

3. PHASE 1 - METHOD SELECTION AND EVALUATION (INCLUDING PILOT STUDY)

Before selecting the sampling and analytical methods, the following essential requirements were identified:

- The method must be able to measure benzene-in-air concentrations of 2-100 $\mu g/m^3$ over a time period up to 24 hours.
- The method should be validated over the range of expected conditions i.e. up to 35°C and high relative humidities.
- The method should use existing proven equipment and technologies.

3.1 REVIEW OF AVAILABLE SAMPLING AND ANALYTICAL MEASUREMENT METHODOLOGIES

An extensive literature review was carried out to identify available methods for the accurate quantification of levels of benzene-in-air. The review covered various sampling and analytical techniques, including direct reading instruments.

The direct reading instruments investigated included transportable instruments which used absorption and mass spectroscopy techniques. However, the limits of detection for these instruments did not meet the identified essential requirements.

Diffusive sampling techniques available at the time of the review were either unable to provide the sensitivity required, or had been insufficiently validated.

Other groups have employed active sampling techniques using a variation of NIOSH (National Institute of Occupational Safety and Health) Method 1501. However, the sampling parameters had not been validated, and without further validation, the technique was considered to be inappropriate for the CONCAWE study.

Because of familiarity and experience with the technique it was decided to extend the CONCAWE Gasoline Method [2] and to validate it over the ranges of concentration and atmospheric conditions expected during the surveys. The method and validation data are given in **Appendix 1**.

3.2 SUMMARY OF SELECTED SAMPLING AND ANALYTICAL METHOD

The sampling technique involved the use of intrinsically safe sampling pumps to draw air through two Chromosorb 106 adsorbent tubes connected in series. The flow rate was set to collect 15 litres of air over a 12 hour period. The sampling tubes, along with quality control samples, were analysed using automatic thermal desorption and a gas chromatograph fitted with a flame ionization detector.

The analytical method was validated over the range 30-1500 ng of benzene on the sampling tubes and the relative standard deviation was 1.8% over this range. The detection limit was 0.3 $\mu g/m^3$. The method was validated over the range 2 to 100 $\mu g/m^3$.

3.3 PILOT STUDY

A pilot study was performed to assist in developing a more detailed sampling protocol for the Phase 2 study. A report of the results of the pilot study is given in **Appendix 2**.

The following are the principal conclusions from the pilot study:

- the main source of benzene-in-air on the service station forecourt was from dispensing gasoline
- benzene-in-air levels downwind of the service station vents were increased for a short period (20-30 minutes) during the bulk delivery of gasoline
- the main source of benzene-in-air around the service station forecourt was considered to be from vehicles using the adjacent road

Other observations which influenced the protocol for the main study related to:

- difficulty in choosing sampling positions at predetermined distances from the forecourt
- maintenance and use of sampling pumps
- logistics of changing sampling units
- effect of excessive moisture on the analysis of samples
- storage and transport of samples prior to analysis
- manpower requirements for each survey

The pilot study confirmed that the methods selected for sampling and analysis were appropriate and also allowed a protocol to be developed for the Phase 2 main study.

4. PHASE 2 - MAIN STUDY

4.1 SAMPLING PROTOCOL

For service stations, two consecutive 12 hour samples were taken during the summer and winter periods. For the purpose of this study summer was defined as the period between the 1 May and 30 September and winter as the period 1 November to 31 March. This also reflected approximately when summer and winter grades of gasoline were sold at service stations.

There were six sampling positions which were selected to determine:

A1: background levels.

A2: background levels. (The sampling device was relocated whenever wind direction changed by more than 90 degrees)

B: the benzene emissions from passing vehicles but not influenced by the service station activities.

C: the contribution from passing traffic and general forecourt activities.

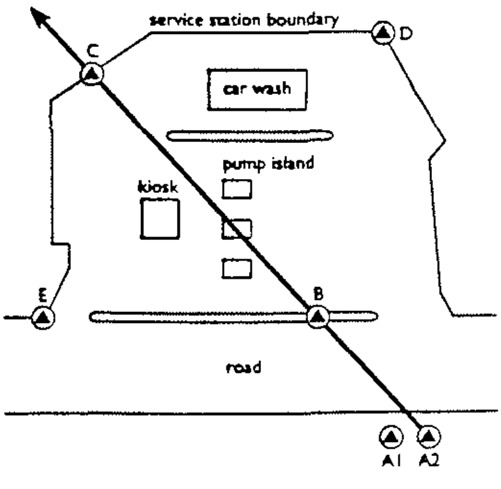
D: supplementary boundary information (approximately 90° to the A-C line).

E: supplementary boundary information (approximately 90° to the A-C line).

The exact position of sampling points was dependent on the layout of the service station, adjacent roads and the wind direction. A layout for one of the service station sites included in the survey is shown in **Figure 1**. This figure indicates the influence of wind direction on the location of sampling positions.

For distribution terminals the sampling positions essentially followed the same protocol as for the service stations. However, the distances between sources of benzene and sampling points were generally greater than for service stations.

Figure 1 Sampling positions at one of the service stations selected for the survey



4.2 LOCATION OF SERVICE STATIONS AND DISTRIBUTION TERMINALS

Eight CONCAWE member oil companies participated in the surveys which were carried out over the period September 1990 to March 1992.

Service stations

Twelve gasoline service stations were included in the study and these were located in the following countries:

Belgium, France, Germany, Greece, Ireland, Italy, Norway, Portugal, Sweden.

Of these, 11 were located in residential areas and one was a motorway service station. Two stations were equipped with Stage 2 vapour recovery systems for vehicle refuelling.

Distribution terminals

Four distribution terminals were included in the study and these were located in the following countries:

Belgium, Italy, United Kingdom.

None of the distribution terminals was located near a residential area; one was located adjacent to a refinery.

4.3 QUALITY ASSURANCE

The following quality assurance procedures were used during the study:

- use of an agreed protocol.
- use of competent persons to perform the sampling and analytical procedures.
- preparation of certified sampling tubes to specific standards (i.e. < 5 ng benzene on the tubes) prior to sampling.
- measurement of flow rates at regular intervals during the sampling period and adjusting them, if necessary to within ± 5% of the original flowrate.
- submission and analysis of four field blanks and four laboratory blanks with each sample set.
- for each batch of samples, analysis of two samples to which known quantities of benzene had been added (spiked samples).
- every fifth tube analysed was a standard. Any result outside ± 10% of the known standard value stopped the analysis cycle.
- analysis cycle stopped on detector "flame out" to prevent loss of subsequent samples.

For consistency a single analytical laboratory was selected. This laboratory was accredited for the analysis under the United Kingdom (UK) Department of Trade and Industry - National Measurement Accreditation Service (NAMAS) and adhered to the principles set out in the UK Health and Safety Executive's (HSE) Methods for the Determination of Hazardous Substances 71 "Analytical Quality in Workplace Air Monitoring". In addition, the laboratory participated in the UK HSE Workplace Analytical Scheme for Proficiency and was consistently rated in the highest category.

Table 1 Results of benzene-in-air measurements at service stations
(All results in microgrammes per cubic metre μg/m³)

Country/season		Background (A1)			Background (A2)			Traffic only (B)			Traffic+forecourt (C)			Boundary (D)			Boundary (E)		
		Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.
Germany	(W)	4.8	3.3	4.1	5.0	6.2	5.6	9.5	5.9	7.7	10.7	8.2	9.5	14.4	9.8	12.1	26.1	12.6	19.4
	(S)	9.8	6.0	7.9	12.8	6.6	9.7	13.8	7.5	10.7	41.4	27.6	34.5	-	-		12.1	9.5	10.8
Belgium	(W)	6.6	5.0	5.8	6.3	-		8.2	7.4	7.8	13.4	8.3	10.9	11.7	7.4	9.6	9.9	6.4	8.2
	(S)	1.9	1.3	1.6	3.9	0.7	2.3	4.3	1.2	2.8	19.3	2.0	10.7	2.3	1.2	1.8	7.9	3.3	5.6
Portugal	(W)	4.5	9.9	7.2	1.7	10.4	6.1	5.1	8.5	6.8	7.6	8.1	7.9	4.4	6.6	5.5	4.8	7.2	6.0
	(S)	9.9	7.0	8.5	2.8	2.3	2.6	5.3	14.4	9.9	-	-		8.9	4.5	6.7	3.2	2.5	2.9
Ireland	(W)	16.0	9.0	12.5	15.8	9.4	12.6	-	18.3		29.8	13.8	21.8	16.1	11.0	13.6	45.8	21.7	33.8
	(S)	5.7	8.6	7.2	5.6	6.9	6.3	5.7	7.7	6.7	15.9	12.5	14.2	17.2	16.2	16.7	5.2	5.6	5.4
France	(W)	18.0	12.8	15.4	18.7	14.2	16.5	76.0	29.4	52.7	24.1	13.4	18.8	-	-		34.6	21.3	28.0
	(S)	-	-		-	-		29.7	14.4	22.1	26.3	10.2	18.3	-	-		34.5	14.7	24.6
Italy 1	(W)	6.8	5.6	6.2	4.5	6.7	5.6	14.4	11.3	12.9	18.6	16.2	17.4	7.4	4.3	5.9	13.8	14.1	14.0
	(S)	10.2	5.8	8.0	-	-		20.5	13.9	17.2	19.0	15.0	17.0	6.4	6.2	6.3	-	-	
Italy 2	(W)	8.4	7.8	8.1	-	5.4		16.1	9.6	12.9	9.8	7.1	8.5	14.8	5.9	10.4	12.0	8.6	10.3
	(S)	5.1	8.1	6.6	-	-		19.1	12.0	15.6	13.7	4.9	9.3	9.3	4.3	6.8	14.9	7.4	11.2
Sweden 1	(W)	4.6	3.9	4.3	4.1	3.8	4.0	6.3	5.6	6.0	10.7	5.7	8.2	9.7	5.1	7.4	10.2	6.3	8.3
	(S)	2.2	2.9	2.6	2.4	2.7	2.6	2.1	3.1	2.6	13.5	17.6	15.6	-	-		-	-	
Sweden 2*	(W)	12.8	-		10.7	-		9.0	-		15.5	-		13.0	-		15.3	-	
	(S)	11.6	-		-	-		16.5	-		3.8	-		9.3	-		17.9	-	
Sweden 3*	(W)	5.0	-		7.1	3.4	5.3	-	4.8		9.7	4.8	7.3	10.1	5.2	7.7	2.6	7.6	5.1
	(S)	6.4	4.8	5.6	-	6.1		4.0	13.1	8.6	-	7.3		8.2	13.9	11.1	9.5	12.7	11.1
Norway	(W)	9.3	6.3	7.8	8.4	6.5	7.5	8.5	5.1	6.8	-	8.7		1.3	7.0	4.2	10.7	9.8	10.3
	(S)	4.5	3.1	3.8	4.5	3.1	3.8	13.5	5.6	9.6	-	3.7	50.5	3.6	3.8	3.7	2.9	3.7	3.3
Greece	(W)	33.9	19.9	26.9	34.6	41.6	38.1	39.9	63.9	51.9	98.4	83.7	91.1	169.0	68.9	119.0	43.2	72.6	57.9
	(S)							9.0	16.5	12.8	77.8	23.1	50.5	68.9	19.1	44.0	10.3	17.1	13.7

NB : - denotes no data
* denotes vapour recovery system installed
Daytime samples were collected between approximately 06.00 and 18.00 h
(W) Winter
(S) Summer
1 ppb benzene = 3.2 μg/m³ (1 ppm = 3,200 μg/m³)

5. RESULTS

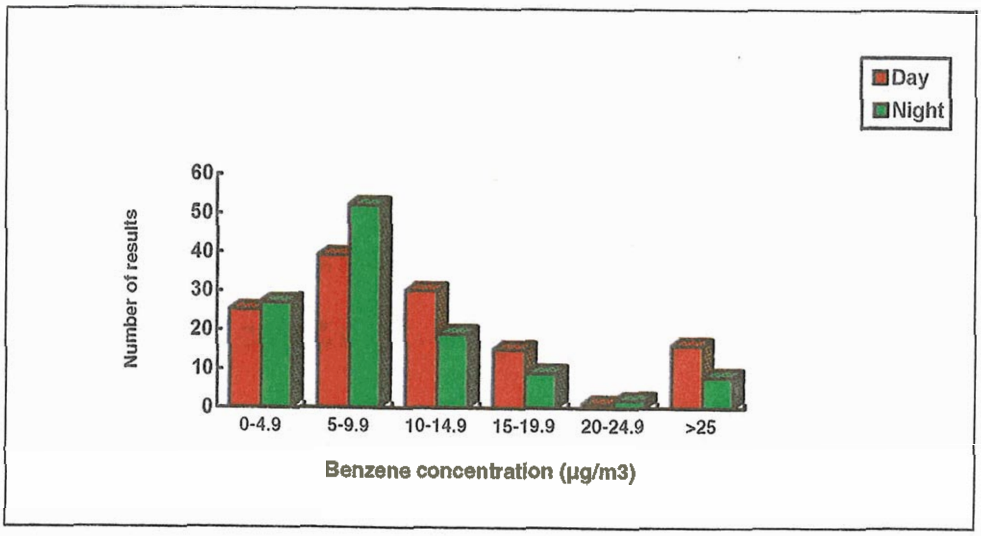
5.1 SERVICE STATIONS

The results of the 12 hour benzene-in-air measurements are shown in **Table 1**, together with the calculated 24 hour average concentrations for those service stations where valid day and night data were obtained.

The number of results (281) was less than the 336 samples taken because following a quality review, certain data were omitted or combined with other data for that location to ensure consistency between surveys. In addition, a few data were lost due to equipment failures, theft, or sampling/analytical inconsistencies or losses.

A histogram of the frequency distribution of all service station data (**Figure 2**) shows that the data were skewed. However, irrespective of the precise distribution of the data, the arithmetic mean value is considered to be the best parameter for assessing long-term average concentrations and therefore has been used to assess the results.

Figure 2 Distribution of the benzene-in-air results for the service station measurements



The calculated 24 hour data are summarized in **Table 2** and shown graphically in **Figure 3**.

Table 2 Summary of 24 hour benzene-in-air data at service stations (summer and winter)

Sample Position		Number of Samples	Range of Results (µg/m³)	Arithmetic Mean (µg/m³)
A1	Background	19	1.6 - 26.9	7.9
A2	Background	15	2.3 - 38.1	8.5
B	Traffic only	20	2.6 - 52.7	14.2
C	Downwind boundary (Traffic plus forecourt)	18	7.3 - 91.1	20.6
D	Boundary	18	1.8 - 119.0	16.2
E	Boundary	20	2.9 - 57.9	14.5

Figure 3 Summary of the arithmetic means of the benzene-in-air data for service stations (summer & winter values combined)

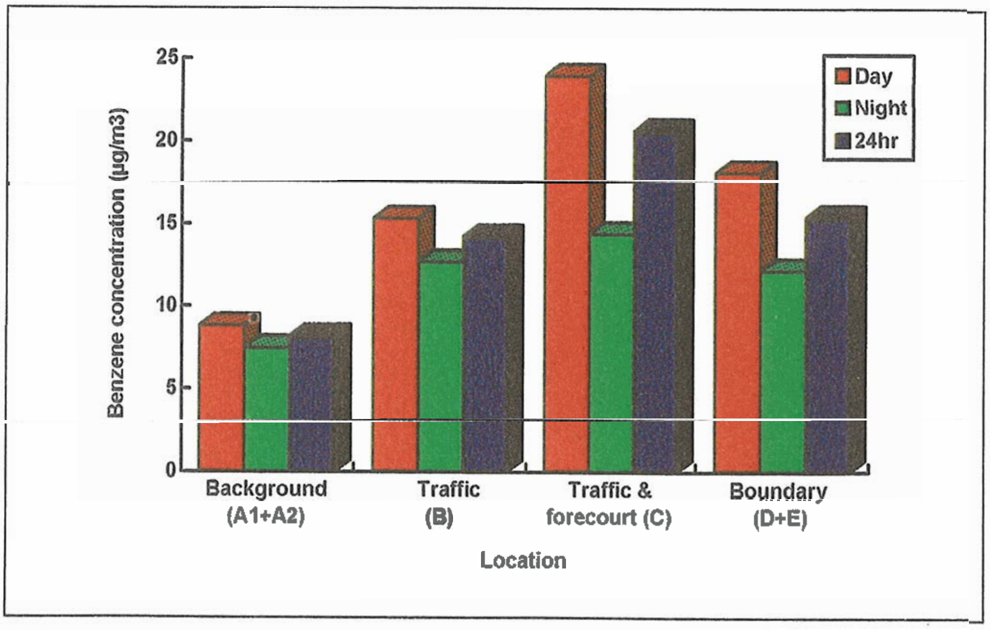
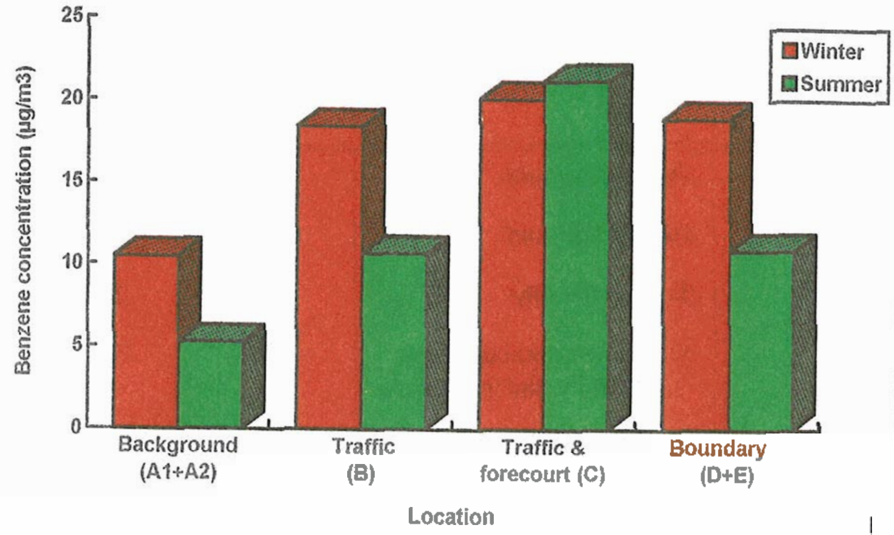


Figure 4 illustrates the difference between benzene-in-air levels during summer and winter.

Figure 4 ***Service stations:*** Comparison of winter & summer benzene-in-air levels



A summary of the ancillary data for each of the service stations is given in **Table 3**.

Table 3: Ancillary data associated with the service stations

Country	Season	Vapour recovery	Fuel delivery*	Benzene Content of gasoline (%$^{v}/_{v}$)		Temperature (°C)		Relative humidity (%)		Wind speed (m/s)		Fuel through-put (l)**
				MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	TOTAL
Germany	W	No	Yes	3.5	2.1	14	7	73	58	2.2	1.0	11 200
Germany	S	No	NR	1.8	1.2	18	11	60	48	1.1	0.8	13 372
Belgium	W	No	NR	2.5	1.5	19	5	73	52	3.0	<1.0	5 755
Belgium	S	No	Yes	1.9	1.1	16	9	89	71	6.0	<1.0	4 778
Portugal	W	No	Yes	2.6	1.9	14	9	95	71	4.0	0.1	4 532
Portugal	S	No	Yes	2.6	1.9	32	18	53	33	2.9	0.8	7 852
Ireland	W	No	NR	4.8	4.5	10	3	80+	NR	1.0	<0.1	11 824
Ireland	S	No	NR	4.8	4.5	18	7	84	39	2.1	<0.4	12 855
France	W	No	Yes	4.1	2.7	2	-3	76	49	2.0	<0.1	8 465
France	S	No	Yes	4.3	2.6	23	9	NR	NR	5.6	2.8	11 269
Italy 1	W	No	NR	2.2	1.1	14	7	76	45	7.8	2.2	5 250
Italy 1	S	No	NR	2.2	1.8	29	20	90	90	0.8	0.1	NR
Italy 2	W	No	Yes	1.5	1.1	18	8	81	51	7.2	0.3	22 890
Italy 2	S	No	Yes	2.3	1.6	28	19	98	98	3.0	0.1	NR
Sweden 1	W	No	No	3.3	1.5	5	-4	20	20	1.0	1.0	NR
Sweden 1	S	No	No	13.1	7.3	25	19	90	47	3.0	0.5	3 890
Sweden 2	W	Yes	No	SAMPLES LOST IN TRANSIT		8	7	83	64	6.0	1.0	7 900
Sweden 2	S	Yes	No			19	19	60	60	1.5	1.5	6 000
Sweden 3	W	Yes	No			10	4	78	75	4.5	1.0	15 200
Sweden 3	S	Yes	No			19	14	85	60	2.0	<0.5	15 000
Norway	W	No	No	2.8	5.0	9	-2	85	68	3.0	<1.0	6 600
Norway	S	No	No	NR	NR	28	20	80	80	0.5	0.5	9 000
Greece	W	No	Yes	3.0	2.7	15	8	89	63	1.0	<0.1	5 800
Greece	S	No	Yes	3.0	2.5	24	19	45	40	2.1	<0.1	7 470

NR = Not reported

* Fuel deliveries were always made during daytime

** Fuel throughput over 24 hours

1 ppb benzene = 3.2 μg/m^3

1 ppm benzene = 3,200 μg/m^3

5.2 DISTRIBUTION TERMINALS

The results of the 12 hour benzene-in-air measurements at four distribution terminals are shown in **Table 4**. As for the service stations, 24 hour average concentrations have been calculated where valid day and night data were obtained.

A histogram of the frequency distribution of all the terminal data (**Figure 5**) shows that the data are skewed. As with the service station data, the arithmetic mean values were used to assess the results despite the nature of their distribution.

Figure 5 Distribution of the benzene-in-air results for the terminal measurements

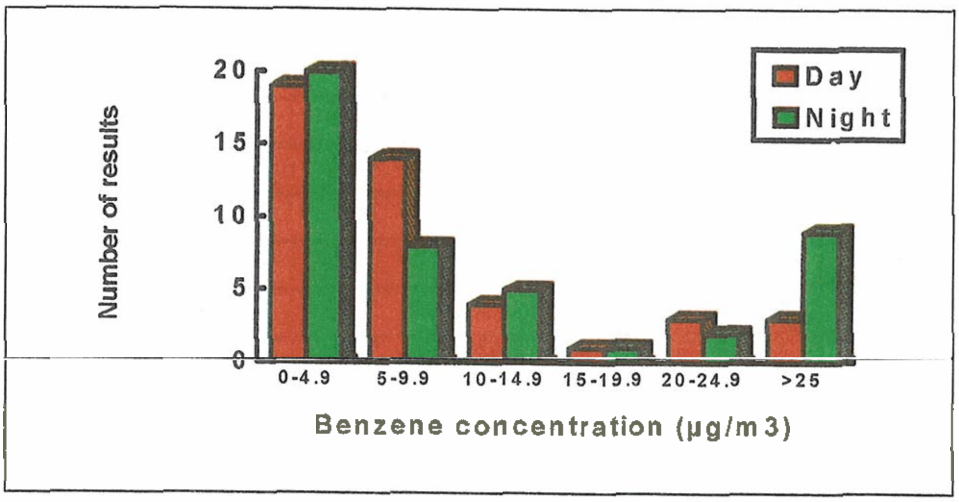


Table 4 Results of benzene-in-air measurements at distribution terminals
(All results in microgrammes per cubic metre µg/m^3)

Country/season		Background (A1)			Background (A2)			Traffic only (B)			Traffic+forecourt (C)			Boundary (D)			Boundary (E)		
		Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.	Day	Night	24hr.
Belgium	(W)	9.8	6.9	8.4	9.7	6.0	7.9	9.8	6.2	8.0	52.4	32.5	42.5	9.2	6.0	7.6	-	-	
	(S)	1.4	0.8	1.1	1.5	1.0	1.3	1.8	1.5	1.7	27.8	16.2	22.0	1.4	1.1	1.3	2.9	1.7	2.3
Italy	(W)	6.9	74.7	40.8	3.6	183.0	93.3	-	-		125.6	32.5	79.1	11.2	10.1	10.7	18.3	52.1	35.2
	(S)	7.3	11.4	9.4	4.5	3.1	3.8	22.1	12.0	17.1	5.7	4.2	5.0	5.1	4.3	4.7	23.5	42.0	32.8
UK 1	(W)	-4.1		-	4.6		7.1	30.5	18.8	14.8	30.6	22.7	9.9	22.7	16.3	23.4	14.2	18.8	
	(S)	2.4	3.7	3.1	2.2	3.8	3.0	4.0	3.8	3.9	12.3	13.7	13.0	5.4	3.9	4.7	3.3	5.5	4.4
UK 2	(W)	1.8	-		1.1	4.7	2.9	1.3	3.7	2.5	9.6	6.6	8.1	3.9	8.2	6.1	3.8	2.9	3.4
	(S)	3.1	3.7	3.4	2.5	3.9	3.2	3.8	4.2	4.0	8.8	24.0	16.4	14.1	6.4	10.3	8.7	32.0	20.4

NB: Daytime samples were collected between approximately 06.00 and 18.00 h.
- denotes no data
(W) Winter
(S) Summer
1 ppb benzene = 3.2 µg/m^3
1 ppm benzene = 3,200 µg/m^3

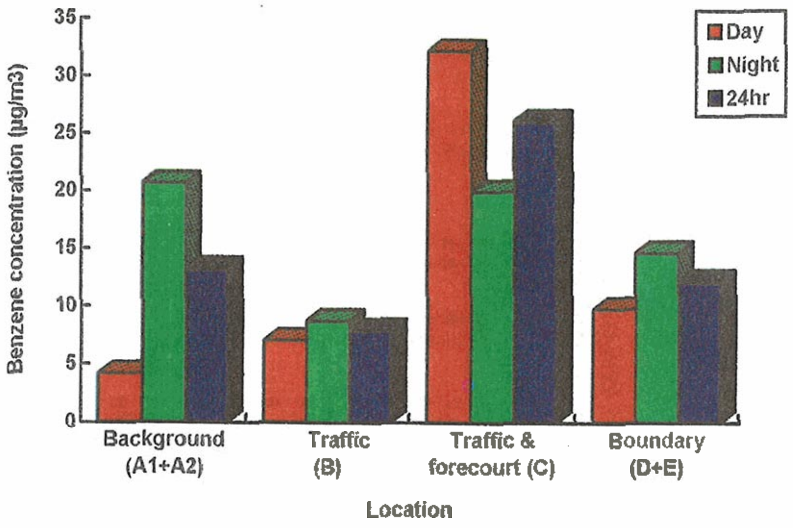
There were a limited number of results and one of the sets was considered to be heavily influenced by the adjacent refinery. The 24 hour data are summarized in **Table 5**.

Table 5 Summary of 24 hour benzene-in-air data at distribution terminals (summer and winter)

	Sample Position	Number of Samples	Range of Results (µg/m³)	Arithmetic Mean (µg/m³)
A1	Background	6	1.1 - 40.8	11
A2	Background	7	1.3 - 93.3	16.5
B	Traffic only	7	1.7 - 18.8	8
C	Traffic plus gantry	8	5.0 - 79.1	26.1
D	Boundary	8	1.3 - 16.3	7.7
E	Boundary	7	2.3 - 35.2	16.7

The data are also shown in **Figure 4** in which the background samples (A1 & A2) and the boundary samples (D & E) have been combined.

Figure 6 Summary of benzene-in-air data at distribution terminals (summer and winter combined)



6. CONCLUSIONS

This preliminary assessment of ambient benzene levels around a number of urban service stations and distribution terminals in Europe has provided an indication of the daily average concentrations that can occur. However, it does not allow **direct** comparison with the long term or annual average Air Quality Standards for benzene that are emerging in some European countries (10 - 16 µg/m^3). Nevertheless, utilising the arithmetic mean for comparison purposes, the data suggest that boundary fence levels may be of a similar order to these emerging values. More detailed study is in progress to gather further information about the variability of ambient boundary fence benzene levels at a service station over similar and extended sampling periods for 12 months.

6.1 SERVICE STATIONS

- The 24 hour benzene levels recorded around the perimeter of the service stations ranged from 1.6 - 119.0 µg/m^3. The variation reflected the relative sampling positions with respect to sources of emission such as dispenser pumps, tank vents and road traffic. In general, the levels were in the rank order expected, with the highest results recorded at the downwind boundary of the service stations (mean 20.6 µg/m^3) and the lowest upwind of the service stations and any adjacent roads (mean 7.9 µg/m^3). The results are similar in magnitude to those reported previously for studies in Italy [3] and the United States. [4]

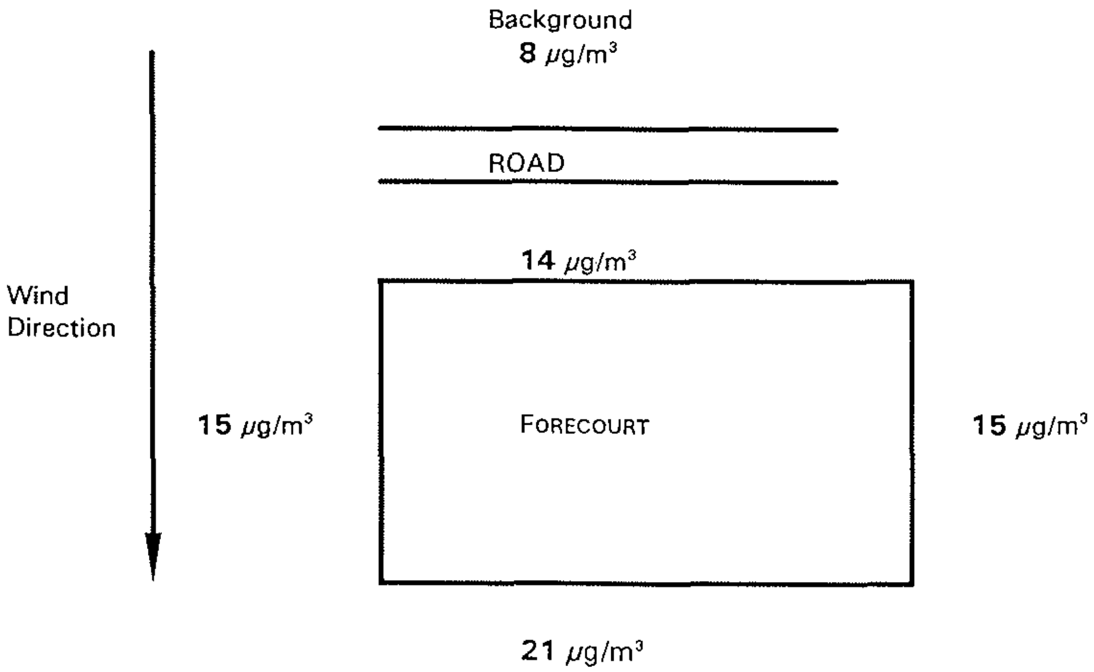
- The daytime ambient benzene levels tended to be higher than those recorded at night. This is probably a consequence of higher traffic densities during the day and the fact that most of the service stations were closed at night.

- The ambient benzene levels recorded in winter around the boundary fence were approximately twice as high as the corresponding concentrations in summer - except for the results obtained at the downwind boundary of the service stations (position C, **Figure 5**). The reason for this difference may be due to greater atmospheric stability during the winter months.

- Excluding the high results obtained in Greece, there was no significant difference between the ambient benzene levels recorded around southern and northern European service stations at corresponding measurement positions.

- Although the effect of vapour recovery facilities at service stations was considered, only two sites were equipped with a Stage 2 vapour recovery system. Consequently it is difficult to draw firm conclusions about differences in the prevailing ambient benzene levels.

- The relative contributions of benzene from forecourt activities and traffic on roads adjacent to the service stations were assessed and these are summarized in the following diagram. It can be deduced that at the downwind boundary of the service station the contributions of benzene from traffic and forecourt activities are essentially similar, (approximately 6 µg/m^3).



- There was no direct correlation between the ambient benzene data and either the volumes of motor gasoline handled, or the benzene content of the gasolines.

6.2 DISTRIBUTION TERMINALS

- The 24 hour benzene levels recorded around the perimeter of the distribution terminals ranged from 1.1 - 93.3 $\mu g/m^3$. The variation reflected the relative sampling positions with respect to sources of emission such as loading gantries, road traffic and in one case an adjacent refinery. In general, the levels were in the rank order expected, with the highest results recorded at the downwind boundary of the distribution terminals (mean 26.1 $\mu g/m^3$).

- Detailed analyses of the data have not been conducted in view of the fact that only four terminals were included in this preliminary study. The results indicate boundary ambient benzene levels of a similar magnitude to those recorded in the vicinity of service stations. However, the overall contribution of the distribution terminal activities was greater than for service stations, whereas that from road traffic was less. The influence of traffic is directly dependent on the nature and usage of the roads adjacent to terminals and thus will need to be considered on an individual terminal basis.

7. REFERENCES

1. CONCAWE (1989) Health risk of exposure to non-occupational sources of benzene. Report N° 8/89. Brussels: CONCAWE

2. CONCAWE (1986) Method for monitoring exposure to gasoline vapour in air. Report N° 8/86. Brussels: CONCAWE

3. AGIP (1993) Meeting on "Evaluation of benzene exposure of employees and customers in filling stations of the AGIP Petroli sector". Private report. Rome: Centro Congressi, 11th February 1993

4. API (1991) Gasoline vapor exposure assessment at service stations. Prepared by Clayton Environmental. API Med Res Publ 40-31151/API Publication 4553. Washington DC: American Petroleum Institute.

APPENDIX 1

METHODOLOGY FOR THE DETERMINATION OF ENVIRONMENTAL LEVELS OF BENZENE IN AIR.

1. SCOPE

This method describes a procedure for the determination of environmental levels of benzene in air. The analytical method has been validated over the range 2-100 µg/m³ for a 15 litre sample of air at a flow rate of 20 ml/min (30-1500 ng benzene collected on tube). The procedure is suitable for personal and fixed location monitoring for periods up to 12 hours, with a maximum sample volume of 15 litres of air, for obtaining time-weighted average levels for benzene in air.

Any compound that co-elutes with benzene at the operating conditions of the gas chromatograph could interfere if present; alteration of chromatographic conditions may remove this interference.

2. METHOD SUMMARY

A calibrated personal sampling pump at a pre-selected flowrate is used to draw a known volume of air through tubes containing preconditioned Chromosorb 106 (80-100 mesh) to adsorb the benzene vapour present in the atmosphere. Two sampling tubes are used in series, one of the tubes acting as a back-up to trap any benzene breaking through the front tube. The collected samples are stored in clean sealed containers.

Each tube is thermally desorbed in a stream of helium, using a two-stage desorption technique. The desorbed benzene is directly introduced into a gas chromatograph, separated by an OV1701 capillary column and detected by flame ionization. The benzene concentration is calculated by comparing peak areas obtained for the samples against the calibration graph derived from areas obtained from the analysis of standards.

3. APPARATUS

It should be noted that whilst specific equipment is described below, any equipment having the same function and meeting the same requirements would be suitable.

3.1. Capillary Gas Chromatograph, a Perkin Elmer 8320 GC, with flame ionization detection, suitable for analysis according to the operating instructions given in Table A-1.

Table A-1 Gas chromatographic conditions used for the analysis of benzene after thermal desorption

Gas Chromatograph	Perkin Elmer 8320
Column	50 m x 0.33 mm OD 0.25 mm ID WCOT capillary OV1701, SGE special thick film 0.25 µm
Oven Temperature	10°C isothermal for 10 minutes rising to 200°C at a rate of 8°C per minute, then held at 200°C for 10 minutes
Detector Type	Flame Ionization
Detector Sensitivity	High
Detector Temperature	250°C
Detector Gases	Hydrogen (89.6 kPa) Air (137.8 kPa)
Carrier Gas/Pressure	Helium (172.3 kPa)

3.2. Perkin Elmer ATD-50 Thermal Desorption Unit, equipped with a thermostatically controlled desorption oven, operated in a direct, two-stage desorption mode according to the operating instructions given in Table A-2.

TABLE A-2 Direct, two-stage thermal desorption unit operating instructions for the analysis of benzene

Thermal Desorber	Perkin Elmer ATD 50
Mode	2
Primary Desorption Temperature	250°C
Primary Desorption Time	5 mins
Box Temperature	150°C
Cold Trap Low Temperature	-30°C
Cold Trap High Temperature	250°C
Cold Trap Programme Rate	1000°C/min
Cold Trap Packing Type	Chromosorb 106
Cold Trap Packing Weight	40 mg
Cold Trap Mesh Size	80/100
Split Flowrates	Input Split Flow 16 ml/min Output Split Flow 19 ml/min Output Split Purge 6 ml/min Column Flow @ 10°C 1.5 ml/min
Split Ratio*	Approximately 35:1

* Split ratio is chosen on the basis of expected concentration levels in the air and required sensitivity. For the range specified in the method, a split ratio of approximately 35:1 is recommended. The use of split ratios outside the recommended range may cause cold trap breakthrough or column overload.

3.3. Adsorption tubes, stainless steel, compatible with the thermal desorption unit used (3.2.). The tubes should be packed (6.1.3.) and conditioned (6.1.4.) according to the instructions given in Sections 10.3 and 10.4. One end of each tube should be marked to indicate the front end. Each tube should have an identification number marked on it; the marking should be resistant to heat and moisture.

3.4. Analytical end caps, with Viton O-ring seals, for capping the adsorption tubes (3.3.)

3.5. Storage end caps, Swagelok ½" blanking nuts fitted with PTFE ferrules.

3.6. Personal sampling pumps, intrinsically safe, flowrate 5 to 50 ml/min, whose average flow is constant within ± 5% at the recommended flowrate.

Note 1: The pump should be tested with the two sample tubes in line to ensure that the required flowrate can be achieved.

Note 2: A suitable pump is the DuPont S205 sampling pump.

3.7. Pipette, 1 ml.

3.8. Precision syringes, plunger in needle type, 1 μl.

3.9. Volumetric flasks, 100 ml, 50 ml, 25 ml (Grade A).

3.10. Gas flow meter, portable, capable of measuring an air flow in the range 5-100 ml/min with an accuracy of ± 2% or better, for calibration of the personal sampling pump (3.6.). A bubble flow meter may be used in flammable areas if required.

3.11. Transportation containers.

3.12. Charcoal cloth to pack tubes into transportation containers as added protection against contamination.

4. REAGENTS AND MATERIALS

4.1. Chromosorb 106, 80/100 mesh

Note 3: Chromosorb 106 should be preconditioned in bulk before being packed into the adsorbent tubes. This is best done in a vertical stainless steel tube, heated at 1°C/min to a temperature of 250°C, and then maintained at 250°C with nitrogen or helium carrier gas flowing through at approximately 10 cm³/min per gram of adsorbent. Carrier gas flow should be maintained while cooling down at the end of the preconditioning period. Store in an air-tight container if not used immediately.

4.2. Benzene (Purity > 99%).

4.3. Cyclohexane, HPLC grade.

Note 4: The cyclohexane should be free from contaminants having similar chromatographic retention times to benzene under conditions listed in Table A-I.

5. SAMPLING

5.1. Immediately prior to sampling, remove the storage end caps from the preconditioned Chromosorb 106 tubes (6.1.4.) and connect the back end of the front tube to the front end of the back-up tube using a Swagelok union fitted with ferrules (the grooved end of the tube is the sample inlet). Connect the back end of the back-up tube to the personal sampling pump using the minimum amount of flexible tubing.

Note 5: The sample tube should be positioned near vertical during sampling to minimize channelling.

Note 6: Air being sampled should not pass through any hose or tubing before entering the adsorption tube. During sampling the end caps should be stored in a clean air-tight container to prevent contamination.

5.2. Adjust the flowrate of the sampling pump, with the two sample tubes in line (5.1.) to the desired sampling rate using a gas flow meter (3.10.). EACH SAMPLE PUMP MUST BE CALIBRATED WITH THE PAIR OF SAMPLE TUBES WHICH WILL BE USED WITH THAT PUMP FOR THE SAMPLING PERIOD.

Note 7: Flowrates should fall within the recommended range of 5 to 50 cm³/min, with the appropriate value being dependent on the total sample volume required (15 litres).

5.3. Record the identification number of each tube, start the pump, measure the exact value of the flowrate. On commencement of sampling, record the sampling start time.

5.4. Ambient temperature, relative humidity, atmospheric pressure, wind direction and velocity etc., should be recorded for an adequate interpretation of the measurements.

5.5. At the end of the sampling period, switch off the pump and record the end of the sampling period. Re-measure the flowrate, disconnect the adsorption tubes, separate the front and back tubes, replace the end caps and store the tubes in the air-tight container, containing charcoal cloth, in which they were supplied.

Note 8: It is important not to overtighten the storage end caps as this will result in damage to the tubes. Finger tightness plus a quarter of a turn is adequate.

Note 9: Tubes are to be stored at minus 20°C wherever practicable, until analysed.

6. ANALYTICAL PROCEDURE

All equipment must be used in accordance with the manufacturer's instructions.

6.1. APPARATUS PREPARATION

6.1.1. Couple the thermal desorption unit (3.2.) to the gas chromatograph by means of a heated transfer line according to the manufacturer's instructions.

6.1.2. Condition a new chromatographic column overnight at 250°C, with helium flow by-passing the detector, using a slow programming rate of 1°C/min and starting at room temperature.

6.1.3. Pack the required number of empty adsorption tubes (3.3.) with 200 mg ± 10 mg of Chromosorb 106 (4.1.) each according to the instructions given in Section 10.

6.1.4. Condition the packed adsorption tubes (3.3.) before use by subjecting them to one or more normal desorption cycles (6.3.), until peak areas from interfering compounds from the tubes, if present, become less than 5% of the peak area of the calibration solution of benzene spiked at the lowest concentration level of interest or lower than the detection limit of the method. Then allow the tubes to cool to room temperature, remove from the thermal desorber and cap with the proprietary end caps, previously conditioned at 100°C for 1 hour. Store in a clean air-tight container at 0°C or lower until use.

6.2. CALIBRATION

6.2.1. Preparation of standard solutions, range 3-150 µg/µl benzene/cyclohexane

6.2.1.1. Stock standard solution 3 µg/µl benzene/cyclohexane

Weigh accurately 0.3 g of benzene into a 100 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.1.2. Stock standard solution 30 µg/µl benzene/cyclohexane

Weigh accurately 1.5 g of benzene into a 50 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.1.3. Stock standard solution 60 µg/µl benzene/cyclohexane

Weigh accurately 3.0 g of benzene into a 50 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.1.4. Stock standard solution 120 µg/µl benzene/cyclohexane

Weigh accurately 3.0 g of benzene into a 25 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.1.5. Stock standard solution 150 µg/µl benzene/cyclohexane

Weigh accurately 3.75 g of benzene into a 25 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.2. Preparation of standard solutions, range 30-1500 ng/µl benzene/cyclohexane

6.2.2.1. Standard solution 30 ng/µl benzene/cyclohexane

Pipette 1 ml of stock standard solution 6.2.1.1. into a 100 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

6.2.2.2. Standard solution 300 ng/µl benzene/cyclohexane

Dilute solution 6.2.1.2. as 6.2.2.1.

6.2.2.3. Standard solution 600 ng/µl benzene/cyclohexane

Dilute solution 6.2.1.3. as 6.2.2.1.

6.2.2.4. Standard solution 1200 ng/µl benzene/cyclohexane

Dilute solution 6.2.1.4. as 6.2.2.1.

6.2.2.5. Standard solution 1500 ng/µl benzene/cyclohexane

Dilute solution 6.2.1.5. as 6.2.2.1.

6.2.3. Calibration

6.2.3.1. Using a 1 µl plunger in needle syringe, inject 1 µl of standard solution (6.2.2.1) directly into the packing material at the back end of a clean Chromosorb 106 sampling tube. Re-fit storage end caps to the tube and store for 24 hours before analyzing. Carry out the spiking procedure in duplicate on separate tubes.

6.2.3.2. Repeat Section 6.2.3.1. by injecting standard solutions 6.2.2.2. to 6.2.2.5. on to separate clean Chromosorb 106 tubes.

6.2.3.3. Analyze each tube (6.2.3.1. and 6.2.3.2.) as described in Section 6.3. Determine the area of the benzene peaks and prepare a calibration graph plotting the areas found against the respective amounts of benzene (in ng) spiked on to the tubes.

6.3. SAMPLE ANALYSIS

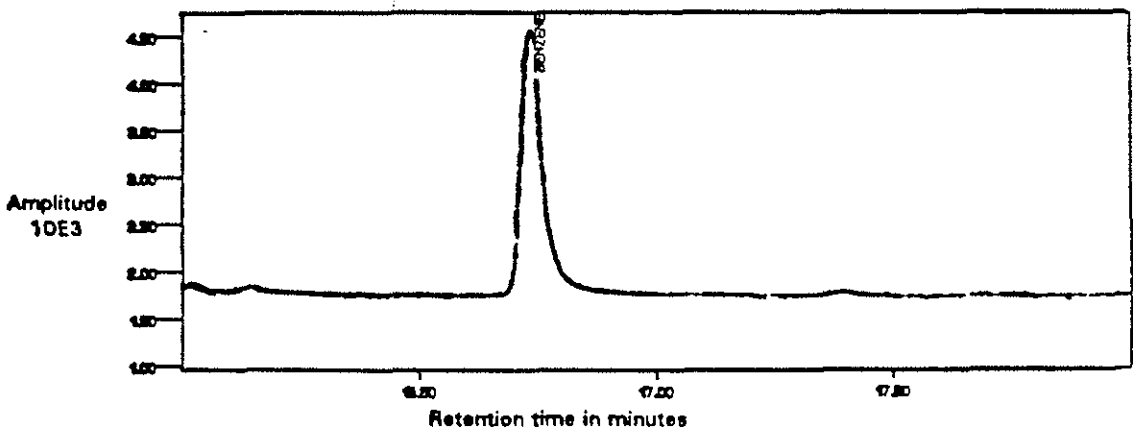
6.3.1. Replace storage end caps with analytical end caps and place the tube onto the autosampler with the scored end facing outermost (i.e. in the "back-flush" mode).

6.3.2. Analyze each sample tube under the conditions given in Tables A-1 & A-2.

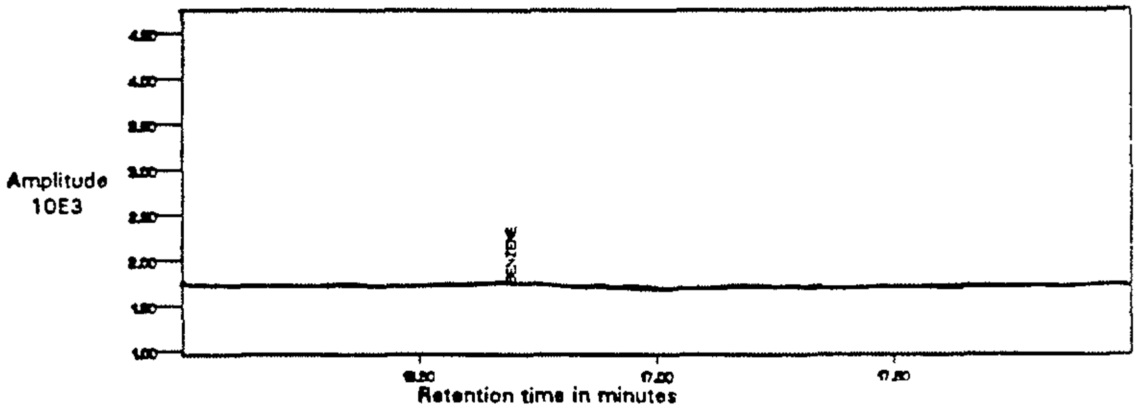
6.3.3. Identify, in the chromatogram, the benzene peak and determine its respective peak area. Determine the amount of benzene (ng) on the tube from the calibration graph (6.2.3.3.). Typical chromatograms are given in **Figure A-1**.

Figure A-1:

Typical standard chromatogram (300 ng benzene on tube)



Typical blank chromatogram (9 ng benzene on tube)



7. CALCULATION

Calculate the concentration of benzene in the air sampled (µg/m³) by means of the following equation:

$$\text{Concentration of benzene} = \frac{W1 + W2}{V} \quad \mu g/m^3$$

where W1 = mass of benzene present on the front tube in ng
W2 = mass of benzene present on the back-up tube in ng
V = volume of air sampled in litres

8. REPORTING

Report the concentration of benzene in µg/m³ to two significant figures.

9. PRECISION

The precision of the analytical method over the range 30-1500 ng tube loading gives a pooled relative standard deviation of 1.8%.

10. PREPARATION, HANDLING AND STORAGE OF PERKIN-ELMER ATD50 THERMAL DESORPTION TUBES

10.1. CONDITIONING OF ABSORBENT PRIOR TO PACKING

The Chromosorb 106 should be preconditioned in bulk before being packed into tubes. See *Note* 3 in Section 4.1.

10.2. HANDLING OF ADSORPTION TUBES

When handling tubes the operator must wear clean gloves to prevent contamination from hands.

10.3. PACKING OF ADSORPTION TUBES

The adsorbent bed is retained between a fine mesh stainless steel gauze screen and a plug of silanised glass wool. The position and size of the bed should be such that it always will fall within the heater zone of the desorber. The screens or plugs should not allow any adsorbent to escape and contaminate the gas line.

The packing procedure is as follows:

- clean the empty tubes with a degreasing solvent and dry them;
- heat the tubes and the metal end caps to 100°C in a clean oven for at least one hour;
- fix the retaining screen at the front end of the tube in such a place that the adsorbent bed will fall approximately in the middle of the heater zone;
- while the tube is held vertically, pour the adsorbent into the tube and tap the tube to allow the adsorbent to settle in;
- with the tube still in a vertical position, press the retaining glass wool plug down onto the bed, ensuring that no free space is left in the bed which might give rise to channelling during sampling;
- cap the tubes with Swagelock end caps fitted with PTFE ferrules.

The tubes are then ready to be preconditioned prior to sampling.

10.4. CONDITIONING OR CLEANING PRIOR TO PRE-ANALYSIS

The tubes are heated for 20 minutes while a stream of pure nitrogen or helium is passed from the back of the tube to the front. The front of the tube is marked with a circular groove (orientation mark). The tubes should not be heated above 250°C as decomposition of the absorbent packing will occur.

10.5. PRE-ANALYSIS PRIOR TO SUPPLY

10.5.1 Each tube is visually examined to check the absorbent has not escaped and the screens or plugs are in the correct position

10.5.2 Each tube is analysed according to Section 6.3.

10.5.3 The tube is clean when the chromatogram shows that the interfering compounds are less than 5% of the peak area of the lowest calibration solution used in the method or below the detection limit of the method.

10.5.4 Every tube is retained with a "conditioned tube chromatogram" showing tube identification number, date of analysis and retention time of compounds for which it is intended.

10.5.5 Tubes spiked with benzene are analysed to show retention time and retained with the "conditioned tube chromatograms".

10.5.6 Eight blank tubes are selected at random, labelled with metal clips which must not be removed. Four blanks are retained by the laboratory and are analysed on return of the samples from the field to demonstrate that degradation or contamination has not occurred over the storage period.

The other four blanks are sent with the sample tubes and they MUST NOT be used as sample tubes. They are analysed as field blanks to demonstrate that contamination has not occurred during transport and storage.

Professional judgement should be used when dealing with results of blank tube analyses showing the presence of interfering compounds at greater than 5% of the peak area of the lowest concentration calibration solution used in the method, or above the detection limit of the method.

10.6. CAPPING

10.6.1 Prior to fitting, the caps are heated in an oven at 100°C for one hour and cooled in a desiccator.

10.6.2 The caps are fitted, then tightened with spanners not more than a 1/4 turn.

NB: Operator must wear gloves to prevent contamination from hands. Tightening caps more than 1/4 turn can result in damage to tubes.

10.7. STORAGE

10.7.1 Adsorption tubes should be stored in clean, air-tight metal containers packed with a small amount of charcoal cloth. Tubes should be stored at the lowest practicable temperature, preferably at 15°C where possible.

10.7.2 If tubes are not used within three months, they should be returned to the laboratory for a new conditioned tube chromatogram.

10.8 TRANSPORT AND STORAGE

10.8.1 Immediately after sampling, the adsorption tubes should be resealed with Swagelock caps according to instructions in section 10.6.2.

10.8.2 The capped tubes and blanks should be stored in a clean airtight metal container at 0°C or lower.

10.8.3 The tubes should be transported back to the laboratory for analysis as soon as possible after sampling and analysed within the recommended storage time of the method, but never later than 21 days.

10.8.4 The metal tin containing the tubes should be well packaged and labelled appropriately.

11. BREAKTHROUGH STUDY AT HIGH TEMPERATURE AND HUMIDITY

11.1. OBJECTIVE

The objective of this study was to demonstrate that under "extreme" sampling conditions i.e. 35°C and 80% relative humidity and while sampling a benzene/air mixture containing 50 $\mu g/m^3$ of benzene at 20 ml/min. for 12 hour periods, that breakthrough of benzene to the backup tubes was $\leq 5\%$.

11.2. SAMPLE TUBE PREPARATION

Six sets of sampling tubes (i.e. 18 tubes) and **4** laboratory blanks, all containing Chromosorb 106 were cleaned by purging with helium at 240°C for a minimum of 2 hours. Test runs were made within 24 hours of cleaning tubes using the analytical method described in 6.3.

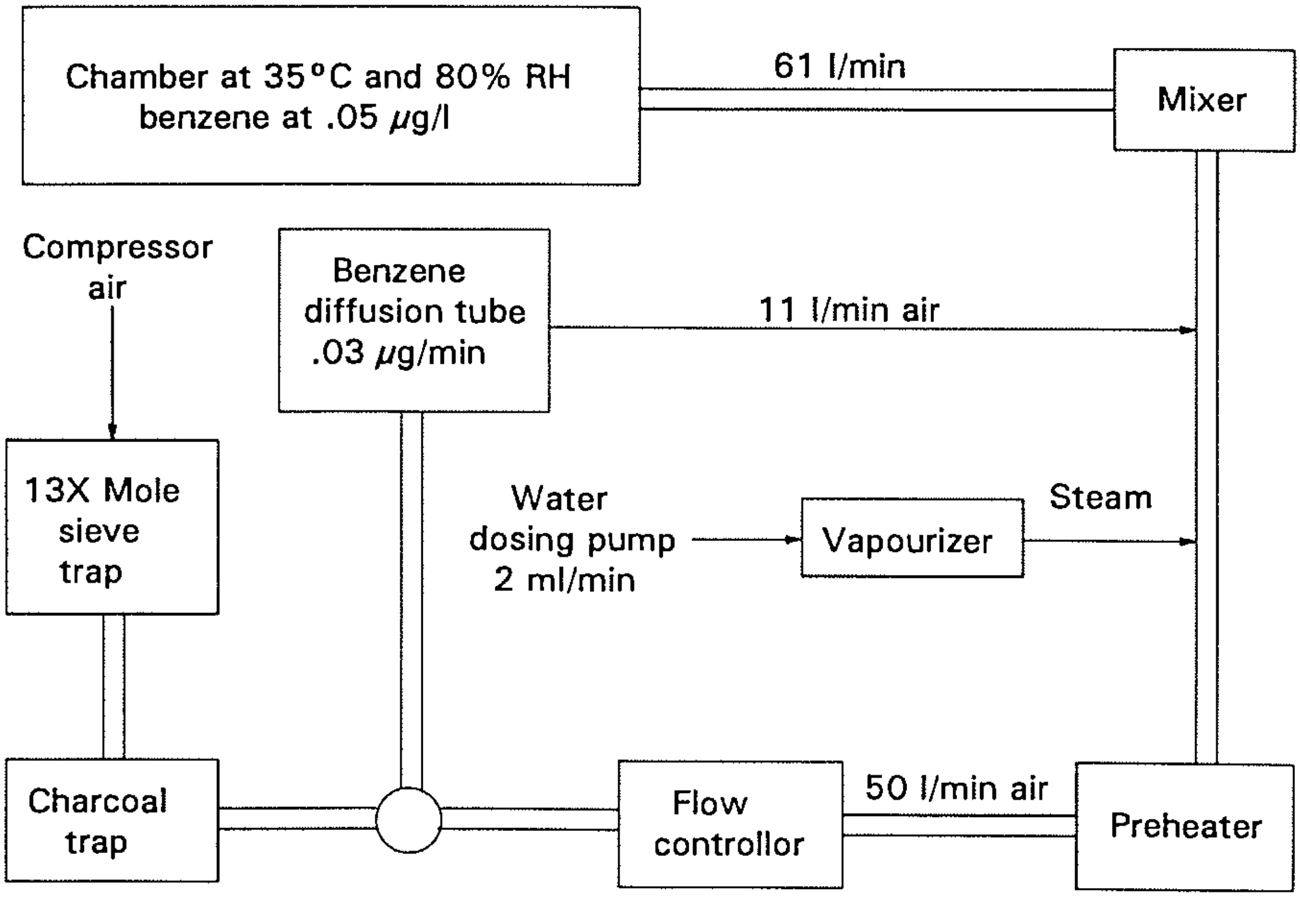
11.3. BENZENE VAPOUR GENERATION

A benzene atmosphere was generated dynamically using the apparatus outlined in Figure A-2. The benzene source was a stabilized capillary diffusion tube in AID Model 360 standards generator. Air was supplied from an air compressor, filtered and cleaned by passing it through molecular sieve 13x and charcoal cartridges.

Flow control was achieved by using a mass flow controller calibrated against a volumetric gasometer.

Six sets of samplers were made up, each set comprising of 3 tubes connected in series. The 3 tubes of each set were retained within the test chamber during the sampling period.

Figure A-2: Benzene standards generation and sampling apparatus



11.4 TEST CONDITIONS

Two 12-hour sampling runs were conducted using the six sets of samplers on each occasion. The average conditions were:

	Run 1	Run 2
Benzene (µg/m^3)	50	50
Relative humidity(%)		
Measured	79	79
Calculated	84	83

The analyses were carried out according to the method described in 6.3.

11.5. RESULTS

Ten out of 12 of the recoveries were within 80 - 100%. One recovery was very low for no apparent reason. The other runs showed a high recovery but the flowrate increased significantly on this sampler during the run. The mean recovery for Run 1 was 91.1% and 89.9% for Run 2. Discounting the two extreme recovery results the mean recovery for Run 2 was 94.5%.

Breakthrough occurred to the middle tube on one sample out of 6 in Run 1 and on 2 out of 6 in Run 2. No breakthrough was detected on the third tube in each sample set.

The detailed results are shown in the following tables.

Table A-3 -	Tube sampling rates and volumes
Table A-4 -	Sampling chamber conditions
Table A-5 -	Benzene diffusion tube emission rates.
Table A-6 -	Sampling chamber data log.
Table A-7 -	Benzene analyses

11.6 CONCLUSIONS

This study showed that under the test conditions i.e. 35°C and 80% relative humidity:

- Breakthrough of benzene from tube 2 to tube 3 would not occur.
- In one case of 12, breakthrough of benzene from tube 1 to tube 2 exceeded the 5% stated in the objectives for the study. However, the mean value was 2.4% (n=6).

Table A-3 Tube sampling rates and volumes

Set	Flow rates			Volume *
	Initial (ml/min.)	Final (ml/min.)	Average (ml/min.)	(litres)
Run 1				
1	20.5	20.5	20.5	14.8
2	23.1	22.4	22.8	16.4
3	20.5	17.1	18.8	13.5
4	18.9	21.1	20.0	14.4
5	25.1	27.6	26.4	19.0
6	19.0	19.3	19.2	13.8
Mean	21.2	21.3	21.3	15.3
Run 2				
1	22.2	21.5	21.8	15.7
2	21.9	21.8	21.9	15.7
3	19.9	16.4	18.1	13.0
4	17.7	17.5	17.6	12.6
5	21.8	29.2	25.5	18.4
6	21.9	21.3	21.6	15.5
Mean	20.9	21.3	21.1	15.2

Tubes were arranged in sets of 3 tubes in series

* Calculated from the mean of the before & after flow rates

Footnote : Sorbent: Chromosorb 106
Weight: 200 mg.
Mesh size: 80/100

Table A-4 Sampling chamber conditions

		Run 1	Run 2
Air flow	l/min	61	61
Temperature	° C	35	35
Mean humidity measured	% RH	79	79
Benzene diffusion rate	µg/min	3.03	3.03
Benzene concentration	µg/l	0.050	0.050
Run time	Min	720	720
Water vaporized	g	1460	1438
Water vapour concentration	µg/l	33.24	32.73
Humidity (theoretical)	% RH	84	83

Table A-5 Benzene diffusion tube emission rates

DATES	TIME	ELAPSED (Mins)	WEIGHT (g)	WEIGHT LOST (g)	BENZENE EMITTED (µg/min)
18/4/91	1.15 pm	0	9.9337		
19/4/91	3.00 pm	1 545	9.9268	0.0069	4.4660
22/4/91	2.15 pm	4 275	9.9116	0.0152	3.5556
29/5/91	1.30 pm	53 280	9.7497	0.1619	3.0387
14/6/91	7.52 am	23 040	9.6799	0.0698	3.0295

Table A-6 Sampling chamber data log

Run 1				Run 2			
Time	Temp (°C)	RH (%)	$H_2$0 (ml)	Time	Temp (°C)	RH (%)	$H_2$0 (ml)
08:20	35.2	81	0	08:00	35.0	81	150
08:24	34.8	78	8	08:04	35.2	79	153
08:50	34.0	79	70	08:15	35.0	78	170
09:18	34.0	85	113	09:00	35.1	76	261
09:49	34.5	80	190	10:38	35.0	82	460
10:18	34.8	80	250	11:55	35.5	79	612
10:46	34.5	80	303	12:32	35.2	80	689
11:32	35.0	79	398	13:54	35.2	80	853
13:01	35.2	74	580	15:09	35.4	74	1005
13:48	35.2	79	673	16:44	34.0	80	1195
14:44	35.2	79	785	17:42	35.6	78	1312
15:39	35.8	79	898	18:48	35.1	81	1445
16:47	35.2	79	1035	20:00	35.0	80	1592
17:32	35.3	80	1126				
18:36	35.6	78	1253				
19:29	36.0	79	1362				
20:00	35.5	81.5	1424				
20:20	35.0	79	1464				
	Mean	Mean	Total		Mean	Mean	Total
	35.0	79	1464		35.1	79	1442
		g Water (d=.997):	1460			g Water (d=.997):	1438
		mg/l Water:	33.24			mg/l Water:	32.73

Table A-7 Benzene analyses

	Run 1			Run 2		
	GC Benzene integrator counts					
	front	middle	back	front	middle	back
set 1	252.2	0.0	0.0	277.6	0.0	0.00
set 2	252.8	0.0	0.0	257.5	24.2	0.00
set 3	210.8	0.0	0.0	299.9	10.7	0.00
set 4	257.6	0.0	0.0	231.3	0.0	0.00
set 5	354.1	5.5	0.0	332.6	0.0	0.00
set 6	253.3	0.0	0.0	109.7	0.0	0.00
	Weight of benzene measured (µg)					
	front	middle	back	front	middle	back
set 1	0.667	0.000	0.000	0.743	0.000	0.00
set 2	0.669	0.000	0.000	0.689	0.065	0.00
set 3	0.558	0.000	0.000	0.803	0.029	0.00
set 4	0.682	0.000	0.000	0.619	0.000	0.00
set 5	0.937	0.015	0.000	0.890	0.000	0.00
set 6	0.670	0.000	0.000	0.294	0.000	0.00
Mean	0.697	0.002	0.000	0.673	0.016	0.00
	Weight of benzene sampled µg (calculated)					
set 1		0.736			0.784	
set 2		0.817			0.785	
set 3		0.675			0.650	
set 4		0.718			0.630	
set 5		0.946			0.916	
set 6		0.687			0.775	
Mean		0.763			0.757	
	Benzene recovery %					
	front	middle	back	front	middle	back
set 1	90.7	0.0	0.0	94.8	0.0	0.0
set 2	91.9	0.0	0.0	87.8	8.2	0.0
set 3	82.6	0.0	0.0	123.5	4.4	0.0
set 4	95.0	0.0	0.0	98.2	0.0	0.0
set 5	99.1	1.5	0.0	97.2	0.0	0.0
set 6	97.5	0.0	0.0	37.9	0.0	0.0
Mean	91.1	0.3	0.0	89.9	2.1	0.0

APPENDIX 2

REPORT OF RESULTS OF PILOT STUDY

SUMMARY

A survey was carried out to measure the levels of benzene-in-air in the atmosphere around a service station forecourt. Measurements were taken at fixed positions during approximately 3 hour periods over a 24 h period.

During the survey the wind direction was from over a busy road and for the most part was in one direction.

Mean levels of benzene-in-air upwind of the adjacent road and the forecourt were 1.2 µg/m^3 (735 mins, 4 samples).

Mean levels of benzene-in-air upwind of the forecourt, between the road and the forecourt were 9.3 µg/m^3 (740 mins, 4 samples).

Levels of benzene-in-air on a 50 metre arc downwind of the forecourt were in the range 2.2 to 14.1 µg/m^3, with a mean level of 7.1 µg/m^3 (896-1113 mins, 29 samples)

Mean levels 100 metres downwind were 5.8 µg/m^3 (961 mins, 5 samples).

When the wind reversed direction early in the morning and with little traffic, levels upwind were in the range 0.4 to 0.5 µg/m^3 (6 samples). Between the forecourt and the road the level was 0.9 µg/m^3. The level of benzene 100 metres downwind of the forecourt and road was 0.9 µg/m^3.

Approximately 14 088 litres of gasoline, with benzene contents ranging from 0.9 to 3.5 % weight/volume, were sold during the survey period.

1. OBJECTIVES

The pilot study objectives were:

1. To develop a sampling protocol for use in the main CONCAWE study.
2. To evaluate the practical aspects of the sampling and analytical methodologies.

2. MEASUREMENTS

Samples were taken by drawing air at 185 ml/min through a Chromosorb 106 (200 mg) adsorbent tube using a Du Pont S200 sampling pump. This pump was found to be able to cope with the high pressure drop imposed by the adsorbent in the sample package. Flow rates were measured using either a Buck Calibrator M5 or a Kurtz model 514S mass flowmeter.

Air movements were checked visually using air current tubes or small smoke bombs and the velocity was measured using either a Deuta anemometer or a Casella air meter. Air temperatures were measured using an Endress and Hauser Hygrolog.

3 SAMPLING STRATEGY

A service station was chosen which had the following attributes:

- a high level sales turnover
- access to areas up to 100 metres from the centre of the forecourt
- level ground
- open 24 hours per day

Nine sampling positions were selected, following an agreed protocol (Figure B-1). The locations are described in the first two columns of Table B-1 and are shown for this forecourt in Figure B-2.

Table B-1 Benzene-In-Air Concentrations around the Service Station µg/m^3

Sampling position *	Sampling position * description	Nominal sampling periods - 29/30 May 1990 and traffic movements for the periods								Mean result	Mean result for constant wind direction
		0600 to 0900	0900 to 1200	1200 to 1500	1500 to 1800	1800 to 2100	2100 to 2400	0000 to 0300	0300 to 0600		
		Very busy	Very busy	Very busy	Very busy	Busy	Light	Light	Light		
A	100 metres upwind of forecourt	Void	1.3	1.0	Void	1.1	1.3	1.0	0.9	1.1	1.2
B	Upwind of forecourt downwind of road on station boundary	12.6	10.6	11.3	Void	Void	2.8	1.5	0.9	6.6	9.3
C	Centre of forecourt	87.5	43.8	9.8	Void	45.5	59.0	25.9	4.9	39.5	49.1
D	50 metres downwind of forecourt far left	6.4	11.9	2.2	5.6	5.5	2.8	1.1	0.5	4.5	5.7
E	50 metres downwind of forecourt left	10.9	9.7	2.6	7.7	4.2	4.6	1.3	0.5	4.5	5.7
F	50 metres downwind	10.4	10.2	5.6	14.1	5.4	3.6	1.3	0.5	6.4	8.2
G	50 metres downwind of forecourt right	8.1	7.6	6.2	9.8	6.2	2.9	1.4	0.5	5.3	6.8
I	100 metres downwind	6.7	5.6	2.9	10.7	Void	3.1	0.7	0.5	4.3	5.8
H	50 metres downwind of forecourt far right	8.0	9.0	7.8	12.5	Void	3.7	1.5	0.4	6.1	8.2
J	30 metres downwind of vent during delivery (1048-1115)		72.9								

▨ Time periods of constant wind direction

- See Figure B-3 for clarification of sampling positions

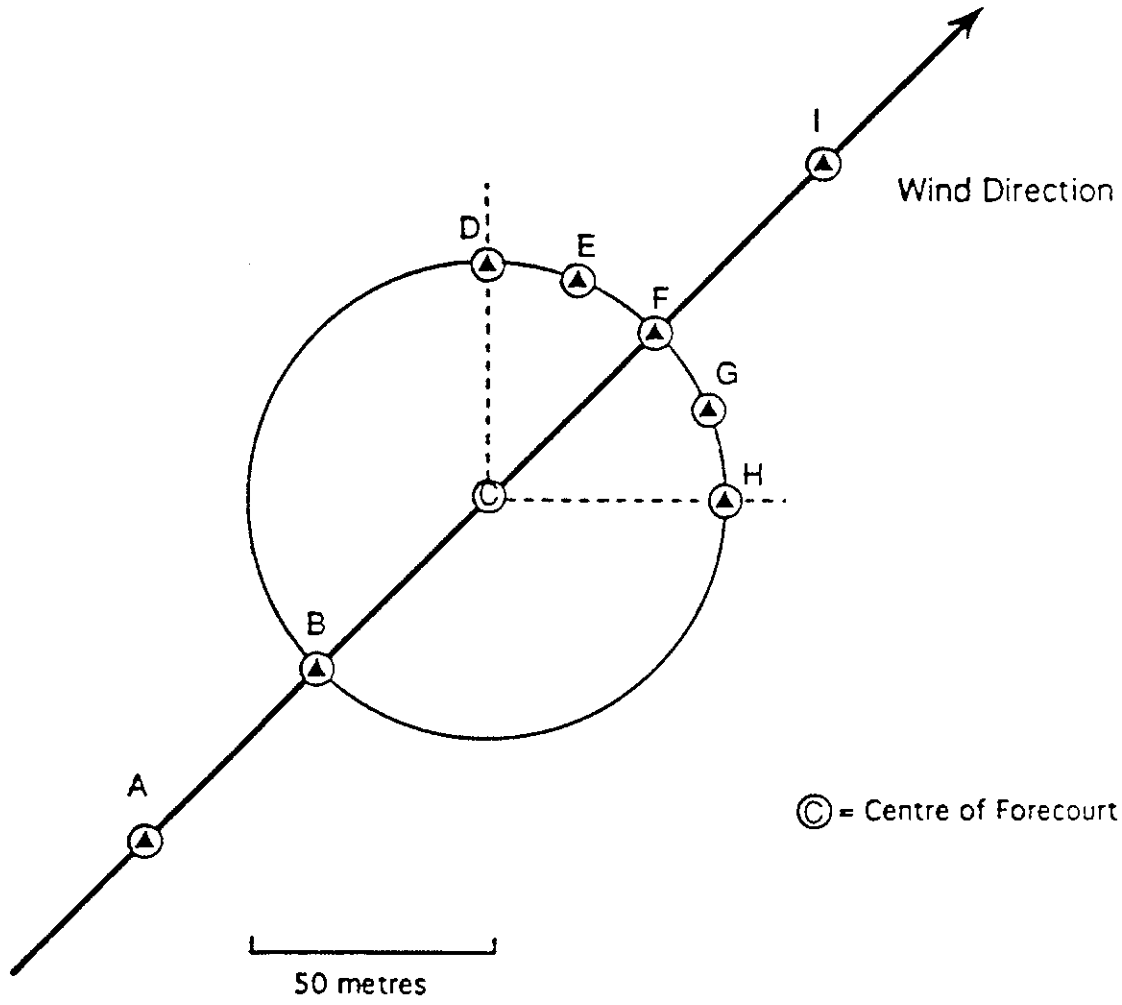


FIGURE B-1 General configuration of sampling positions

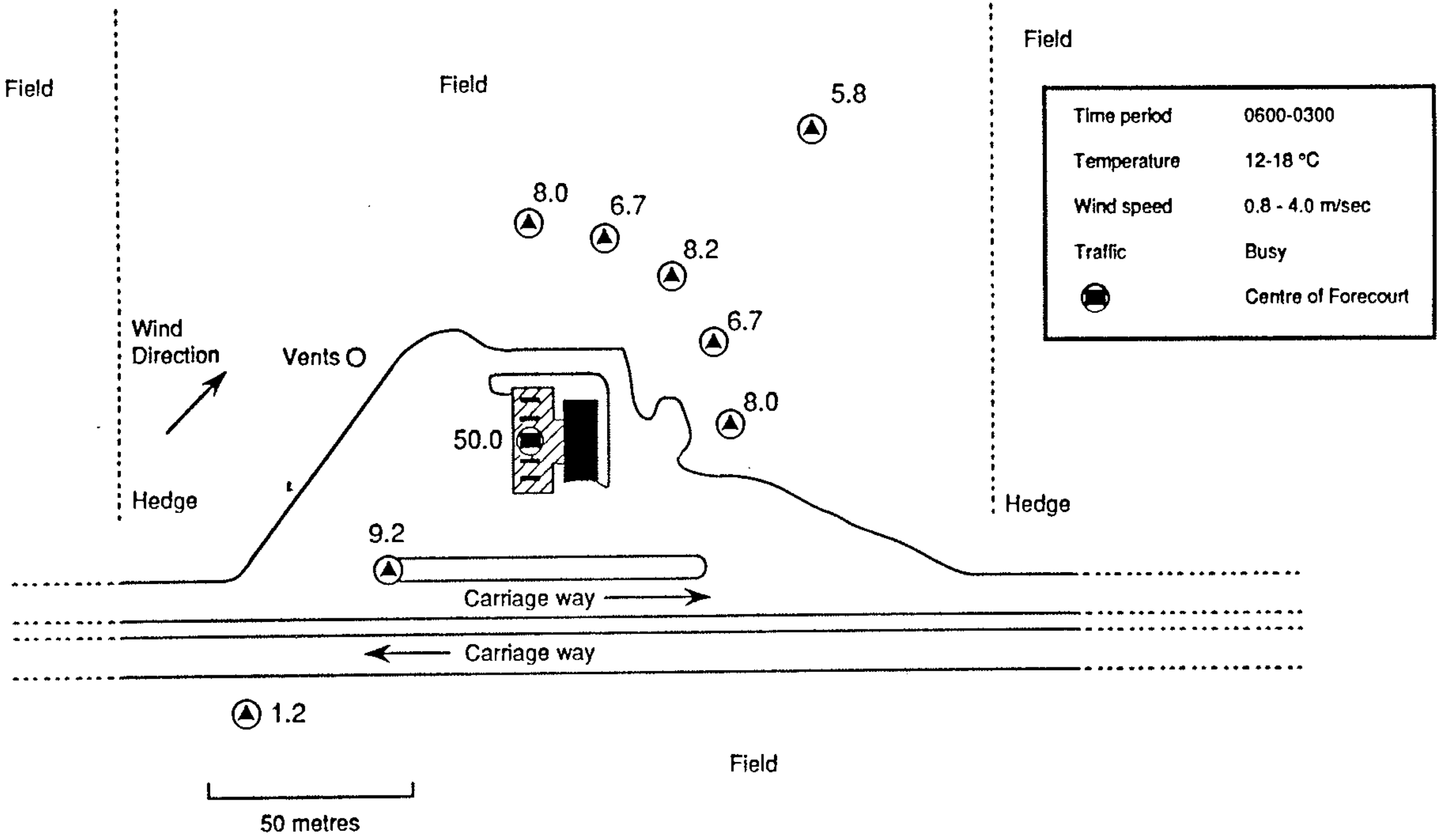


Figure B-2 - Benzene-in-air concentrations (µg/m^3) for constant wind direction

Prior to the beginning of the survey the aim was to physically move the samples so as to maintain their respective positions relative to the wind direction and the centre of the forecourt. When fuel was delivered a sample of air was collected 30 metres downwind of the vent pipes from the site storage tanks and roadcar (20 mins).

The sampling tubes were mounted pointing downwards at a height of 1.75 metres above the ground by attaching them to wooden canes slotted into 0.5 metre tubes which had been hammered into the ground at the appropriate place.

The sampler at the centre of the forecourt was attached to a fuel dispensing pump housing by tape.

At the onset of rain the sampling pumps were covered with polythene bags but the sampling tubes were left unprotected to minimize the potential for contamination. The flow rates of each pump and tube combination were checked before and after sampling and at least once during the sampling period.

Sampling tubes were changed approximately every 3 hours during a continuous 24 hour period beginning at 06:00. Samples were submitted for analysis, together with unused sample tubes; which were used for control purposes.

Details of weather conditions and approximate sales figures were noted.

The volume of traffic was estimated by the observation of traffic movement on the forecourt and on the adjacent road. The results were expressed as light, busy and very busy.

72 samples were collected of which 66 samples were analysed successfully. (See Section 5.2)

Bulk samples of the gasolines being sold were collected at 22:00 hrs from the pumps and transported to the laboratory for quantification of the benzene content. Bulk samples were transported separately from the sampling tubes to avoid the possibility of cross contamination.

4. RESULTS

4.1 BENZENE-IN-AIR CONCENTRATIONS

Benzene-in-air concentrations obtained during this study are shown in Table B-1. The mean values for each position and the mean values for a constant wind direction (06:00 - 24:00 hrs) are provided along with traffic movement information. The benzene-in-air concentrations for constant wind direction are shown in Figure B-2.

During a period of constant wind direction:

- The highest levels of benzene-in-air measured were in the centre of the forecourt, and were in the range 9.8 to 87.5 μg/m³ and 30m downwind of the vents during gasoline delivery, 72.9 μg/m³.

- The lowest benzene-in-air levels were 100 metres upwind of both the forecourt and the road and were in the range 1.0 to 1.3 µg/m^3. (735 mins, 4 samples).
- Levels of benzene-in-air in between the road and the forecourt but upwind of the pumps were in the range 2.8 to 11.3 µg/m^3. (740 mins, 4 samples).
- Levels on an arc 50 metres downwind of the forecourt were in the range 2.2 to 14.1 µg/m^3 over nominal 3 hour periods (29 samples).
- Levels of benzene-in-air 100 metres downwind were in the range 2.9 to 10.7 µg/m^3 (5 samples).

When the wind reversed direction early in the morning, and with little traffic, levels upwind were in the range 0.4 to 0.5 µg/m^3 (6 samples). The wind was then blowing from the direction of a wide river estuary and open fields. Between the forecourt and the road the levels were 0.9 µg/m^3. The level of benzene 100 metres downwind of the forecourt and downwind of the road was 0.9 µg/m^3.

4.2 FUELS

The volumes of fuels and their benzene contents are given in Table B-2.

Table B-2 Benzene content and sales volumes of fuels during the study

TIME PERIOD (29/30 May 1990)	FOUR STAR (litres)	UNLEADED (litres)	SUPER UNLEADED (litres)
0700-1400	3250	2627	299
1400-2200	3671	2085	528
2200-0700	1039	443	146
Benzene content (% wt/vol) (sampled at 2200)	0.9	2.8	3.5

Total gasoline sales - 14 088 litres

4.3 METEOROLOGICAL CONDITIONS

The dry bulb temperature, wind speeds and comments are given in Table B-3.

Table B-3 Weather conditions (29/30 May 1990)

TIME	TEMPERATURE (°C - dry bulb)	WIND SPEED (m/sec)	DIRECTION	COMMENT
6:50	12	0.8	SW	-
7:25	12	0.0	SW	-
8:30	14	1-2	SW	-
9:50	17	-	SW	-
11:20	18	1-2	SW	-
14:00	-	-	SW	Rain
14:25	15	2-4	SW	Rain
17:00	14	2-4	SW	Rain
19:00	-	-	SW	Rain stopped
19:30	-	-	SW	Rain
20:30	14	2-3	SW	Rain
21:00	-	-	SW	Rain stopped
22:00	12	1.0	SW	-
1:30	-	-	Still	-
2:00	-	-	NE	-
5:00	13	5.0	NE	-

Over the first 19 hours (six full sampling periods) the wind direction was constant. During the seventh sampling period the wind direction reversed over a 30 minute period. As it was not possible to forecast further changes in the wind direction the sampling points were not changed for the last 3 hour sampling period.

5. DISCUSSION

5.1 LOCATION

The chosen forecourt met the requirements for the study in terms of sales volumes and accessibility to suitable sampling locations. The prolonged constant wind direction did not allow the feasibility of moving the sample locations to be tested.

Although a 50 metre downwind arc was chosen on an arbitrary basis for sampling in this study, the criteria for other forecourts will vary depending on local conditions.

The service station was self service.

The road and forecourt were approximately two miles downwind of the nearest conurbation and clear of any other major roads and industrial areas.

5.2 ANALYSIS

Some samples were lost during analysis due to equipment failure (flame out on the detector of the gas chromatograph). This failure was attributed to the collection of excessive quantities of water onto the samples arising from fine water spray from the road surface during and immediately after rain. This affected the sample at Location B. This caused the loss of the sample being analysed and some subsequent samples. This was not the case with samples from other positions collected whilst it was raining.

5.3 BACKGROUND DATA

The sales volumes from this forecourt were obtained from the computerised printout made by the forecourt staff at the end of each work shift. This did not relate directly to the sampling periods used. More detailed information could have been gathered by reading the analogue counters fitted to the individual dispensing pumps. However, this would have been more time consuming and may have led to some spillages.

It was found that taking readings of temperature and wind speed etc. was feasible every hour.

There were significant problems experienced in recording traffic movements along the adjacent road due to vehicles travelling at speeds of about 70 mph in opposite directions on different carriageways, vehicles overtaking, variable types, e.g. heavy goods vehicles and diesel and petrol driven vehicles. The movement of vehicles along the road was affected greatly by traffic lights approximately 400 metres from the forecourt.

The above had some bearing on the number and rate of vehicles entering and leaving the forecourt.

5.4 BENZENE-IN-AIR CONCENTRATIONS

The results of the benzene-in-air levels at the different sampling time periods are shown in Figures B-3 to 10.

The highest concentrations of benzene-in-air were in the centre of the forecourt and the lowest 100 metres upwind of the station.

In general the benzene levels on the 50 metres downwind arc appeared to be influenced by the distance from the road. This is clearly seen in figures B-5 and B-6. The centre point on the arc appeared to be influenced by emissions from the forecourt.

Positions D and E were unlikely to be influenced by emissions from the forecourt because of the wind direction except for a short period when there was a delivery of bulk fuel to the forecourt at which time they were downwind of the roadcar and the vent pipes.

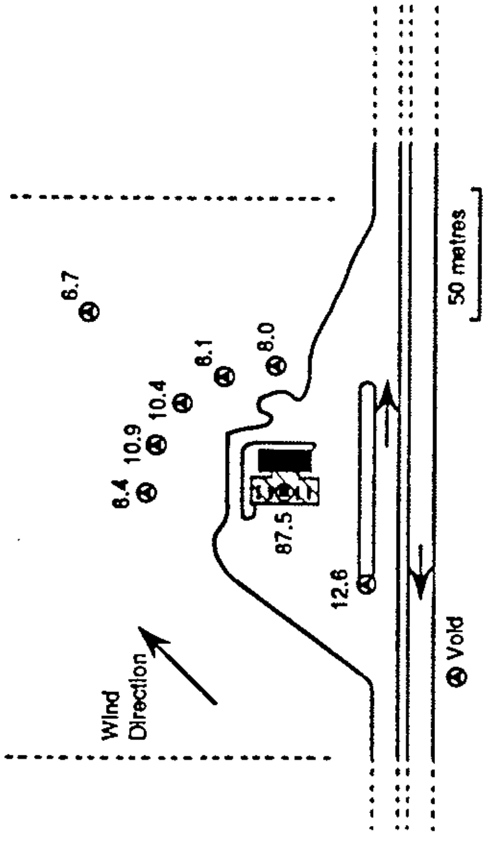


Figure B-3 : Benzene-in-air concentrations (µg/m³) for sampling period 0600-0900

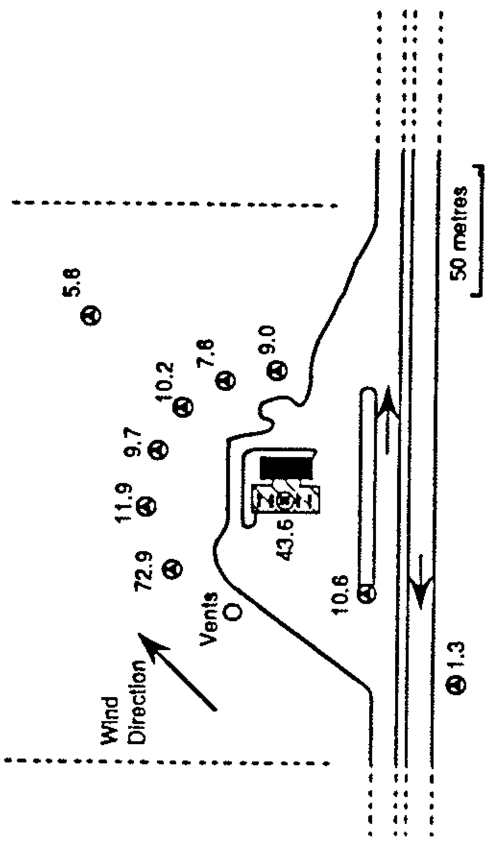


Figure B-4 : Benzene-in-air concentrations (µg/m³) for sampling period 0900-1200 (fuel delivery during this period)

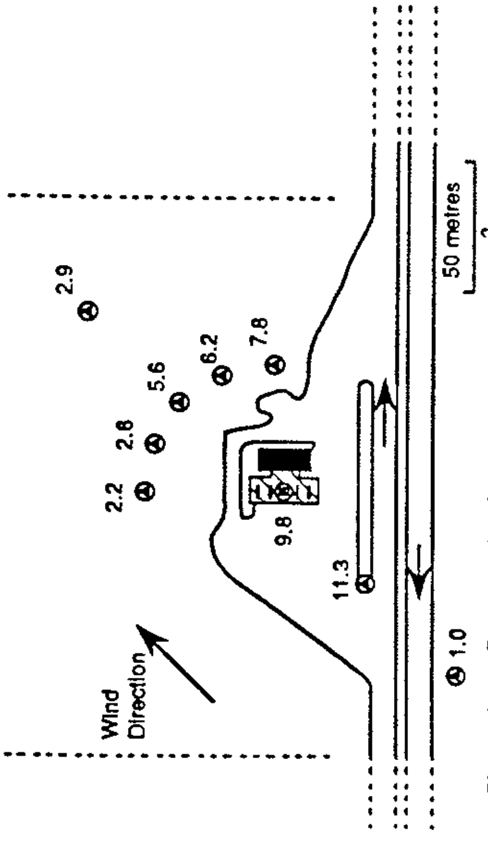


Figure B-5 : Benzene-in-air concentrations (µg/m³) for sampling period 1200-1500

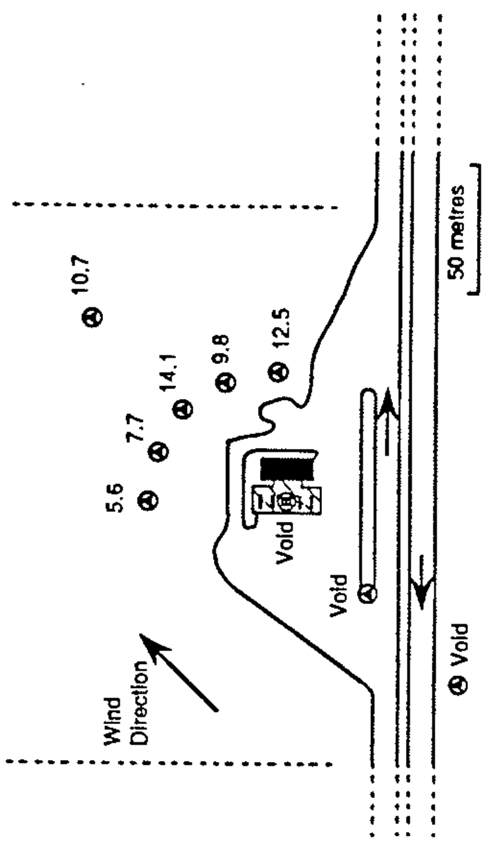


Figure B-6 : Benzene-in-air concentrations (µg/m³) for sampling period 1500-1800

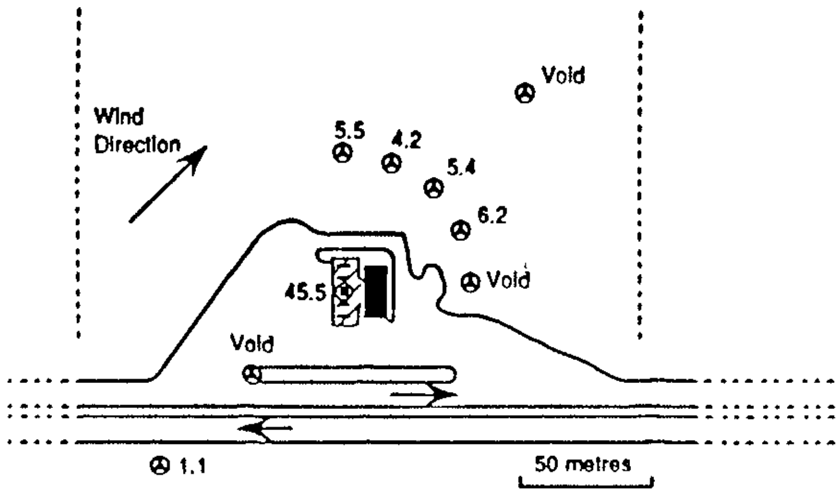


Figure B-7 : Benzene-in-air concentrations (µg/m³) for sampling period 1800-2100

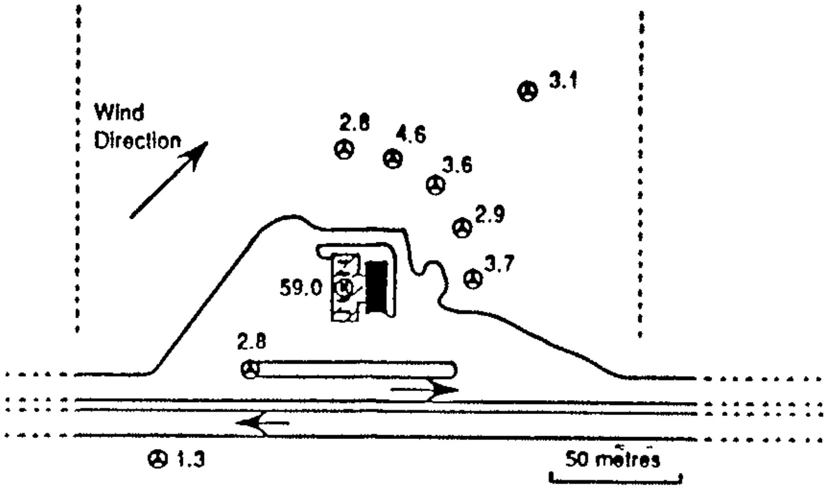


Figure B-8 : Benzene-in-air concentrations (µg/m³) for sampling period 2100-0000

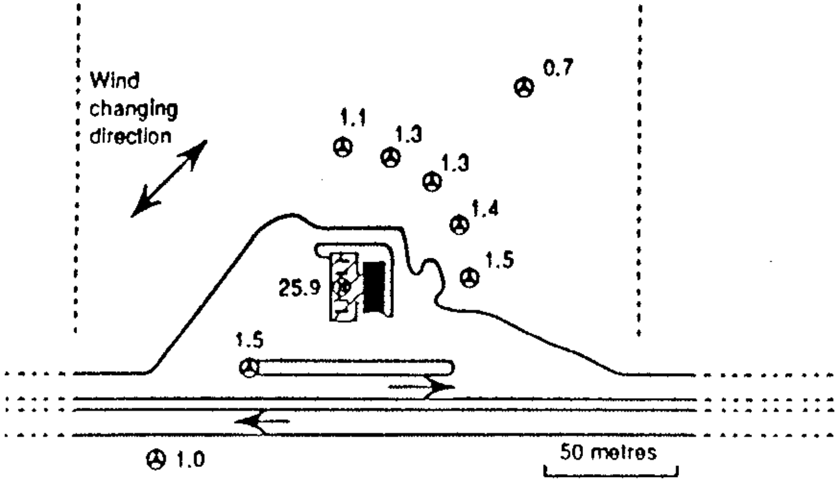


Figure B-9 : Benzene-in-air concentrations (µg/m³) for sampling period 0000-0300

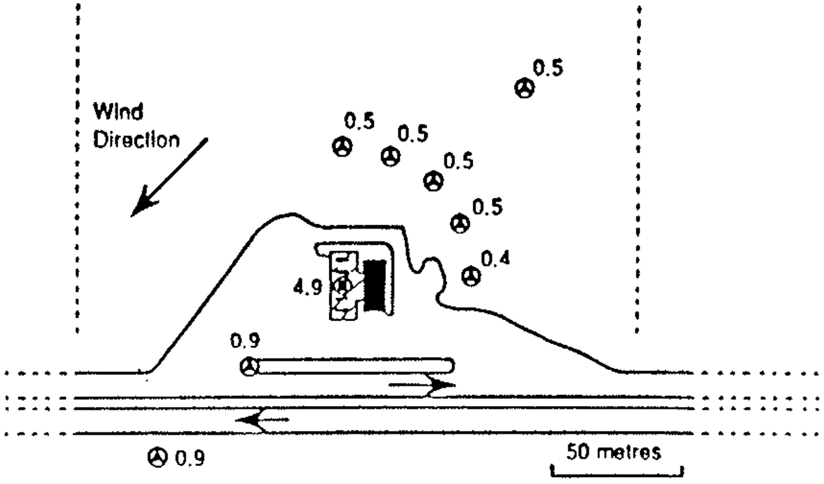


Figure B-10 : Benzene-in-air concentrations (µg/m³) for sampling period 0300-0600

6 CONCLUSIONS

The "pilot" study indicated that wind speed and direction had a major impact on ambient air levels of benzene at the service station perimeters. Other factors which influenced the benzene concentration included:

- the layout of the pumps on the site and their proximity to each other;
- buildings on site and off site:
- distance of the sampling points from the road:
- delivery of fuels by roadcar:
- emissions from the forecourt such as from vehicle exhausts, tanks, carburettors and spillages at the pumps

The main source of benzene on the forecourt was considered to be from dispensing gasoline.

No spillages of fuel were noted during the survey and hence the effects of spillage were not recorded.

The main source of benzene around the forecourt was considered to be from the vehicles using the adjacent road. This can be seen from the general reduction in levels along the 50 metre downwind arc from location H to location D. Superimposed on this is the main contribution from the forecourt represented by location F.

The emission from the vent pipes during roadcar off-loading had an impact on the levels downwind but the influence would have been for a short duration only.

The benzene level immediately upwind of the forecourt is expected to be variable and dependent on the sampling position with respect to roads and any industrial sources of benzene in the area.

The results of the 24 hour study showed that, in general, ambient air benzene levels around the perimeter of the service station forecourt were less than 10 $\mu g/m^3$. However, levels around the gasoline dispensing pumps averaged 5 times this value.

The roadside benzene levels (upwind of the service station) averaged 9.2 $\mu g/m^3$. This value indicates that the benzene arising from exhaust emissions may have a significant impact on the service station itself.

The ambient air benzene content of samples collected away from the influence of the service station and exhaust emissions was approximately 1.0 $\mu g/m^3$.

It was not possible in this short study to investigate the dispersion profile of the benzene release from this forecourt.

The information gained from this study indicated that the adsorption capacity of the sampling tube would be adequate to allow for 12-hour sampling periods. This would represent a significant reduction in costs for sample tube preparation and subsequent analysis.

The survey required one person to be on site at all times for security of the samples, to ensure the validity of the samples collected and to collect relevant data in accordance with the protocol. Changing of samples, including flow rate checks after each sampling period and flow checks on new tube/pump combinations at ten sampling points took up to one hour.

Continuous relocation of all the samplers in varying wind conditions would not have been viable.

The results of the samples oriented around the service station forecourt indicated that it would be sufficient to place samplers at the four compass points on the service station perimeter in order to estimate the average emission from the service station. The pilot study also noted the influence of refilling of underground storage tanks.

To recognise significant changes in wind direction duplicate samplers were proposed for the "background" sample position. In the event of a wind change greater than 90°, one sampler would be moved to the new upwind background position.