environmental levels of benzene at the boundaries of three european refineries

Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Benzene Monitoring at Refinery Fenceline (AQ/STF-45)

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ABSTRACT

A year-long study of benzene-in-air concentrations at the boundaries of three refineries has been carried out.

The sampling technique employed was passive diffusion tubes. Sampling locations were fixed at 12 or 16 points around the refineries.

Continuous samples were collected for 26 two-week periods to provide the annual averages for each sampling location. Two-weekly wind direction data were also gathered at each refinery.

The results reflect the relative sizes and complexities of the three refineries. Variations between the two-weekly samples reflect changes in wind direction and occasional operational events and incidents.

KEYWORDS

Air quality, refinery, monitoring, benzene, survey, passive diffusion tubes.

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SUMMARY

CONCAWE has conducted two previous studies to determine benzene levels in air at locations adjacent to service stations and distribution terminals[1,2]. The present report extends these studies to the boundaries of three refineries covering a period of one year from September 1994 to September 1995.

The principal objective was to determine annual levels of benzene in air at refinery boundaries, since actual and proposed air quality standards consider annual average concentrations. A secondary objective was to assess possible sources of emissions and their dispersion.

In view of the large sizes of refineries compared to facilities studied previously, and of the logistics of supplying and analysing many hundreds of sample tubes over the course of a year, the planning phase was important to the overall success of the project.

Three refineries were selected ranging from small, compact and relatively simple to a large, dispersed and complex refinery, with an intermediate refinery in terms of size, throughput and complexity.

The technique employed was passive diffusion tubes. Sampling locations were fixed at a height of 1.5 m at 12 or 16 points around the refineries. A number of sampling locations were arranged across the refineries, external sampling locations were arranged at one refinery. Continuous samples were collected for 26 two-week periods to provide the annual averages for each sampling location. Two-weekly wind direction data were also measured at each refinery.

Quality control samples included field blanks, duplicate tubes and ‘spiked’ samples, i.e. with known additions of benzene. In total, 2325 samples were submitted to the laboratory for analysis; 99.2% were successfully analysed.

Sampling locations are identified as land boundary, marine boundary, marine operational boundary (i.e. adjacent to the loading of volatile organic compounds (VOCs)), and internal and external gradients.

The data reflect the relative sizes and complexities of the three refineries. Variations between the two-weekly samples reflect changes in wind direction, the influence of marine loading, and occasional operational events and incidents.

Although the 14-day data provide a useful insight into the variations in benzene levels, particularly where these can be explained, the key data are the annual averages since these are the basis for proposed air quality standards.

Most of the refinery boundary annual averages are within the typical levels for urban background sites (at or below 5 µg/Nm^3); the remainder are at levels currently experienced at street sites (10-20 µg/Nm^3). With the exception of marine operational boundaries, these higher levels were only found at the larger, complex refinery (Refinery A).

1. INTRODUCTION

A number of countries have issued regulations or proposals for air quality standards for benzene expressed as an annual average limit[3]. Within the EU, the Framework Directive on Ambient Air Quality Assessment and Management[4] is the enabling directive for a series of daughter directives which will set air quality standards for a range of pollutants including benzene. A proposal for a Council Directive relating to limit values for benzene (and carbon monoxide) in ambient air (1999/C53/07) has been submitted by the European Commission on 20 January 1999.

CONCAWE has conducted two previous studies to determine benzene levels in air at locations adjacent to service stations and distribution terminals[1,2]. The present report extends these studies to the boundaries of three refineries covering a period of one year from September 1994 to September 1995.

2. OBJECTIVES

The principal objective was to determine annual levels of benzene in air at refinery boundaries since actual and proposed air quality standards consider annual average concentrations.

A secondary objective was to assess possible sources of emissions and their dispersion.

3. PLANNING

In view of the large sizes of refineries compared to facilities studied previously, and of the logistics of supplying and analysing many hundreds of sample tubes over the course of a year, the planning phase was important to the overall success of the project.

3.1. REFINERIES

There is no such thing as a typical refinery and hence those chosen cover a range of installations with respect to complexity, size, age, location and climate so that the results obtained could allow some general inferences to be drawn from the refinery-specific data. Depending on the scope of refinery activities and site geography, parts of the refinery boundaries can be differentiated as land boundary, marine boundary (adjacent to waterways), and marine operational boundary (normally adjacent to the loading of products into ships and/or barges at quays or jetties during which emissions can occur).

CONCAWE approached a number of refineries and three were selected to participate in the study. The types of the three refineries were as follows:

Refinery A: A large complex refinery with some associated petrochemical processes; its crude oil throughput is above 10 Mt/y.

Refinery B: A small, modern and very compact site occupying about a tenth of the area of Refinery A; its crude oil throughput is about 5 Mt/y.

Refinery C: Intermediate between Refineries A and B in terms of both throughput and plot size.

3.2. METEOROLOGICAL DATA

It was agreed that hourly wind direction, wind speed, and air temperature data should be collected locally throughout the study period at the three refineries. Wind distribution plots for 12 x 30^0 or 16 x 22.5^0 sectors were to be supplied or compiled from diskette for each of the 14-day sampling periods.

3.3. MONITORING STRATEGY

Diffusive sampling tubes were used in the study. To provide a logical and representative distribution of boundary samples, tubes were to be deployed in fixed positions on the boundaries in each wind sector and across the sites to give representative 14-day average levels. All samples collected for each 14-day period comprised a set. For the year-long study, 26 sets were used at each site. A sampling protocol was prepared (see **Section 4.1**). The role of each refinery in providing the resources necessary for the study was discussed in a briefing session (see **Section 3.7**).

3.4. ANALYSIS OF TUBES

Invitations to tender for the specialist analytical services required for the study were prepared. It was agreed at the outset that the analytical facility to be engaged should not only have an immediate capability to perform the analysis but also a strong reserve capability to handle any unforeseen problems which could lead to delays or the loss of data.

3.5. LOGISTICS

Although not immediately apparent, a proposal to appoint a CONCAWE Special Task Force (STF) member as “logistics” manager to handle the many tubes passing to and from the three refineries and the analytical centre proved to be very important. At this planning stage, attention was paid to packaging and shipment of the tubes.

3.6. QUALITY ASSURANCE

The analytical laboratory was to meet appropriate national accreditation requirements and demonstrate a satisfactory quality control performance. Attention was also paid to the quality assurance requirements which were the specific responsibilities of the site personnel and of the logistics manager. STF members would also visit each refinery during the study for quality assurance purposes following an agreed checklist.

3.7. REFINERY PLANNING VISITS

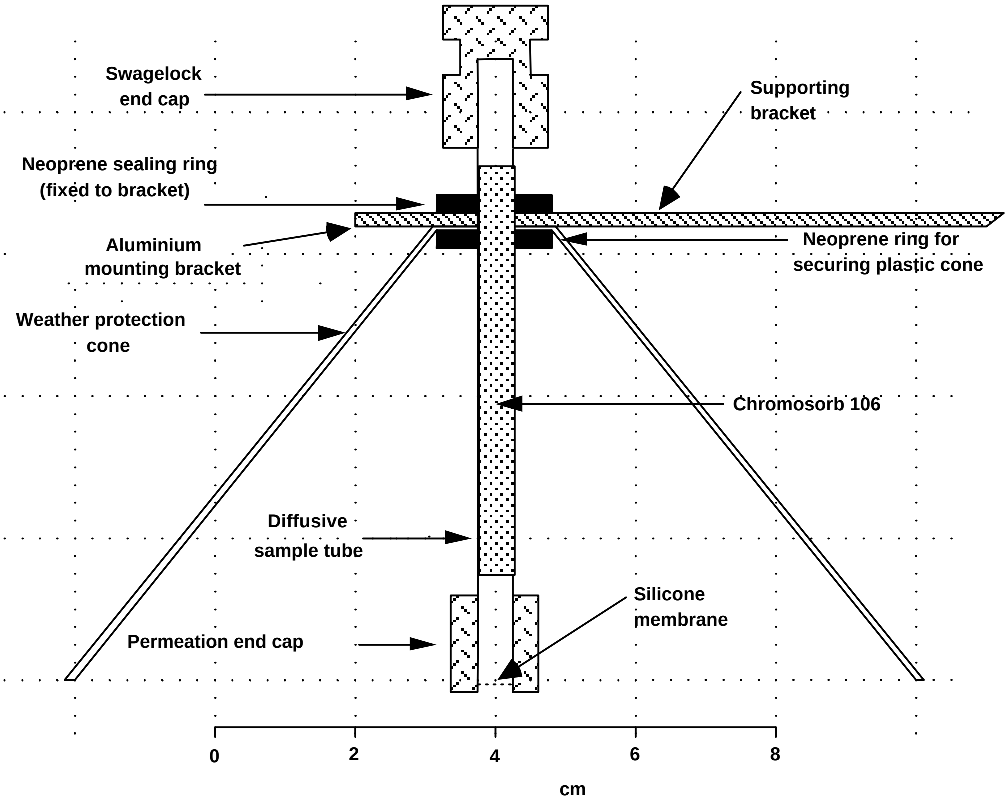
A briefing for the staff of the three participating refineries was arranged to acquaint them with their role in the study as well as the roles of the analytical centre and STF members. An important aspect of this was their responsibility to set up the monitoring sites in accordance with the project proposal and sampling protocol. The general briefing was followed by visits to each of the refineries by members of the STF at which the locations of monitoring sites were proposed. Refinery staff then provided marked-up copies of refinery plot plans showing the location and identification of each monitoring site.

4. MEASUREMENT - SAMPLING AND ANALYSIS TECHNIQUES

A sampling protocol, including sampling locations and tube mounting and dismounting was developed by the STF; the tube handling protocol was developed by the STF in conjunction with the analytical centre; the analytical protocol was developed by the analytical centre. These protocols are discussed in the following sections.

4.1. SAMPLING (see also Appendix 1)

Figure 1 Sampling assembly, including weather shield



At each refinery, the diffusive sampling tubes fitted with weather protection were mounted in each of the sampling positions at a height of 1.5 m above ground level. They were mounted by attachment to a lamp post, fence or fence post, or a dedicated post in the absence of any available support. The decision to use weather protection for the tubes was made on the basis of the certainty of frequent and, occasionally heavy, rainfall occurring at the three locations during the year-long study.

In general, the sampling end of the diffusive tube was flush with the lower edge of the weather cowl, but for one refinery it was necessary to withdraw the tube one third of its length into the cowl to ensure that water droplets were not deposited on the end of the tubes.

Continuous 24 hours per day ambient air samples were taken for 26 consecutive two-week periods over one year.

Sampling began on 29 September 1994 and was completed on 29 September 1995.

4.2. TUBE PREPARATION AND CERTIFICATION (see also **Appendix 2**)

The sampling tubes were each prepared, cleaned and certified using the full analytical procedure. The chromatograms associated with each certified tube were retained **(Table 1).**

Each set of tubes was sent by the analytical centre to the co-ordination centre.

A full set of samples for each 2-week sampling period comprised:

Table 1 Number of sampling tubes in the different locations at each refinery

TYPE OF TUBE	REFINERY		
	A	B	C
Boundary	16	12	12
Gradient	8	8	8
Quality Control duplicate	1	1	1
Field Blank (unused tube)	2	2	2
Field Spike (unused tube with added benzene)	1	1	1
Field Spike (exposed tube with added benzene)	1	1	1
Spike (laboratory tube with benzene added by an accredited laboratory)	1	1	1
TOTALS	30	26	26

The analytical centre had additional laboratory standards and blanks as defined by its quality assurance practices which are referred to below.

The field blanks and standards sent to the refineries by the co-ordination centre remained unexposed and provided an indication of any contamination resulting from storage or transport of the samples.

The exposed and unexposed sampling tubes were returned via the co-ordination centre to the laboratory with an additional three independent quality control samples.

4.3. ANALYSIS (see also **Appendix 3**)

The analytical centre ensured that all tubes from each set were returned. The analytical system was calibrated at at least five different levels, between 10 and 1500 nanogrammes and check samples were analysed. The exposed and unexposed tubes and quality samples were analysed with a check standard inserted every tenth sample. If the check standard was outside ± 10% of the 'true' value the analytical cycle was halted.

In total, 2325 samples were submitted to the laboratory for analysis. Of these, 99.2% were successfully analysed. 18 results were not reported, 12 being due to instrument failure, 3 due to poor packing of the Chromosorb, and 3 due to damage in the field.

4.4. CO-ORDINATION CENTRE ACTIVITIES

The co-ordination centre's role proved crucial in the management of this study. The centre ensured the smooth running of the study and removed unnecessary burdens on the participating refineries and the analytical centre. The centre’s activities included:

- receipt of unexposed tubes from the analytical centre;
- recording tube identification data for each set of samples and ensuring sufficient sampling tubes were sent to the refineries two weeks before the start of the allotted sampling period;
- cross-checking the condition of exposed sampling tubes and any supporting information from the refineries and recording any deviations from good sampling practice;
- recording sampling information for each exposed tube;
- providing exposed tubes and independent quality assurance standards to the analytical centre within two weeks of completion of the sampling;
- collating and checking the results from the analytical laboratory;
- calculating the final atmospheric concentrations and submitting them to the relevant refineries; and
- providing summaries of the final results to assist in the interpretation of the study.

4.5. CALCULATION OF RESULTS (see also **Appendix 3**)

Blank (i.e. unexposed) samples were analysed for each of the 26 sets of samples throughout the study. The benzene results were calculated by subtracting the mean blank value for the relevant set of samples from the individual results obtained for the exposed samples. The diffusive uptake rate for benzene on Chromosorb 106, using a membrane, was predicted using the method of van den Hoed and Halmas[5]. The figure used was 0.502 ml min^{-1}.

All results were quoted to two significant figures. For convenience all values below 1.0 µg m^{-3} are quoted as <1.0 µg m^{-3}. A value of 0.5 µg m^{-3} was used for calculations of annual means when the quoted values were <1.0 µg m^{-3}.

5. RESULTS

The following nomenclature and format are used for the main data:

- The types of sampling locations are identified as:

  L = land boundary
  M = marine boundary
  M* = marine operational boundary

  and

  E = external gradient

  I = internal gradient

- A plot showing:

  the arrangement of the refinery facilities;

  annual average benzene data and ranges for each boundary sample location, with the various types of sampling location as above; and

  the annual wind direction rose showing the proportion of the time the wind was blowing from each wind direction sector.

- Tables showing annual means and minimum and maximum values for all sample locations giving the full data for all 26 data sets throughout the year.
- Figures showing:

  the full data in a three-dimensional plot to give an overall picture of the complete boundary data sets; and

  wind direction data for each data set to show the seasonal variations.

In assessing the data with respect to wind direction, it is important to recognise that any refinery has a number of potential emission sources dispersed throughout its area. Hence, consideration of the effect of any particular wind direction indicated by the wind rose for any of the three refineries must consider all of the possible downwind sampling locations relative to the potential upwind sources. In some instances, a particular source may effect a number of downwind sampling locations.

5.1. REFINERY A

Refinery A is typical of large complex refineries as it has been developed in more than a single phase of construction. Crude oil and volatile products are stored in external floating roof tanks. Product distribution is both inland and via ship’s cargo.

The annual averages for each boundary sample location are shown in **Figure 2** and the benzene data tabulated in **Table 2**. All benzene data are shown in **Appendix 4.1** and plotted for the boundary locations in three-dimensional form in **Figure 3**. The wind direction data for each data set are shown graphically in **Figure 4**.

Figure 5 shows the variation throughout the year at various sampling locations.

Table 2 and **Figure 2** show that the higher annual average benzene levels occur here. Excluding marine operational locations, 60% of sampling locations had annual averages of less than 10 µm/Nm^3 with all falling below 20 µm/Nm^3.

Reference to the wind rose in **Figure 2** shows winds primarily from directions 11 to 14.

The annual wind direction pattern, **Figure 4**, shows the variations between each of 14-day periods throughout the study.

Figure 3 shows that sample points M2 and L3 were generally higher during the first half of the study period. Significantly increased levels occurred in Set 3 when a spill affected sample points M2, L3 and L4.

Figure 3 also shows that land boundary sample points L7, L8 and L9 were generally higher during the second half of the study period. Rather than a general increase, there appear to have been discrete periods of elevated levels. This can be seen in **Figure 5** which, although the wind directions were very similar, indicated possible different sources. An examination of the compositional data supported this view.

The impact of an operational incident for sample point M1*, a marine operational boundary site, in Sets 9 and 23 is evident; no explanations were available for the two other excursions at this point in sets 20 and 25 during the second half of the study period (**Appendix 4.1**).

A number of internal sample points dispersed throughout the refinery show an occasional increase in ground level concentrations but since adjacent locations do not reflect similar rises, the sources appear to be discrete and small (**Appendix 4.1**).

Table 2 Refinery A: Benzene in air concentration (µg/Nm^3)

Sampling Position	Annual Mean	Minimum 14 day Average	Maximum 14 day Average
M1*	31	3.7	190
M2	15	6.4	40
L3	13	3.6	73
L4	11	3.5	58
L5	6.7	3.1	14
L6	5.5	<1.0	12
L7	12	2.1	68
L8	18	2.5	57
L9	12	1.4	65
L10	3.5	1.2	7.8
L11	2.4	<1.0	5.0
L12	2.4	<1.0	4.1
L13	2.1	<1.0	4.8
L14	3.5	<1.0	6.6
L15	3.0	<1.0	8.8
M16*	7.2	<1.0	21
I 1	12	2.7	25
I 2	19	4.6	81
I 3	87	7.6	180
I 4	15	1.4	45
I 5	19	6.2	55
I 6	28	9.9	66
I 7	7.2	1.6	58
I 8	15	<1.0	34

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
I	Internal gradient

Figure 2 Refinery A: Plot Plans Showing Boundary Benzene Levels, Annual Averages

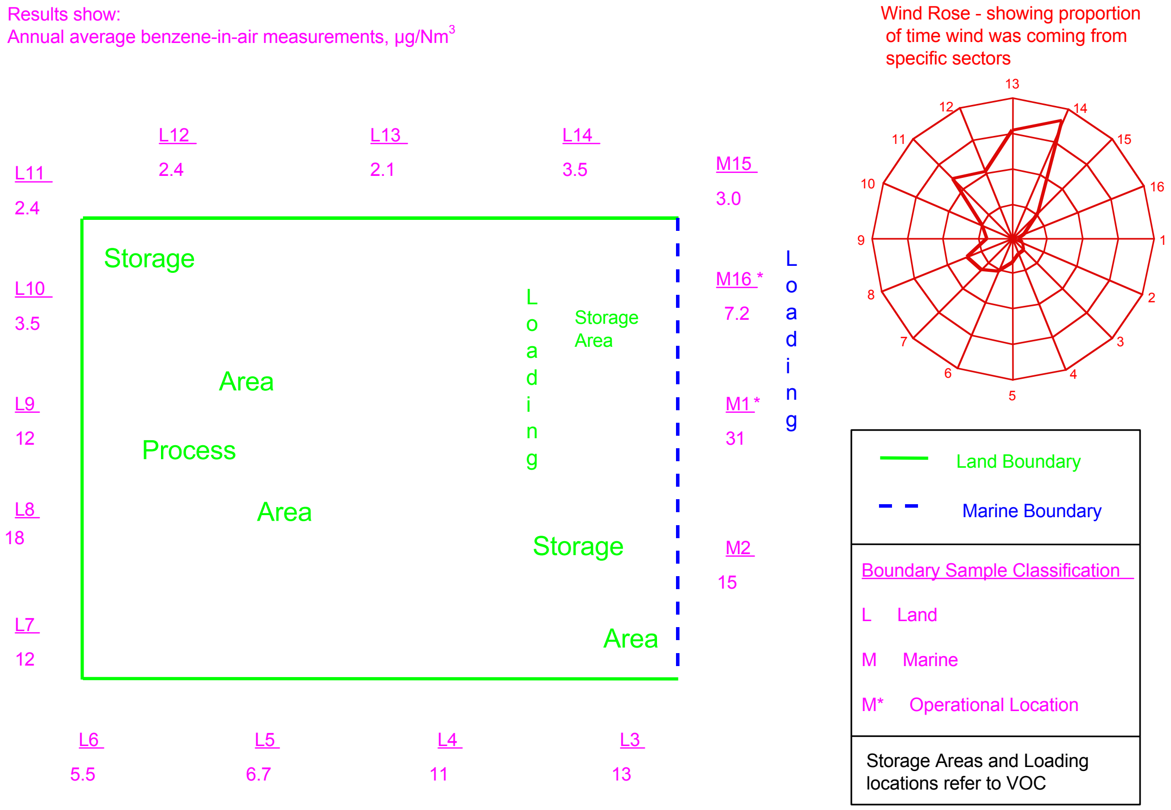


Figure 3 Refinery A: Boundary Benzene Levels, 14-Day Averages and Annual Means

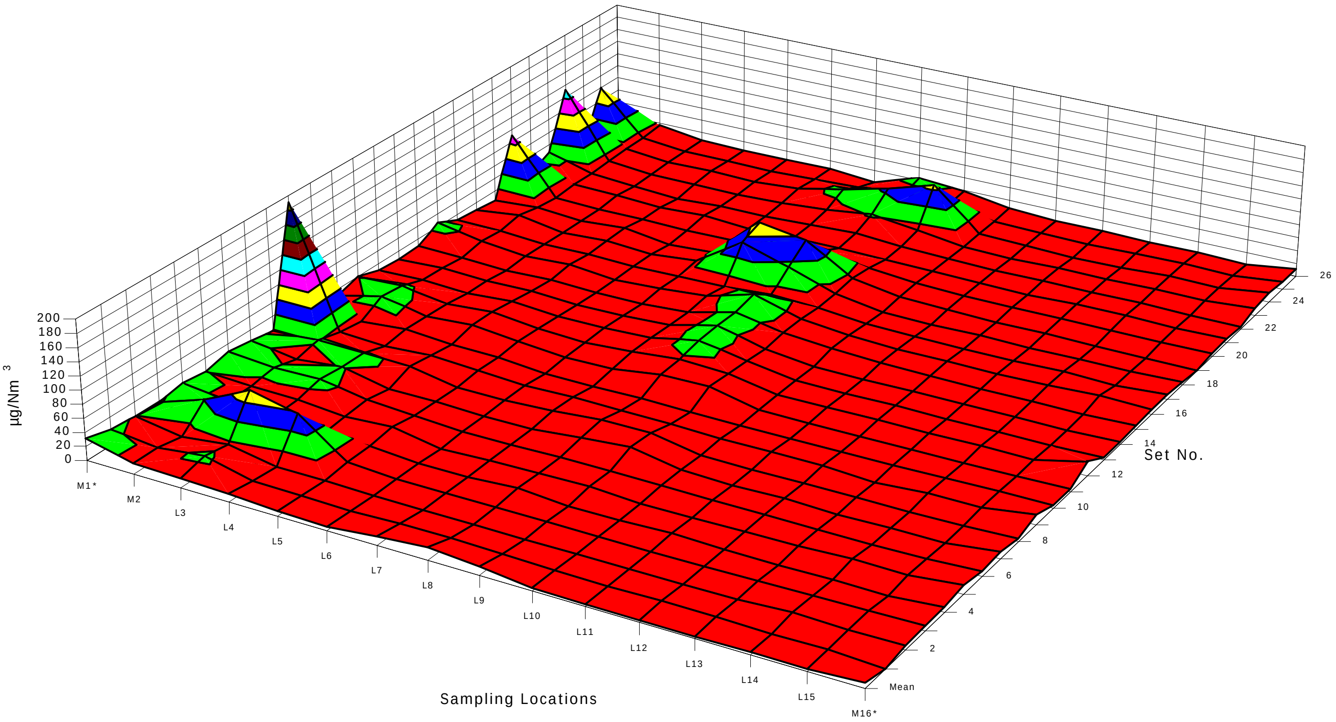


Figure 4 Refinery A: Wind Direction, 14-Day Averages

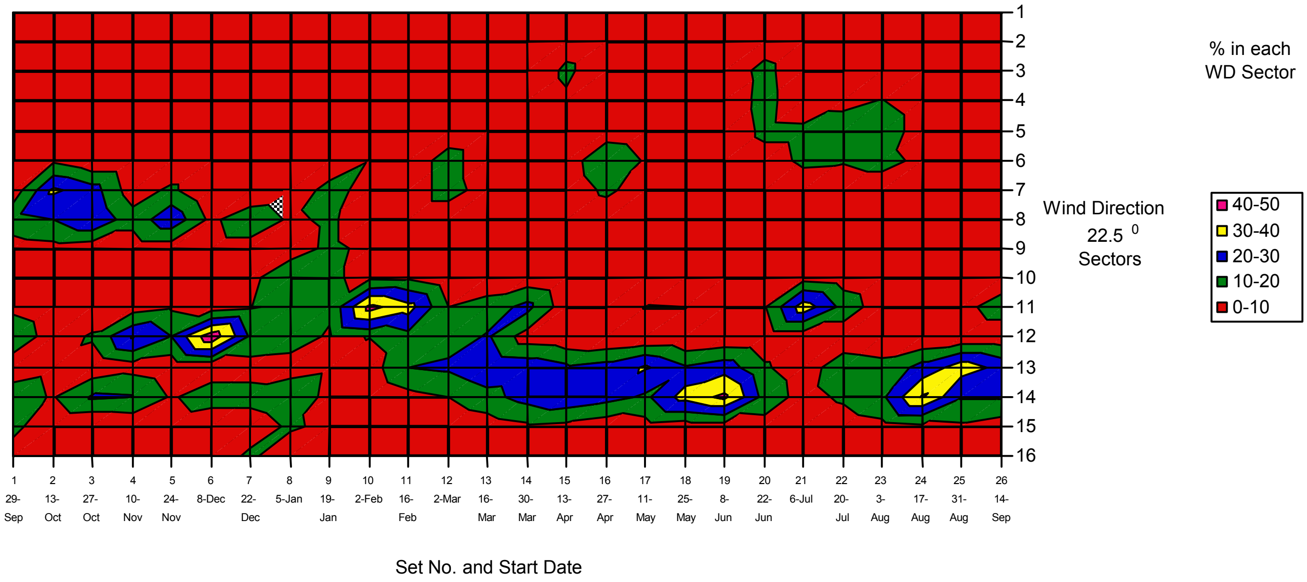
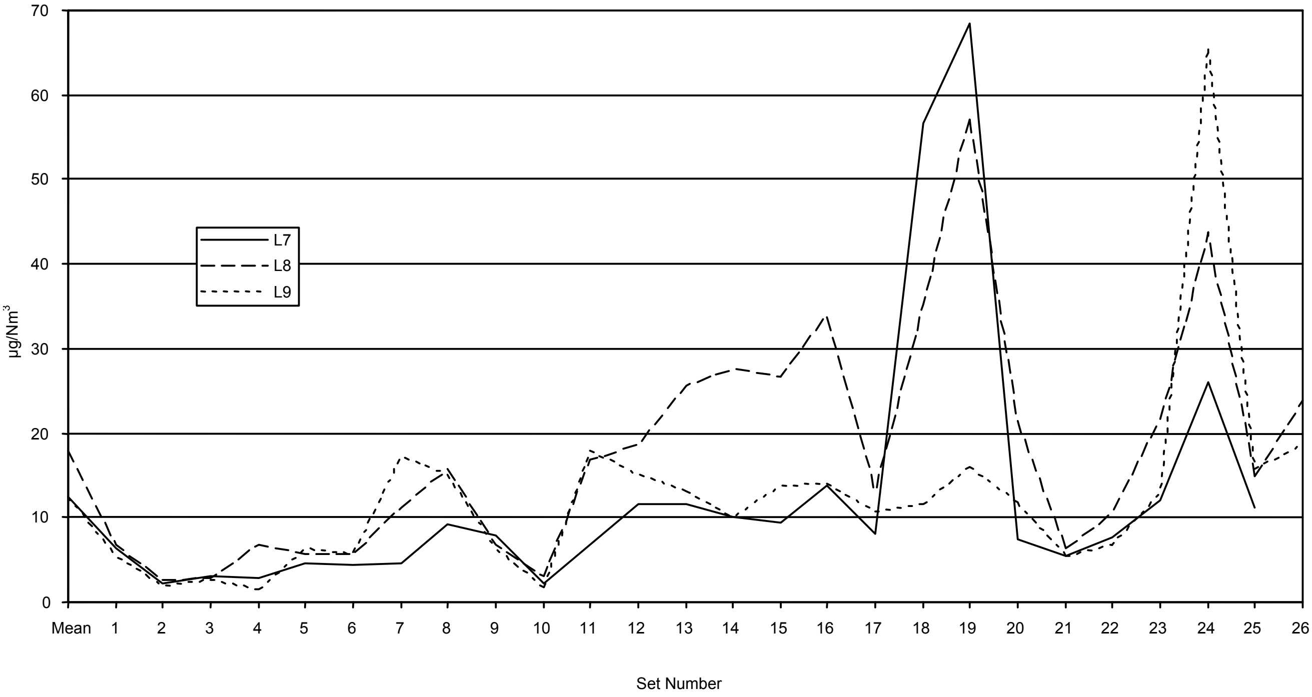


Figure 5 Refinery A: Benzene Levels for Sampling Locations L7, L8 and L9, 14-Day Averages



5.2. REFINERY B

The very compact nature of Refinery B, occupying about a tenth of the area of A, is typical of a generation of small modern and fully integrated refineries which have been built in Europe. Here, the relatively small tank farm contains few external floating roof tanks; vapour recovery is fitted to road and barge loading facilities.

The annual averages for each boundary sample location are shown in **Figure 6** and the benzene data tabulated in **Table 3**. All benzene data are shown in **Appendix 4.2** and plotted for the boundary locations in three-dimensional form in **Figure 7**. The wind direction data for each data set are shown graphically in **Figure 8**.

Annual average benzene levels were lowest at this refinery; all annual boundary values were below 10 μm/Nm^3.

Many individual 14-day boundary values were <1 μm/Nm^3; annual averages were 2-3 μm/Nm^3 (**Appendix 4.2**).

Reference to the wind rose in **Figure 6** shows winds primarily from directions 8/9 and, to a lesser extent, 2/3.

The annual wind direction pattern, **Figure 8**, clearly shows the variations in the 14-day periods between these sectors.

The marine operational boundary sample point, M5*, in the vicinity of a gasoline loading jetty, see **Figures 6 and 7**, shows some slightly elevated levels but the annual average lies below 10 μm/Nm^3. It was suggested that the higher levels might be attributed to the vapour recovery unit not being in commission. Sampling location M6* was adjacent to non-volatile loading operations and was affected to a lesser extent by gasoline loading (**Appendix 4.2**).

A number of internal sample points dispersed throughout the refinery show generally low levels with only the process area sampling location **I** 14 exceeding 20 μm/Nm^3 (**Appendix 4.2**).

The increased levels at internal sample point **I** 16 may have been attributable to operations in the fire training area or to emissions from the adjacent tankage (**Appendix 4.2**).

Sample points M5* and M6* were alternately affected as the wind direction changed through 180^0; in general, 14 day average levels at sample point M6* were less than at M5* since it is more distant from the gasoline loading jetty (**Figure 7**, **Appendix 4.2**).

Table 3 Refinery B : Benzene in air concentration (μm/Nm^3)

Sampling Position	Annual Mean	Minimum 14 day Average	Maximum 14 day Average
L1	2.3	<1.0	5.2
L2	2.9	<1.0	5.7
L3	3.3	<1.0	5.8
L4	2.7	<1.0	5.6
M5*	8.0	<1.0	22
M6*	3.4	1.0	7.5
L7	3.0	1.0	5.8
L8	2.6	<1.0	5.3
L9	2.3	<1.0	8.7
L10	2.6	<1.0	22
L11	1.9	<1.0	4.5
L12	2.1	<1.0	5.8
I 13	3.7	<1.0	8.6
I 14	14	4.9	27
I 15	4.0	<1.0	6.5
I 16	10	1.0	18
I 17	4.4	1.7	6.9
I 18	4.9	<1.0	10
I 19	4.1	<1.0	7.8
I 20	3.8	<1.0	9.7

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
I	Internal Gradient

Figure 6 Refinery B: Plot Plans Showing Boundary Benzene Levels, Annual Averages

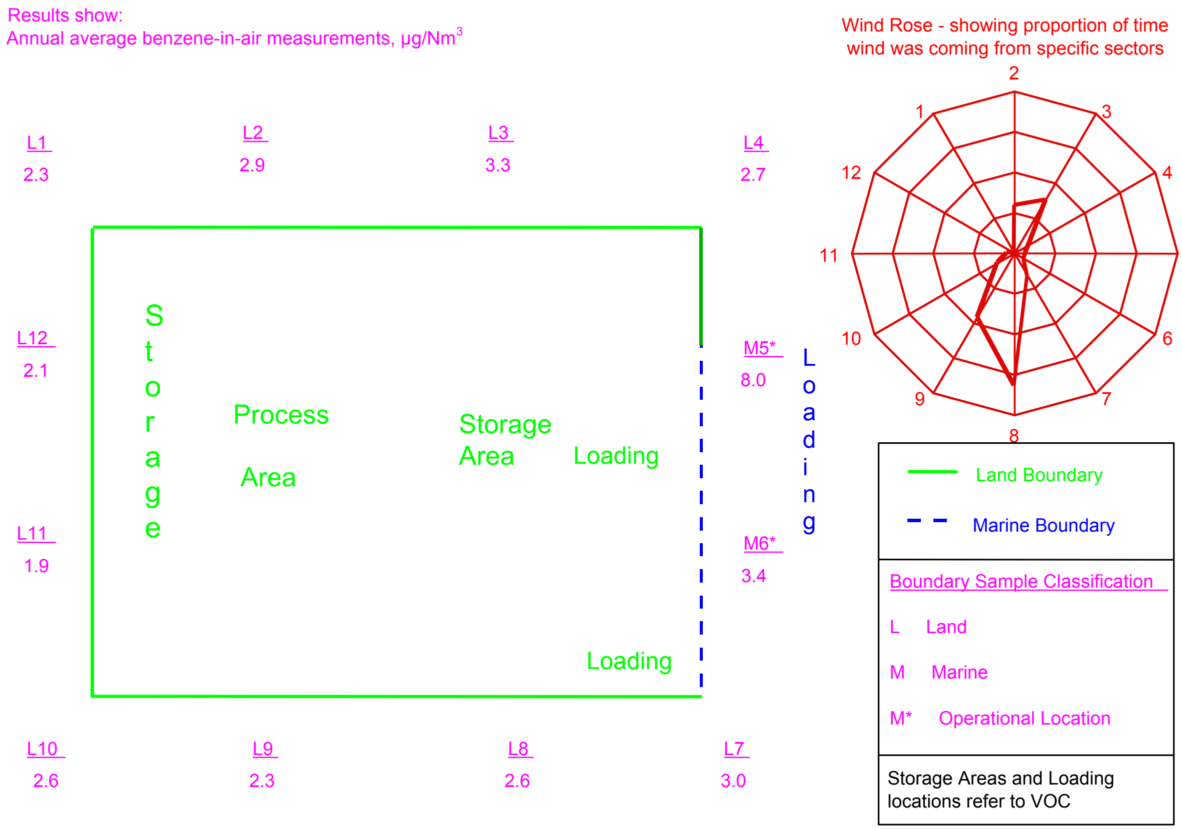


Figure 7 Refinery B: Boundary Benzene Levels, 14-Day Averages and Annual Means

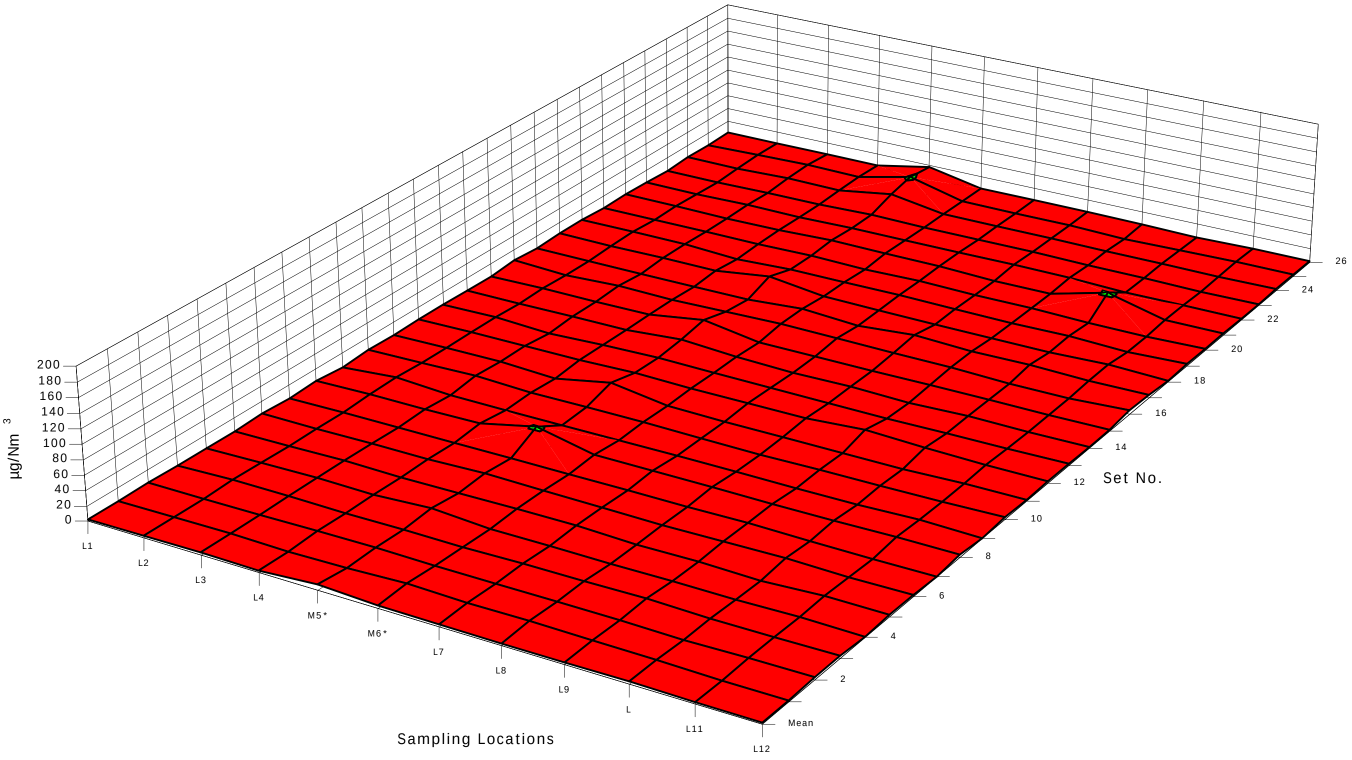
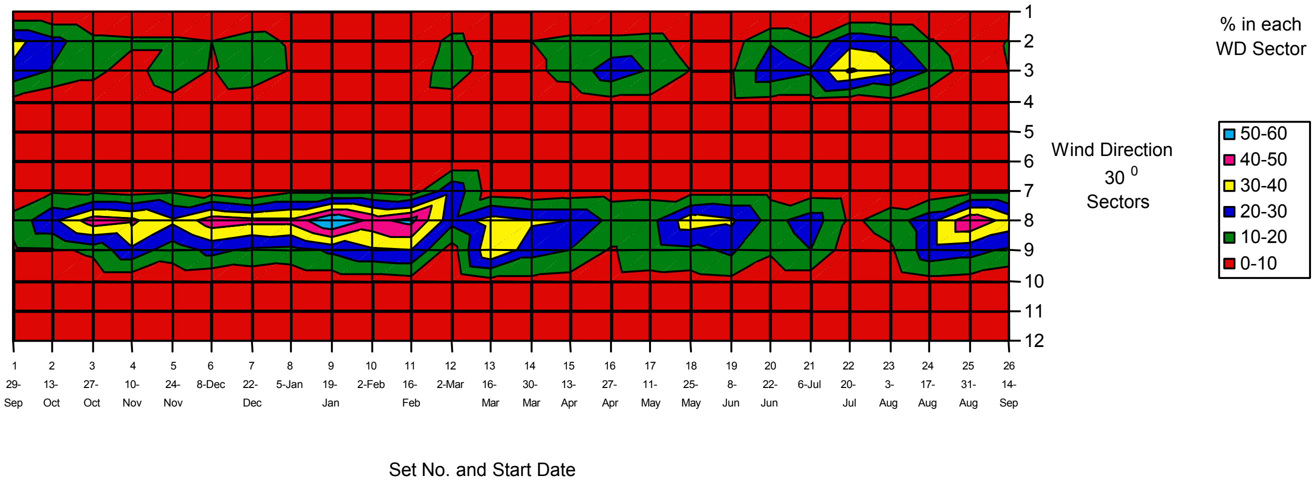


Figure 8 Refinery B: Wind Direction, 14-Day Averages



5.3. REFINERY C

Refinery C is intermediate between A and B in terms of both throughput and plot size. As for B, it is a modern integrated refinery. Crude oil storage has vapour balancing to minimise emissions; gasoline is stored in internal floating roof tanks. It has road and marine loading facilities.

The annual averages for each boundary sample location are shown in **Figure 9** and the benzene data tabulated in **Table 4**. All benzene data are shown in **Appendix 4.3** and plotted for the boundary locations in three-dimensional form in **Figure 10**. The wind direction data for each data set are shown graphically in **Figure 11**.

Excluding marine operational locations, all annual average boundary values were below 10 μg/Nm^3.

Some annual averages are <1 μg/Nm^3 which is taken to be the absolute background value for this site.

Reference to the wind rose in **Figure 9** shows prevailing winds from directions 2, 3 and 4 and to a lesser extent from directions 8 and 9.

The annual wind direction pattern, **Figure 11**, also shows that for much of the year, the prevailing wind direction is from direction 3 with components from 2 and 4 and, in the early summer, direction 9 with a component from 8.

The two marine operational sample points, M6* and M7*, show elevated average 14-day levels and annual means which are associated with the gasoline loading into sea-going vessels, **Figures 9 and 10**.

A number of internal sample points were dispersed throughout the refinery with three external sampling locations, E2, E3, E4, beyond L2, L3 and L4. The external sample concentrations show the effect of the sampling locations relative to the various emitting sources. For example, for Set 20 with the three sample points downwind of the refinery, E4 was influenced by the jetties, E3 by the process area, and E2 not influenced at all.

Table 4 Refinery C: Benzene-in-air concentration (µg/Nm^3)

Sampling Position	Annual Mean	Minimum 14 day Average	Maximum 14 day Average
L1	<1.0	<1.0	1.8
L2	1.1	<1.0	4.5
L3	3.6	1.0	6.9
L4	3.6	<1.0	7.8
M5*	4.8	<1.0	8.7
M6*	16	5.5	35
M7*	17	6.4	34
M8*	6.1	<1.0	20
M9	4.0	<1.0	13
M10	3.1	<1.0	24
L11	<1.0	<1.0	4.7
L12	<1.0	<1.0	3.7

E2	<1.0	<1.0	2.1
E3	1.0	<1.0	2.3
E4	2.2	<1.0	4.5
I 7	6.1	2.2	14
I 8	7.1	1.5	17
I 9	3.8	<1.0	13

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
E	External gradient
I	Internal gradient

Figure 9 Refinery C: Plot Plans Showing Boundary Benzene Levels, Annual Averages

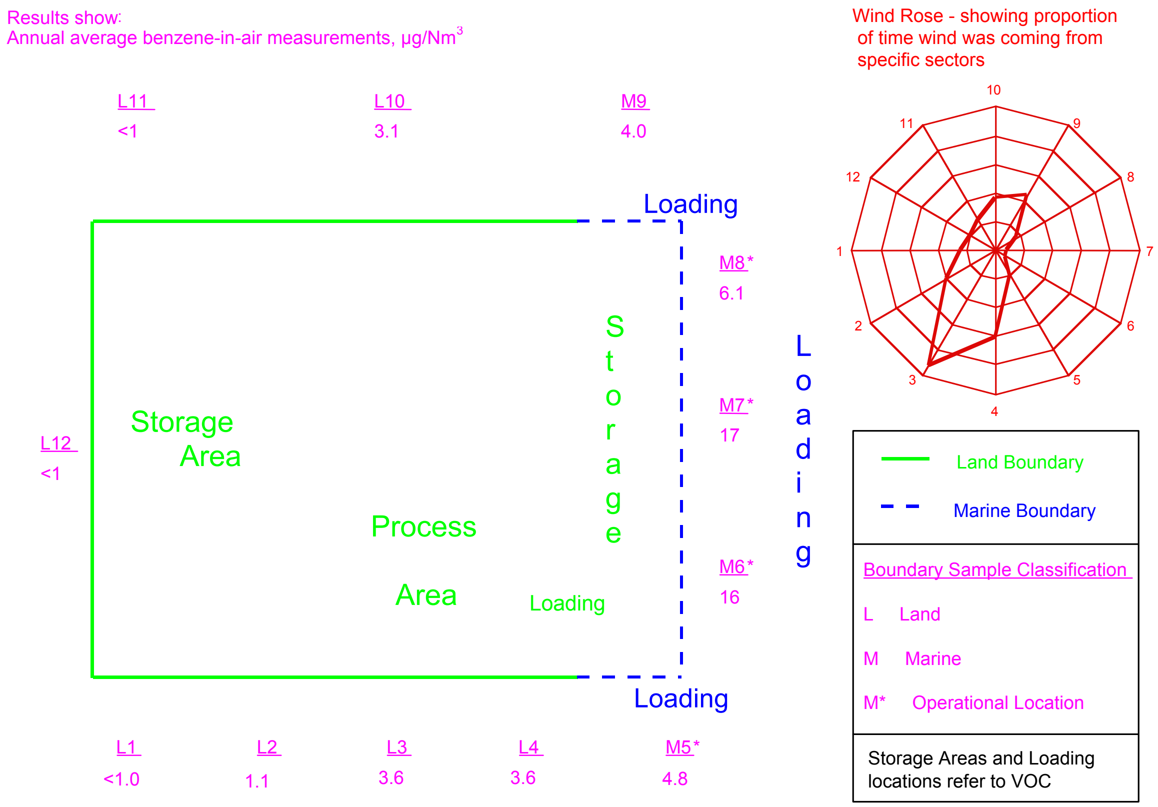


Figure 10 Refinery C: Boundary Benzene Levels, 14-Day Averages and Annual Means

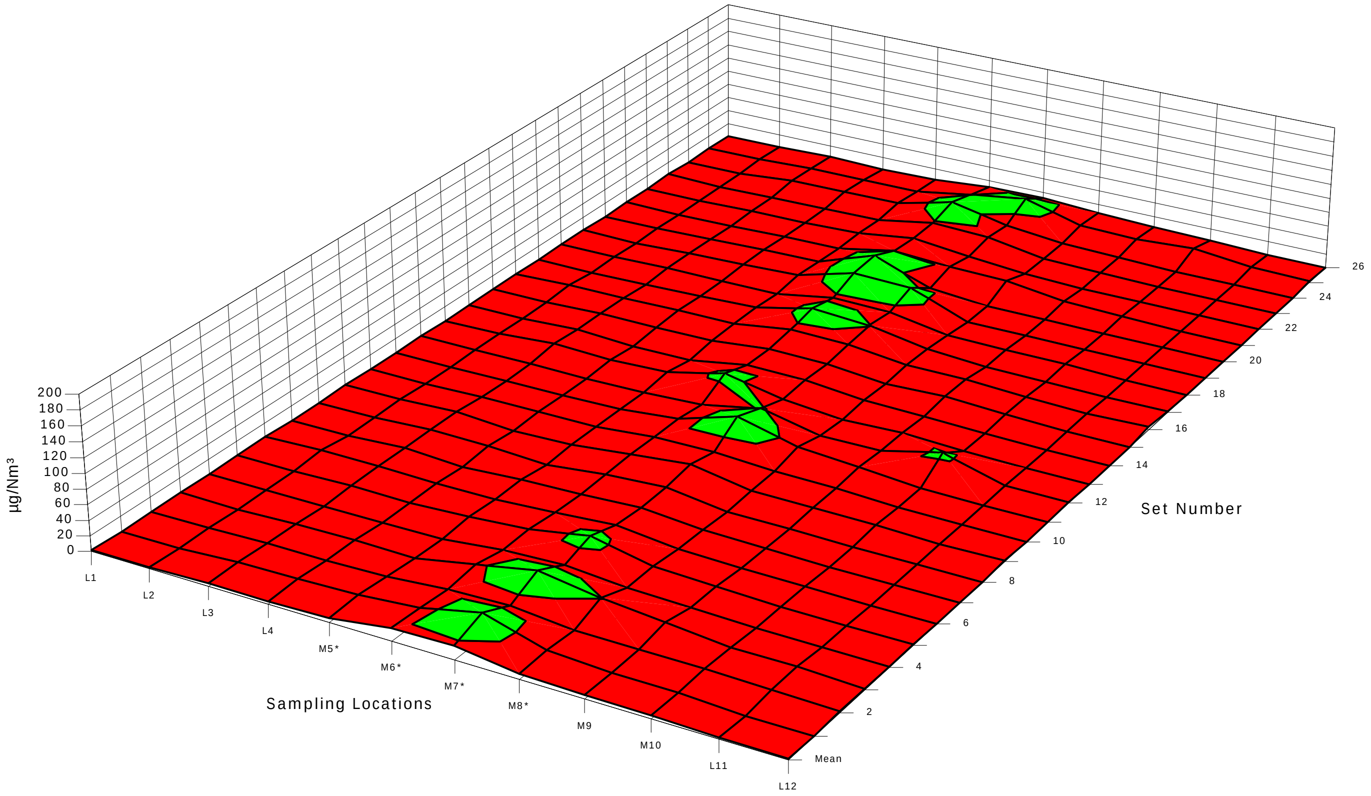
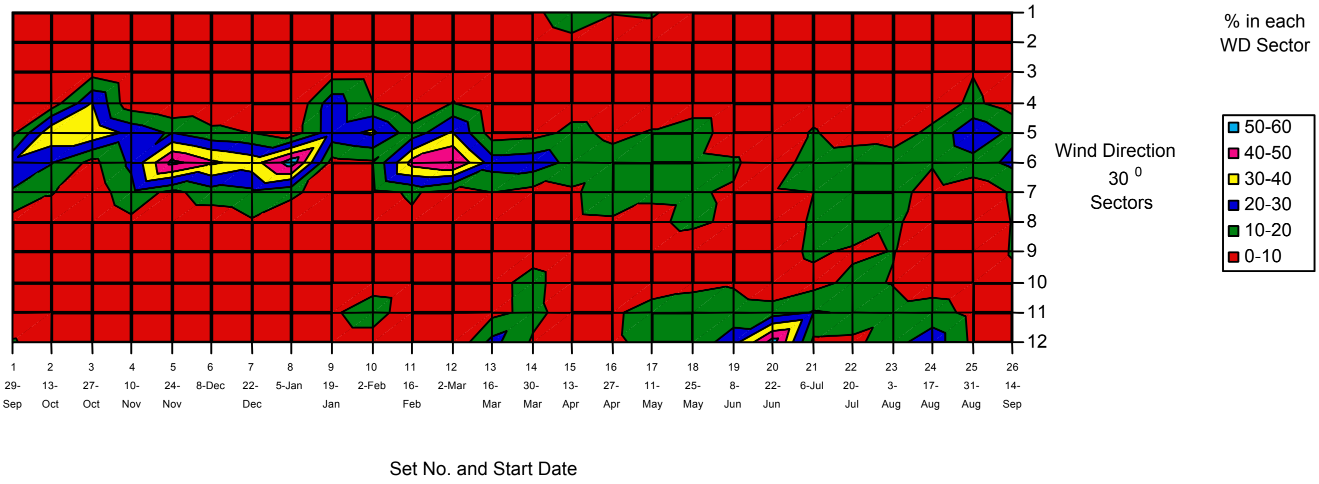


Figure 11 Refinery C: Wind Direction, 14-Day Averages



5.4. GENERAL OVERVIEW

Annual mean data for the boundary sampling locations, excluding marine operational locations, at the three refineries are shown as frequency distributions in **Figure 12**.

All of the values for the boundary sampling location (non-operational) at refineries B and C and 60% at refinery A were less than 10 μm/Nm^3. For refinery A of the six points between10-20 μm/Nm^3, three are downwind of marine operations and/or crude oil storage and three adjacent to gasoline tankage and process plant.

The impacts of known events are clear in the data. Although some high data has no explanation, combined with the wind data it has allowed prioritisation of future investigative effort.

Events which could have led to excursions in 14-day non-operational boundary levels, but in fact did not, were:

> At Refinery A, during the prolonged use of a mobile diesel generator adjacent to a sampling point;
>
> At Refinery B, during the cleaning of a crude oil tank; and
>
> At Refinery C, during a major shutdown and start-up of the refinery, although levels at two internal sampling points were slightly elevated during one sampling period. (This information was available due to the extension of the year-long study to cover the event.)

No remote background levels were measured in this study. However, upwind boundary levels suggest that background levels for these sites fall within the range of <1 to 3μm/Nm^3 depending on upwind sources.

A recent report of the European Environmental Agency[6] contained a tabulated summary of urban benzene measurements in Europe in recent years. The table is reproduced overleaf (**Table 5**).

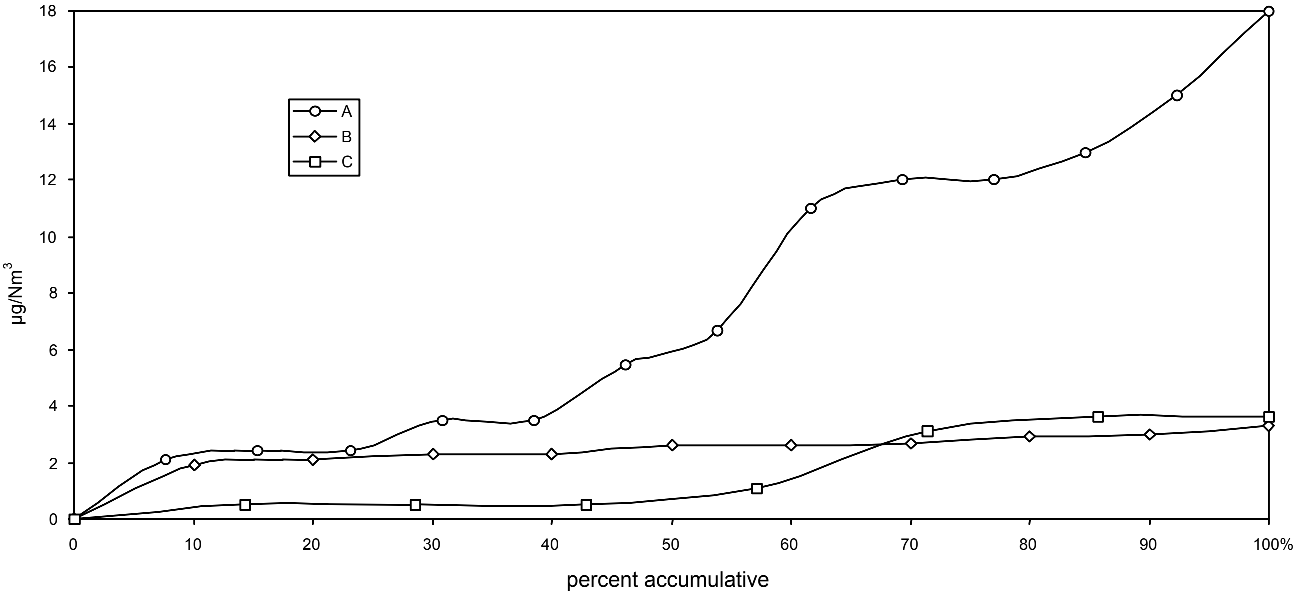
Table 5 Recent European Urban Benzene Measurement

	Urban Background Sites		Street Sites	
Belgium (De Saeger et al., 1995)	Brussels, 68 sites 1994	1.6-11.3	street	15
Denmark (IVL, 1996)	Copenhagen 1995-96		street, winter	15.8
Italy (Foa V, 1994) (Cavallero A. et al., 1995)	2 cities Bari, 8 sites, 1993 Milano, 2 sites		 street street	 18-47 22
Germany (Niedersachsen, Sachsen-Anhalt, Sachsen, 1994	13 cities 1993	2.0-4.9	Hannover, 2 streets	10-12
Sweden (IVL, 1996)	28 cities, winter 1995-96	2.1-5.0	3 streets, winter	6.7-10.3
The Netherlands (RIVM, 1995-96)	3 cities 1993, 1994	2.4-4.7	7 streets, various cities	3.5-8.7
UK (Bower et al., 1995)	6 cities 1994	2.2-4.8	London street	5.8

N.B.: Values are annual averages unless otherwise noted (µm/Nm^3)

Comparison of the data with the frequency distributions of the annual average boundary levels at the three refineries in **Figure 11** shows that most of the refinery data fall within the typical levels for urban background sites. The remainder are at the levels experienced at street sites.

Figure 12 Frequency Distribution of Annual Boundary Values (excluding Marine-Operational Locations)



6. CONCLUSIONS

Although the data are not directly transferable to other refineries of similar throughput and size, they are of value as indicators which can identify refinery operations which require attention to benzene as a specific emission.

The impacts of a number of incidents causing an increase in emissions are reflected in the data and demonstrate the value of incident reporting during such studies.

The impact of marine loading is clearly illustrated at each refinery.

The impact of emissions from tankage and/or the process area is possibly significant at Refinery A; neither is very significant at Refineries B and C.

The data indicate that the siting of the different types of facilities, i.e. process plant, tankage and loading jetties, will influence boundary results from different refineries.

Gradient measurements over 14 days were not an appropriate method for identifying sources of emissions. In general, they mainly reflected the impact of significant seasonal changes in wind direction although in one case, the rapid fall-off in concentrations at adjacent sampling points indicated a small, discrete source.

The fitting of weather protection for the tubes was considered essential to the year long study. The issue should be referred to the EC's European Diffusion Tube Sampling Initiative (EDSI) which will involve long term studies of diffusion tubes for a range of pollutants.

A number of unpublished data sets for refineries have been produced in the past but different sampling and analytical approaches mean that direct comparison may not be appropriate. This study, in defining sampling and analytical protocols and the associated quality assurance requirements, provides a sound basis for comparing data from the different sites and locations. The results are considered to reflect the adequacy of the method for measurement of long term data.

Although the 14-day data provide a useful insight into the variations in benzene levels, particularly where they can be explained, the key data are the annual averages since they are the basis for air quality standards.

Most of the refinery boundary annual averages were within the typical levels for urban background sites (at or below 5 µg/Nm^3); the remainder were at levels currently experienced at street sites (10-20 µg/Nm^3). With the exception of marine operational boundaries, these higher levels were only found at the larger, complex refinery (Refinery A).

7. ACKNOWLEDGEMENTS

The success of the project was due to the significant input and interest shown by the participating refineries, to the extensive input and professionalism of the analytical centre, and to the additional manpower provided by and to the logistics manager. Their inputs are gratefully acknowledged.

8. REFERENCES

1. CONCAWE (1994) A preliminary study of ambient air concentrations of benzene around service stations and distribution terminals in Europe. Report No. 94/53. Brussels: CONCAWE

2. CONCAWE (1995) A year long study of ambient air concentrations of benzene around a service station. Report No. 95/63. Brussels: CONCAWE

3. Department of the Environment and The Scottish Office (1997) The United Kingdom National Air Quality Strategy, March 1997

4. EU (1996) Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management. Official Journal of the European Communities No. L296, 21.11.1996

5. van den Hoed, N. and Halmas, M.T.H. (1987) Prediction of uptake rates for tube type samplers. In: Berlin, A. et al (Eds). Diffusing sampling; an alternative approach to workplace air monitoring, p. 131-142. Publ. No. 10555 EN. Brussels-Luxembourg: Co-ordinating European Council

6. EEA (1997) Air pollution in Europe 1997. EEA Environmental Monograph No. 4. Copenhagen: European Environment Agency

APPENDIX 1 BENZENE FENCELINE SAMPLING PROTOCOL

1. OBJECTIVE

The objective is to measure ambient benzene concentrations around the boundaries of three refineries from which annual average concentrations can be calculated.

2. SAMPLING

Diffusive sampling tubes will be supplied to the nominated contact at each refinery. The sample tubes are constructed of stainless steel tubing, 6 mm outside diameter, 5 mm inside diameter and 90 mm long. They are pre-packed with Chromosorb 106 by the analytical laboratory; each tube is inscribed with a discreet reference number and “a certificate of cleanliness” for each is retained by the laboratory. The tubes are sealed by fitting Swagelock end caps to finger tightness with a further quarter turn using spanners. During sampling, one of the Swagelock caps is replaced with a permeation end-cap.

3. SAMPLING LOCATIONS

To avoid bias and to provide a representative and logical distribution, boundary sampling locations will be positioned within discreet sectors of the compass. Sectors may be selected on the basis of available wind direction data, e.g. 12 sampling locations each located in a 30° sector or 16 locations in 22.5° sectors, providing all-round 360° coverage.

Some sampling locations at the nominal refinery boundary may be within, or adjacent to operational areas, e.g. marine loading of gasoline at jetties or quays, leading to higher than normal benzene levels. Such locations are to be identified.

Sample tubes are to be mounted at a height of 1.5 m above ground level by attachment to convenient lamp standards, fence posts or, if necessary, dedicated support posts. Generally in locating the sites, care is taken to avoid obstructions to free air flow.

Refinery staff and STF members are to agree sampling locations and fixing points during refinery tours for this purpose. Plot plans are to be provided which identify each sampling location and its reference number.

4. WIND DIRECTION ROSES

Hourly average wind direction data are normally available at refinery or from a nearby source, e.g. airport, from which periodic wind roses may be compiled, see attached **figure**. Since in such a study diffusion tubes are to be exposed for 14 day periods, wind roses based on hourly average wind direction data may be constructed over the same period.

Wind direction data for each 14-day sample set are to be supplied to the STF.

Reference to a wind rose when assessing analytical data from individual sites can provide useful information on possible sources of emissions.

5. SAMPLE TUBE PROTECTION

Since in Western Europe rainfall may be both frequent and heavy, rain protectors are provided for the tubes. Initial experience showed that with the permeation end-cap level with the bottom of the shroud as recommended (see paragraph), wind-driven rain could form droplets on the diffusion head. To avoid this, it was decided that, if necessary, the tube should be withdrawn one third of its length into the shroud. A simple laboratory test by an STF member indicated that this should not present a problem.

20 single (24 for Refinery A) and 3 double sample tube weather protector kits (includes spares) will be sent to the refinery focal points at least 3 weeks prior to the planned date of commencement of the study.

6. PERMEATION END-CAPS

Approximately 30 end-caps (includes spares) will be sent to the refinery site focal points with the first set of sampling tubes.

7. SAMPLE SETS

A full set of samples for each 2 week sampling period will comprise:

	Refinery		
Type of tube	A	B	C
Boundary	16	12	12
Gradient	8	8	8
Quality Control duplicate	1	1	1
Field Blank (unused tube)	2	2	2
Field Spike (unused tube with added benzene)	1	1	1
Field Spike (exposed tube with added benzene)	1	1	1
[Spike (laboratory tube with benzene added by an accredited laboratory) see note]	1	1	1
TOTALS	30	26	26

[Note: An independent laboratory will provide 1 sample tube per site which has been "spiked" with a known amount of benzene. These will be retained by the Co-ordination Centre and inserted into each batch of site samples submitted for analysis as laboratory quality control samples.]

All tube movements will be via the Co-ordination Centre which will be responsible for their overall management.

All tubes will be contained in a sealed metal container which in turn will be transported in an outer container.

The two ‘field spikes’ containing a known amount of benzene are identified by steel clips labelled:

- Blank Spike: not to be used
- Blank Spike: to be used

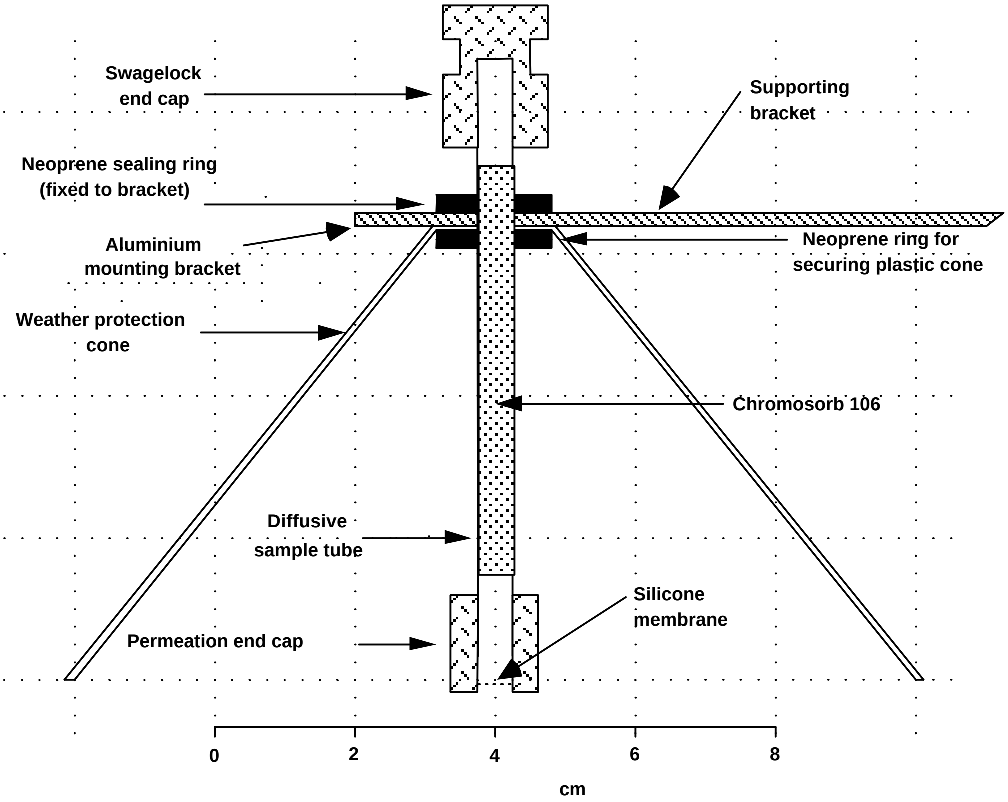
8. RECEIPT OF SAMPLE TUBES

On receipt of sample tubes, identification numbers should be checked off against the list accompanying the tubes. Tightness of end caps should be checked. If any are loose these should be reported to the focal point who will supply replacements. The tubes should be stored in a cool place (preferably a refrigerator) until required. Note: Do not store tubes with any hydrocarbon materials.

9. ASSEMBLY OF SAMPLER (see **Figure 13**)

For ease of location / recognition on site, it may be helpful to number the outside face of each protector with the sample position number, using a "permanent" marker.

Figure 13 Sampling assembly, including weather-shield*:*



9.1. EACH SAMPLING UNIT WILL CONSIST OF THE FOLLOWING ITEMS:

- Diffusion sample tube complete with "Swagelock" end caps.
- 1 permeation end cap
- 1 cone shape white plastic weather protector
- 1 aluminium holding bracket with neoprene sealing ring attached
- 1 neoprene sealing ring for securing diffusion tube inside plastic weather protector
- Plastic covered wire and screws to fix samplers

9.2. ASSEMBLE THE SAMPLER AS FOLLOWS:

Remove "Swagelock" end cap assembly from that end of the diffusion which has 2 rings marked on it. During wet weather prevent any rain from entering sample tube.

Note: The relevant Swagelock end cap is marked with a red X.

Insert the tube through the neoprene seal fixed to the aluminium bracket.

Slide the white plastic cone over the diffusion tube and secure cone to the tube with a neoprene sealing ring.

Place the permeation end cap over the tube and adjust height of tube in its protecting cover such that the bottom side of the permeation cap is flush with the edge of the weather protector.

The sampling unit should be fixed at approximately 1.5 metres above ground level.

Keep “Swagelock” end cap in a safe place.

10. RECORD KEEPING

Complete sample record sheet as per attachment.

11. FIELD BLANKS AND SPIKED TUBES

Two diffusion sample tubes must be retained during each 2 week sampling period as designated field blanks. End caps MUST NOT be removed and the tubes should be retained in a cool area free from contamination.

Two diffusion tubes will have been "spiked" with a known amount of benzene. These will be labelled. One tube will be used as a field quality control sample in a double sampler unit, the other tube should be retained along with the field blanks. Swagelock end caps MUST NOT be removed from this retained sample.

12. SAMPLE TUBE CHANGEOVER

Sample tubes will be changed over every 14 days. Sampling will commence at 0900h on the 29 September 1994 with the 26th sampling set finishing at 0900h on 29 September 1995.

Remove used tube from weather protector assembly and refit "Swagelock" end cap finger tight then secure with one 1/4 turn using spanners.

During wet weather dry the sample tube assembly with clean tissue paper before removing tube from weather protector. Avoid any water entering the tube and connect end cap immediately.

13. SAMPLE TUBE DESPATCH

Used sample tubes, "spiked" tubes and field blanks should be despatched to the Co-ordination Centre together with a completed copy of the sample record sheet, as soon as possible on completion of each 2 week sampling period. For speed of delivery it is advised to use a reputable courier service. A facsimile should be sent to the Co-ordination Centre advising the date and method of despatch. A copy of the sampling record sheet should accompany the sample tubes.

Notes for Guidance

Do not:

- store sample tubes in any area which contains volatile hydrocarbon material
- transport sample tube around site in any vehicle which is, or may be contaminated with hydrocarbons
- transport sample tubes in boot of vehicle
- remove or loosen Swagelock end caps until immediately prior to installing them at the sampling location

Do:

- store sample tubes in cool area
- prevent water from entering tube during sample tube installation / changeover
- ensure the sample record sheets are completed correctly
- arrange for transport of used sample tubes field blanks and "spiked" control sample(s) to the focal point as soon as possible on completion of each 2 week sampling period
- use same site numbers on sampling schedule sheet (1st column) for sample point locations as those used on the site plan.

APPENDIX 2 PREPARATION, HANDLING, CERTIFICATION, TRANSPORTATION AND STORAGE OF THERMAL DESORPTION TUBES

1. PURPOSE

To provide instructions on the preparation, handling certification, transportation and storage of thermal desorption tubes used for occupational hygiene and environmental studies.

2. SCOPE

Can be used to prepare any thermal desorption tubes for pumped or diffusive sampling of airborne organic vapours. The most common tube used is the Perkin Elmer (PE) tube which is designed for the PE ATD50 and ATD400 automatic thermal desorbers.

3. REFERENCES

None

4. DEFINITIONS

None

5. PROCEDURE

5.1 METHOD SUMMARY

Adsorbents are preconditioned and then packed into thermal desorption tubes and further conditioned. Prior to supply, the tubes are analysed using the selected method and a certificate (chromatogram) produced showing the absence of interference at or around the retention time of the compounds of interest. Further instructions on transportation and storage are also given.

5.2 APPARATUS/INSTRUMENTATION

- Gas chromatography capable of being temperature programmed at 1°C per minute up to 250°C.
- Oven capable of heating to 100°C.
- Stainless steel tube.

- Dessicator.
- Stainless steel adsorption tubes.
- Storage end-caps, Swagelock ¼ inch blanking nuts fitted with PTFE Ferrules.
- Transportation/storage containers.

5.3 REAGENTS & MATERIALS

- Adsorbents suitable for thermal desorption type sampling and analysis of airborne organic vapours [e.g. Tenax TA (35/60 mesh); chromosorb 106 (60-80 mesh); Sutcliffe Speakman charcoal (60-80 mesh)].

  Note: If tubes are to be used on the ATD 400 then the mesh size **MUST NOT** be less than 60-80 (80-100 mesh is too fine and will cause failure of the ATD 400).

- Degreasing Solvent.

5.4 SAMPLING/SAMPLE PREPARATION

5.4.1 Conditioning of Adsorbent Prior to Packing

The adsorbent should be preconditioned in bulk before being packed into tubes. It is packed into a stainless steel tube and heated slowly up to its maximum safe operating temperature with pure nitrogen or helium carrier gas at a flow rate of 10 cm^3/min/gram of adsorbent. It is held at this temperature overnight. Carrier gas flow should be maintained while cooling down at the end of the preconditioning period. Store in an airtight container if not used immediately.

5.4.2 Packing of Adsorption Tubes

The adsorbent bed is retained between a fine mesh stainless steel gauze screen and a plug of glass wool. The position and size of the bed should be such that it will always 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 (i.e. 15mm from end);
- while the tube is held vertically, pour the conditioned adsorbent into the tube and tap tube to allow the adsorbent to settle in;
- with the tube still in a vertical position, press the retaining glass wool plug down on 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 certified prior to sampling.

5.4.3 Conditioning or cleaning prior to certification

The tubes are heated 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 grove (orientation mark). The tubes should not be heated above the maximum operating temperature of the adsorbent packing as decomposition will occur.

5.4.4 Certification prior to supply

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

Each tube is analysed by the analytical method for which it has been selected. Tubes will only be analysed for compounds covered by the method as indicated on the "certified tube chromatogram".

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.

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

Tubes spiked with the compounds of interest are analysed to show retention time and supplied with the "certified tube chromatograms".

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 samples. They are analysed as field blanks to demonstrate that contamination has not occurred during transport and storage.

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, should be investigated. Findings and conclusions should be reported to the client.

5.4.5 Capping

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

The caps are fitted, then tightened with spanners not more than a degree turn to prevent damage.

5.4.6. Storage

Adsorption tubes should be stored in clean, air-tight metal containers at the lowest practicable temperature.

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

5.4.7 Sample Collection

Sample collection should be carried out according to the instructions in the selected validated sampling and analytical method which can be supplied by the Laboratory on request.

5.4.8 Transport and Storage

Immediately after sampling, the adsorption tubes should be resealed with Swagelock caps according to instructions in **Section 5.4.5**.

The capped tubes and blanks should be stored in a clean airtight metal container at the temperature recommended in the analytical method.

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.

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

5.5 ANALYTICAL PROCEDURE

Samples are analysed according to the selected sampling and analytical method.

5.6 EXPRESSION OF RESULTS

See analytical method selected.

5.7 PRECISION AND ACCURACY

See analytical method selected.

5.8 REPORTING

See analytical method selected.

5.9 SAFETY

See analytical method selected.

Attention is drawn to the hazards associated with the use of organic solvents.

Various parts of the instruments each carry their own hazards and these must be considered when using the equipment (heated zones, pressurised gases etc.).

APPENDIX 3 DETERMINATION OF LOW LEVELS OF BENZENE IN AIR USING DIFFUSIVE SAMPLING AND THERMAL DESORPTION

1. PURPOSE

This method is suitable for the determination of airborne vapours of benzene for environmental monitoring studies.

2. SCOPE OF APPLICATION

The analytical method has been validated over the range 30-1500 ng benzene collected on the tube (equivalent to 2-100 µg/Nm^3 of benzene in the atmosphere). The procedure is suitable for fixed location monitoring for periods up to 14 days.

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 or it may be necessary to use mass spectrometry detection.

3. REFERENCES

Appendix 2 - Preparation, Handling, Certification, Transport and Storage of Thermal Desorption Tubes.

MDHS 66 Mixed Hydrocarbons (C5 to C10 in Air)

BP in house method MT-HSE-06: The Collection and Determination of Volatile Organic Compounds in Air Using Diffusive Tubes.

COSHH Assessment No. 25, Task Appraisal Nos. 54 and 55.

4. DEFINITIONS

None.

5. PROCEDURE

5.1 METHOD SUMMARY

Benzene vapour is collected onto preconditioned Chromosorb 106 (60-80 mesh) by means of molecular diffusion. The collected samples are transported and 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 ionisation. 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.

5.2 APPARATUS

Capillary Gas Chromatograph, a Perkin Elmer 8000 GC or HP5890 GC, with flame ionisation detection, suitable for analysis according to the operating instructions given in **Table 1**.

Perkin Elmer ATD-50 or ATD-400 Thermal Desorption Unit, equipped with a thermostatically controlled desorption oven, operated in a direct, two-stage, desorption mode according to the operating instruction given in **Table 2**. Instructions on the construction of the capillary interface are given in Annex I.

Adsorption Tubes, stainless steel, compatible with the Thermal Desorption Unit used. The tubes should be packed and conditioned according to the instructions given in PT62: GM61. One end of each tube should be marked to indicate the front end. Each tube should have an identification number marked on it, resistant to heat and moisture.

Analytical End Caps, Swagelock 1/4" blanking nuts fitted with PTFE ferrules.

Pipette, 1 ml.

Precision Syringes, plunger in needle type, 1 µl.

Volumetric Flasks, 100 ml, 50 ml, 25 ml.

Transportation Containers.

5.3 REAGENTS AND MATERIALS

5.3.1 Chromosorb 106, 60-80 mesh

Note 1 Chromosorb 106 should be preconditioned in bulk before being packed into the adsorbent tubes, see **Appendix 2**.

WARNING: If tubes are to be used on the ADT-400 then the mesh size **MUST NOT** be less than 60-80 (80-100 mesh is too fine and will cause failure of the ATD-400).

5.3.2 Benzene, (Purity >99%).

5.3.3 Cyclohexane, HPLC grade.

Note 2 The cyclohexane should be free from contaminants having similar chromatographic retention times to Benzene under conditions listed in **Table 1**.

5.4 SAMPLING/SAMPLE PREPARATION

Immediately prior to sampling remove the storage end cap from the grooved end of the tube and fit a diffusion head fitted with a membrane.

Note 3 The sample tube should be positioned near vertical during sampling to minimise channelling.

Note 4 During sampling the end caps should be stored in a clean air-tight container to prevent contamination.

Record the identification number of each tube on commencement of sampling; record the sampling start time

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

At the end of the sampling period record the sampling time and replace the end caps and store the tubes in an air-tight container

Note 5 It is important not to over-tighten the storage end caps as this will result in damage to the tubes. Finger tightness plus a 1/4 turn is adequate.

Note 6 Tubes are to be stored at minus 20°C wherever practicable, until analysed.

5.5 ANALYTICAL PROCEDURE

The following procedure should be followed in conjunction with **Appendix 2**.

5.5.1 Apparatus Preparation

Couple the thermal desorption unit to the gas chromatograph by means of a heated transfer line according to the manufacturers' instructions.

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

After conditioning, connect the column to the detector, set the operating conditions according to **Table 1** and monitor the baseline at the operating sensitivity to check stability.

Pack the required number of empty adsorption tubes with 200 mg ± 10 mg of preconditioned Chromsorb 106 each according to PT62: GM61.

5.5.2 Preparation of Standard Solutions, Range 1-150 µg/µl of Benzene in Cyclohexane

5.5.2.1 Stock Standard Solution 1 µg/µl Benzene.

Weigh accurately 0.1 g of Benzene into a 100 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

5.5.2.2 Stock Standard Solution 2 µg/µl Benzene.

Weigh accurately 0.2 g of Benzene into a 100 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

5.5.2.3 Stock Standard Solution 3 µg/µl Benzene.

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

5.5.2.4 Stock Standard Solution 30 µg/µl Benzene.

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

5.5.2.5 Stock standard Solution 60 µg/µl Benzene.

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

5.5.2.6 Stock standard solution 120 µg/µl Benzene.

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

5.5.2.7 Stock Standard Solution 150 µg/µl Benzene.

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

5.5.3 Preparation of Standard Solutions, Range 30-1500 ng/µl of Benzene in Cyclohexane

5.5.3.1 Standard Solution 10 ng/µl Benzene.

Pipette 1 ml of stock standard solution 5.5.2.1 into a 100 ml volumetric flask containing cyclohexane and make up to the mark with cyclohexane.

5.5.3.2 Standard Solution 20 ng/µl Benzene.

Dilute solution 5.5.2.2 as in 5.5.3.1.

5.5.3.3 Standard Solution 30 ng/µl Benzene.

Dilute solution 5.5.2.3 as in 5.5.3.1.

5.5.3.4 Standard Solution 300 ng/µl Benzene.

Dilute solution 5.5.2.4 as in 5.5.3.1.

5.5.3.5 Standard Solution 600 ng/µl Benzene.

Dilute solution 5.5.2.5 as in 5.5.3.1.

5.5.3.6 Standard Solution 1200 ng/µl Benzene.

Dilute solution 5.5.2.6 as in 5.5.3.1.

5.5.3.7 Standard Solution 1500 ng/µl Benzene.

Dilute solution 5.5.2.7 as in 5.5.3.1.

5.5.4 Calibration

5.5.4.1 Using a SGE/1 µl plunger in needle syringe inject l µl of standard solution

5.5.3.1 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 analysing. Carry out the spiking procedure in duplicate on separate tubes.

5.5.4.2 Repeat **Section 5.5.4.1** by injecting standard solutions 5.5.3.2 to 5.5.3.7 onto separate clean Chromosorb 106 tubes.

5.5.4.3 Analyse each tube (5.5.4.1 and 5.5.4.2) as described in 5.5.5

Determine the area of the Benzene peaks. Prepare two calibration graphs (1 to 60 ng and 60 to 1500 ng) by plotting the areas found against the respective amounts of Benzene (in ng) spiked on to the tubes.

5.5.5 Sample Analysis

5.5.5.1 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).

5.5.5.2 Analyse each sample tube under the conditions given in **Tables 1 and 2**.

5.5.5.3 Identify, in the chromatogram, the benzene peak and determine its respective peak area. Determine the amount of benzene (ng) on the tube from the relevant calibration graph (5.5.4.3).

5.6 EXPRESSION OF RESULTS

Calculate the concentration of Benzene in the air samples (µm/m³) by means of the following equation:-

Concentration of Benzene C = $\frac{W_1 - W_b}{Uxt} = mg / m^3$

where W_1 = mass of benzene present on sample tube in ng

U = Uptake rate for benzene (cm3/min) (see below)

14 days with membrane 0.50

8 hrs. with membrane 0.57

8 hrs. without membrane 0.63

t = Exposure time (mins)

Note to express concentrations reduced to specified conditions e.g. 25°C and 101 kPa Then:

$$\frac{Cx101xT}{Px298} = mg / Nm^3 \quad \text{corrected}$$

5.7 PRECISION

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

5.8 REPORTING

The Report the concentration of benzene in µm/Nm^3 to two significant figures;

5.9 SAFETY

See references in **Section 3**.

Attention is drawn to the hazards associated with the use of organic solvents during sample preparation. Samples must carry hazard-warning labels and directions must be adhered to.

Various parts of the instrumentation each carry their own hazards and these must be considered when performing the analysis (heated zones, pressurised gases, etc).

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

Gas Chromatograph	Perkin Elmer 8000 Series
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 Ionisation
Detector Sensitivity	High
Detector Temperature	250°C
Detector Gases	Hydrogen (13 psi) Air (20 psi)
Carrier Gas/Pressure	Helium/25 psi
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 25:1

* 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 25:1 is recommended. The use of split ratios outside the recommended range may cause cold trap breakthrough or column overload.

Table 2 Direct two-stage thermal desorption unit operating instructions for ATD 50 or ATD 400 for the analysis of benzene

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 Packing Rate	1000°C/min
Cold Trap Packing Type	Chromosorb 106
Cold Trap Packing Wt	40 mg
Cold Trap Mesh Size	80/100

ANNEX I

CONSTRUCTION OF THE CAPILLARY INTERFACE

Couple the thermal desorption unit to the gas chromatograph by means of a thermostated transfer line (150°C).

Lead an empty capillary column through the transfer line so that the inlet of the empty column is close to the packing of the secondary trap. The splitter system effectively flushes the space around the capillary inlet, which leads to clearly define injection profiles.

Set the split ratio to such a value that sufficient material enters the column to achieve the required sensitivity without column overload. For high tube loadings, a high split ratio (e.g. 100:1) is required, while at low tube loadings, a lower split ratio should be used.

NOTE: For the range specified, a split ratio of approximately 25:1 is recommended.

APPENDIX 4.1: Refinery A

Benzene-in-air concentration: 14 day Averages and Annual

Sampling Position	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Set 8	Set 9	Set 10	Set 11*	Set 12**	Set 13	Set 14	Set 15	Set 16	Set 17	Set 18	Set 19	Set 20	Set 21	Set 22	Set 23	Set 24	Set 25	Set 26	Annual Mean
M1*	22	19	18	24	20	28	24	18	190	11	10	20	10	6.9	8.4	26	11	7.8	3.7	91	13	28	110	8.2	80	5.5	31
M2	15	8.2	40	17	17	23	14	22	13	8.9	27	23	12	10	6.9	14	10	16	8.9	6.4	8.7	8.5	10	12	12	16	15
L3	22	17	73	14	15	25	21	21	9.9	15	14	12	8.6	7.4	3.6	6.5	6.3	5.1	4.4	4.2	7.8	3.9	4.2	5.7	5.7	6.3	13
L4	5.9	3.5	58	5.8	9.4	13	6.7	19	14	9.7	18	18	14	9.0	6.2	10	6.7	8.9	9.6	4.6	4.4	-	3.6	7.7	5.3	5.3	11
L5	5.2	3.8	7.4	7.9	14	8.3	7.4	6.3	10	8.8	12	10	8.7	5.8	4.1	3.8	5.4	4.3	-	3.1	7.7	4.2	3.6	5.7	4.4	5.2	6.7
L6	3.8	2.5	3.6	2.6	<1.0	4.1	4.8	6.4	5.6	2.8	5.6	7.0	8.8	6.4	4.6	8.2	6.8	12	3.5	4.4	3.4	3.8	6.0	11	7.5	6.6	5.5
L7	6.3	2.1	3.0	2.9	4.1	4.3	4.6	9.2	7.7	2.2	6.8	12	12	10	9.4	14	8.0	57	68	7.6	5.1	7.4	11	26	11	-	12
L8	6.6	2.5	2.9	6.7	5.3	5.7	11	16	6.6	3.2	17	19	26	28	27	34	13	35	57	21	6.1	10	21	43	15	24	18
L9	5.4	1.9	2.7	1.4	6.0	5.6	17	15	6.1	1.7	18	15	13	10	14	14	11	12	15	12	5.1	6.5	12	65	15	19	12
L10	3.4	2.0	2.5	1.6	2.3	4.2	4.7	2.1	3.7	1.4	1.6	2.4	2.6	1.9	7.5	6.7	4.1	1.2	3.8	5.8	4.0	3.6	2.6	4.6	3.9	7.8	3.5
L11	3.0	2.0	2.3	4.1	1.5	4.0	1.6	1.1	3.9	1.3	1.3	3.1	1.6	1.1	5.0	3.6	2.2	<1.0	1.7	3.2	2.2	2.2	<1.0	2.5	2.6	3.5	2.4
L12	4.1	2.0	2.9	1.8	2.7	3.5	3.0	1.4	3.6	1.3	1.0	3.4	2.3	1.6	3.3	4.1	1.8	1.5	<1.0	3.2	1.6	3.4	3.2	<1.0	1.6	3.6	2.4
L13	4.2	2.7	3.4	<1.0	<1.0	2.5	<1.0	1.1	<1.0	1.5	1.6	2.7	1.7	1.6	2.0	3.4	2.0	<1.0	<1.0	3.5	4.8	3.2	2.9	1.6	3.7	2.2	2.1
L14	2.6	6.6	5.2	1.9	6.5	2.5	2.1	1.1	4.5	2.9	1.9	4.4	2.0	1.6	3.5	5.5	4.2	1.8	<1.0	3.2	5.0	4.1	4.4	5.4	5.2	3.7	3.5
L15	3.8	4.3	5.8	<1.0	4.5	3.2	1.7	1.6	3.8	3.8	2.7	3.5	1.8	1.6	2.8	8.8	1.9	1.3	<1.0	3.5	3.4	2.6	4.2	4.5	3.4	1.3	3.0
M16*	<1.0	5.4	7.4	7.1	12	6.9	9.6	4.6	14	4.2	4.0	21	3.7	3.9	5.5	6.9	7.3	3.8	<1.0	4.8	5.1	3.2	11	14	11	11	7.2
I 1	15	9.9	16	9.8	21	18	18	25	16	8.5	5.0	12	-	4.6	3.4	11	8.5	5.5	2.7	8.5	9.9	7.4	14	15	14	9.9	12
I 2	17	11	23	16	49	81	57	23	19	15	6.4	22	8.8	5.9	7.7	19	15	9.7	4.6	9.0	20	14	19	15	11	5.9	19
I 3	180	76	64	85	140	180	120	88	72	69	78	120	45	57	32	100	55	40	7.6	77	130	78	150	76	110	48	87
I 4	8.8	20	9.1	7.2	13	45	11	8.7	12	11	2.7	9.0	3.9	3.9	32	14	5.7	3.6	1.4	26	32	32	29	24	11	5.3	15
I 5	13	15	12	31	26	49	18	27	35	55	34	19	15	16	6.9	10	8.8	9.1	6.2	6.7	-	8.5	10	11	11	9.5	19
I 6	12	20	20	9.9	15	19	23	18	25	31	24	36	19	24	27	23	23	26	39	40	31	66	50	48	27	32	28
I 7	4.3	5.9	7.6	2.3	8.8	58	3.5	2.4	4.9	3.9	1.6	6.2	3.6	3.0	5.3	9.5	4.7	1.9	1.9	4.3	4.3	3.2	10	6.8	7.7	12	7.2
I 8	20	8.9	12	10	19	28	24	20	6.9	25	15	21	12	7.7	6.7	34	10	7.8	<1.0	12	23	9.8	23	11	13	7.1	15

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
I	Internal gradient

APPENDIX 4.2: Refinery B

Benzene-in-air concentration: 14 day Averages and Annual Mean

Sampling Position	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Set 8	Set 9	Set 10	Set 11	Set 12	Set 13	Set 14	Set 15	Set 16	Set 17	Set 18	Set 19	Set 20	Set 21	Set 22	Set 23	Set 24
L1	2.0	2.9	2.4	1.9	1.1	3.3	1.2	3.8	<1.0	2.5	1.7	2.6	2.5	2.2	1.6	5.2	1.5	3.9	3.1	2.1	2.9	1.9	<1.0	1.9
L2	2.9	2.8	4.5	3.2	2.0	3.0	2.5	4.6	5.7	3.9	3.3	4.1	3.9	2.0	2.8	1.7	1.9	3.6	3.2	2.1	2.7	1.1	<1.0	1.0
L3	3.2	3.3	4.4	4.7	3.6	3.9	2.4	4.3	1.3	5.8	3.4	4.2	-	2.4	2.5	4.9	1.8	4.1	3.3	2.1	1.9	2.3	<1.0	3.9
L4	2.1	4.6	3.6	3.7	2.3	3.6	2.0	5.6	<1.0	2.7	<1.0	3.8	3.4	2.8	3.3	3.4	5.0	3.7	<1.0	1.8	2.3	1.8	1.0	2.9
M5*	3.8	5.0	3.7	7.4	3.0	5.7	2.5	22	<1.0	2.7	14	5.5	5.0	8.4	15	5.0	14	14	3.3	3.6	5.8	3.6	3.3	14
M6*	6.4	4.1	3.0	2.2	4.1	4.4	2.4	4.8	1.0	2.9	2.3	3.8	3.6	4.1	2.7	7.5	3.9	3.9	3.0	2.0	4.0	3.8	2.0	2.7
L7	4.6	3.6	4.5	2.2	4.1	3.5	2.5	4.7	1.0	1.6	1.2	4.1	2.6	1.7	2.6	5.8	2.0	2.7	3.2	3.5	3.8	3.6	2.2	2.7
L8	5.0	3.6	4.7	1.2	1.5	2.5	2.1	4.5	<1.0	-	1.0	3.8	1.6	2.3	2.0	5.3	2.0	2.0	2.3	2.0	1.5	4.6	2.3	2.2
L9	4.1	3.8	5.4	1.8	1.3	3.0	2.7	3.4	<1.0	1.4	<1.0	8.7	1.1	<1.0	2.2	4.6	1.9	1.5	<1.0	2.2	1.5	3.8	1.2	1.4
L10	3.4	2.2	2.8	<1.0	1.5	3.7	1.6	3.2	<1.0	1.3	<1.0	5.4	1.9	2.6	1.9	1.4	1.8	1.4	1.9	<1.0	22	1.2	<1.0	1.6
L11	1.7	3.3	2.9	2.4	3.3	2.2	<1.0	4.0	1.9	2.0	2.1	2.8	1.8	1.5	1.3	1.8	1.7	4.5	<1.0	1.0	1.6	1.9	<1.0	1.0
L12	1.9	3.5	3.2	<1.0	2.4	2.0	<1.0	3.2	<1.0	3.1	1.9	2.5	2.5	1.5	1.8	5.8	1.5	1.4	2.2	1.9	2.1	1.2	1.0	2.3
I 13	2.5	3.3	3.2	1.5	3.1	2.7	-	4.7	5.0	5.5	3.3	4.4	4.0	2.2	4.1	8.6	2.0	6.0	<1.0	3.6	7.2	4.2	<1.0	2.8
I 14	13	9.2	17	10	12	19	23	17	20	21	27	19	20	13	14	9.6	7.6	10	9.9	11	16	6.7	4.9	9.3
I 15	3.0	4.1	5.6	5.1	4.1	4.8	4.2	6.5	3.9	4.7	6.5	5.4	5.2	3.1	3.5	5.7	2.4	4.2	4.6	2.8	3.7	1.0	<1.0	2.4
I 16	4.7	9.2	13	15	7.6	8.3	7.1	11	11	15	16	11	16	7.2	6.4	9.0	8.0	15	12	6.4	-	3.6	1.0	11
I 17	3.0	4.5	5.0	5.7	5.8	4.8	2.5	5.6	1.8	4.8	5.1	4.7	5.9	4.1	3.4	3.3	4.6	5.4	6.3	3.6	6.0	3.3	1.7	3.8
I 18	10	6.6	5.2	4.3	2.9	3.5	3.1	6.0	<1.0	2.9	3.4	6.8	3.0	3.6	3.8	8.1	6.1	6.2	6.0	6.5	5.2	9.8	7.1	3.9
I 19	7.8	7.0	4.1	2.4	3.9	3.5	2.1	5.1	<1.0	2.7	4.2	4.9	2.7	3.2	3.8	6.8	3.9	4.5	2.8	3.4	4.7	5.9	4.0	2.2
I 20	9.7	5.2	6.9	6.2	2.6	3.6	2.6	4.7	<1.0	2.3	<1.0	3.8	2.2	3.2	2.6	5.9	4.4	4.8	3.2	3.7	2.2	4.7	5.6	3.7

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
I	Internal Gradient

APPENDIX 4.3: Refinery C

Benzene-in-air concentration: 14 day Averages and Annual Mean

Sampling Position	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Set 8	Set 9	Set 10	Set 11	Set 12	Set 13	Set 14	Set 15	Set 16	Set 17	Set 18	Set 19	Set 20	Set 21	Set 22	Set 23	Set 24	Set 25	Set 26	Annual Mean
L1	<1.0	<1.0	1.3	<1.0	<1.0	1.8	<1.0	<1.0	1.7	<1.0	<1.0	1.2	<1.0	<1.0	1.1	1.0	<1.0	1.6	1.1	<1.0	<1.0	<1.0	1.8	<1.0	1.2	<1.0	<1.0
L2	<1.0	1.2	<1.0	<1.0	<1.0	4.5	<1.0	1.2	2.1	<1.0	<1.0	1.1	1.1	<1.0	1.1	3.8	<1.0	1.3	<1.0	1.3	<1.0	<1.0	<1.0	<1.0	1.9	1.1	1.1
L3	4.5	3.0	3.0	1.0	2.5	4.8	4.8	5.0	5.5	2.5	1.1	1.6	7.0	4.6	4.4	4.5	1.7	3.6	3.5	3.6	1.3	2.5	2.0	6.9	5.2	3.0	3.6
L4	5.5	3.4	4.2	1.0	1.5	3.1	<1.0	3.9	-	2.3	1.3	1.1	4.0	-	3.8	6.4	3.8	3.7	5.4	6.0	3.4	3.2	3.3	7.8	5.3	1.5	3.6
M5*	8.1	5.6	3.0	2.0	5.2	3.2	4.5	3.1	2.4	2.7	3.3	1.8	6.9	<1.0	5.0	6.5	7.1	4.6	8.7	7.8	4.8	6.4	4.6	8.6	5.6	3.1	4.8
M6*	15	12	17	10	11	7.6	6.6	8.0	10	9.7	10	5.5	25	14	13	18	25	18	30	35	20	17	19	28	19	9.6	16
M7*	32	14	32	13	24	14	11	13	18	10	34	21	10	13	12	17	20	17	29	6.4	16	9.0	15	12	30	11	17
M8*	8.5	6.2	20	7.0	7.8	4.4	4.1	2.0	4.1	6.0	14	5.0	2.9	5.3	4.5	7.5	6.7	3.4	<1.0	<1.0	14	2.4	2.3	3.6	8.9	7.2	6.1
M9	4.1	5.8	13	4.6	4.5	2.3	1.7	1.5	3.8	4.9	8.3	5.7	2.7	3.6	7.4	7.3	2.0	2.4	<1.0	1.0	3.6	<1.0	<1.0	2.1	6.8	4.4	4.0
M10	3.6	5.6	4.6	2.0	1.6	1.6	<1.0	<1.0	2.6	1.4	1.2	24	1.5	1.3	4.0	4.1	1.3	2.8	<1.0	<1.0	1.2	<1.0	<1.0	<1.0	12	2.8	3.1
L11	<1.0	3.4	4.7	1.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.1	<1.0	<1.0	1.1	1.4	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.5	<1.0	<1.0
L12	<1.0	1.2	1.4	<1.0	<1.0	1.0	<1.0	<1.0	1.2	<1.0	<1.0	1.2	<1.0	<1.0	<1.0	3.7	1.2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.4	<1.0	<1.0
E2	2.1	1.0	1.2	<1.0	<1.0	1.2	<1.0	<1.0	1.8	<1.0	1.6	<1.0	1.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.2	<1.0	<1.0
E3	1.7	1.2		<1.0	<1.0	1.1	<1.0	1.1	<1.0	<1.0	1.1	<1.0	2.3	1.5	1.7	1.1	1.3	<1.0	<1.0	2.0	<1.0	<1.0	<1.0	2.1	2.1	<1.0	1.0
E4	3.4	2.6	3.4	<1.0	<1.0	1.6	2.0	2.2	2.7	1.5	<1.0	<1.0	3.2	2.0	2.5	2.4	2.3	3.8	3.2	4.5	1.6	1.6	2.1	2.9	-	1.3	2.2
I 7	6.7	7.2	14	4.6	5.6	3.7	3.1	4.4	7.3	2.4	14	10	4.5	3.6	4.1	7.8	6.6	8.7	5.2	3.0	6.9	2.8	3.2	2.2	12	4.1	6.1
I 8	3.7	13	17	7.4	11	6.9	8.7	6.2	9.6	6.7	11	14	4.1	5.4	6.7	8.5	3.7	3.9	2.6	1.5	3.8	3.0	3.4	2.6	10	10	7.1
I 9	2.2	12	8.7	5.3	2.5	2.6	3.3	1.6	3.8	1.7	1.8	6.4	2.1	1.9	4.2	5.1	1.7	4.4	<1.0	1.4	4.5	<1.0	1.4	2.1	13	2.9	3.8

Sampling Position Key	
L	Land boundary
M	Marine boundary
M*	Marine operational boundary
E	External gradient
I	Internal gradient