ERRATA

page iv, line 8, delete 'acknolwedge', include 'acknowledge'

page v, line 20, delete 'withe', include 'with'

page 4, Fig. 1.2, delete 'λ 300-400 mm', include 'λ 300-400 nm'

page 24, line 9, delete 'lead', include 'led'

page 34, line 27, delete 'lead', include 'led'

page 65, after the 2.2.2.2 insert '(a) Adsorption Capacity'

page 102, Fig. 3.5, delete '$y = 0.623 + 0.416\ x_1$'
include '$y = 0.0623 + 0.416\ x_1$'

page 117, Fig. 3.12, delete '$y = -0.0100 + 0.017\ x$'
include '$y = -0.0100 + 0.0107\ x$'

page 162, line 14, delete 'less EDB(20%)', include 'less EDB (~10%)'

page 193, Table 5.11, delete 'xyelene', include 'xylene'

VEHICLE-ASSOCIATED AIR POLLUTANTS

A thesis submitted to the University of London
in partial fulfilment of the requirements for
the degree of Doctor of Philosophy in
the Faculty of Engineering
and for the Diploma of Imperial College

by

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ABSTRACT

Analytical techniques involving adsorption onto porous polymers have been developed for the estimation of the concentrations of individual hydrocarbons and halocarbons in ambient air.

Sixteen individual aromatic hydrocarbons and two halocarbons - vehicle generated - have been studied in different locations and correlations between them have been related to air quality.

Detailed dynamometer studies have been undertaken utilizing different vehicles operating in various modes, and exhaust emission concentrations have been related to both engine operation and contribution to ambient levels in different situations.

The analytical techniques developed have also been used as a means of identifying possible alternative combustion sources, together with an assessment of the relative contribution that they make to ambient air quality. In this context a detailed study was undertaken of a large international airport and an assessment was made of the contribution made by the aircraft to the overall atmospheric pollution loadings.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

litre		1
millilitre	(10^{-3}1)	ml
microlitre	(10^{-6}1)	μl
gram		g
milligram	(10^{-3}g)	mg
microgram	(10^{-6}g)	μg
nanogram	(10^{-9}g)	ng
kilogram	(10^{3}g)	Kg
parts per million		ppm
parts per billion		ppb
parts per trillion		ppt
parts per hundred million		pphm
minute		min
hour		h
metre		m
kilometre	(10^{3}m)	km
centimetre	(10^{-2}m)	cm
millimetre	(10^{-3}m)	mm
inch	(25.4 mm)	in
kilometres per hour		Kmph
miles per hour	(1.61 Km)	mph
Solid smokeless fuel		SSF
Therm	(10^{5}Btu, 1.05506×10^{8}J)	therm
Constant volume sampling		CVS
Air to fuel ratio		A/F
Aircraft movement		ACM
Gas chromatography		GC
Mass spectrometry		M/S
Flame ionization detectors		FID

Electron capture detectors	ECD
Non-dispersive infra red	NDIR
Support coated open tubular column	SCOT
Air quality chromatograph	AQC

Hydrocarbons	HC
Total hydrocarbons	THC
Non-methane hydrocarbons	NMHC
Halogenated hydrocarbons	HCX_n
Carbon monoxide	CO
Oxides of nitrogen	NOx
Benzene	C_6
Toluene	C_7
1,2 Dichloroethane	EDC
1,2 Dibromoethane	EDB
Vinyl Chloride	VCl
Tetramethyl lead	TML
Tetraethyl lead	TEL
Peroxyacylnitrates	PAN

Environmental Protection Agency	EPA
World Health Organization	WHO
Economic Commission for Europe	ECE
United Kingdom	UK
United States	US

CHAPTER 1 : INTRODUCTION

1.1 Air Pollution

All air is contaminated to some extent, arising in many instances from the activities of man. Although a definition of AIR POLLUTION would be a worthy prerequisite of a study of the subject, it is becoming increasingly difficult to define what is meant by both, the term air pollutant and more particularly the concentration level at which the pollutant becomes unacceptable. In attempting such a definition the Engineers Joint Council of the United States in issuing a policy statement on air pollution (1) made the following comment:

> "Air pollution means the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odour, smoke or vapour in quantities of characteristics and of duration such as to be injurious to human, plant or animal life or to property, or which unreasonably interfere with the confortable enjoyment of life and property".

Following many incidents in the 1950's and the introduction of the term smog - a combination of the words smoke and fog - there was greater public awareness of the seriousness of air pollution and the need for controls. This term is however used rather loosely in the popular press where it has become a means of describing any air pollution event that is accompanied by a decrease in visibility.

In chemical terms however, smog includes two widely varying atmospheric conditions and the well known London smogs for instance are completely different in character to those reported in Los Angeles.

Even as far back as 1661, air pollution in London was described by John Evelyn in his book "Fumifugium" (2) which set out the problems arising from the inefficient combustion of soft coal. These processes continued and indeed expanded with increasing industrial activity until the well recorded London smog of December 1952 when many hundred people, suffering with respiratory problems, died prematurely as a result of the air pollution levels in the city. Build up of atmospheric concentrations of both sulphur dioxide and smoke under a temperature inversion which persisted for many days accounted for the high death rate (3) and a clear correlation between these factors was seen (Fig. 1.1).

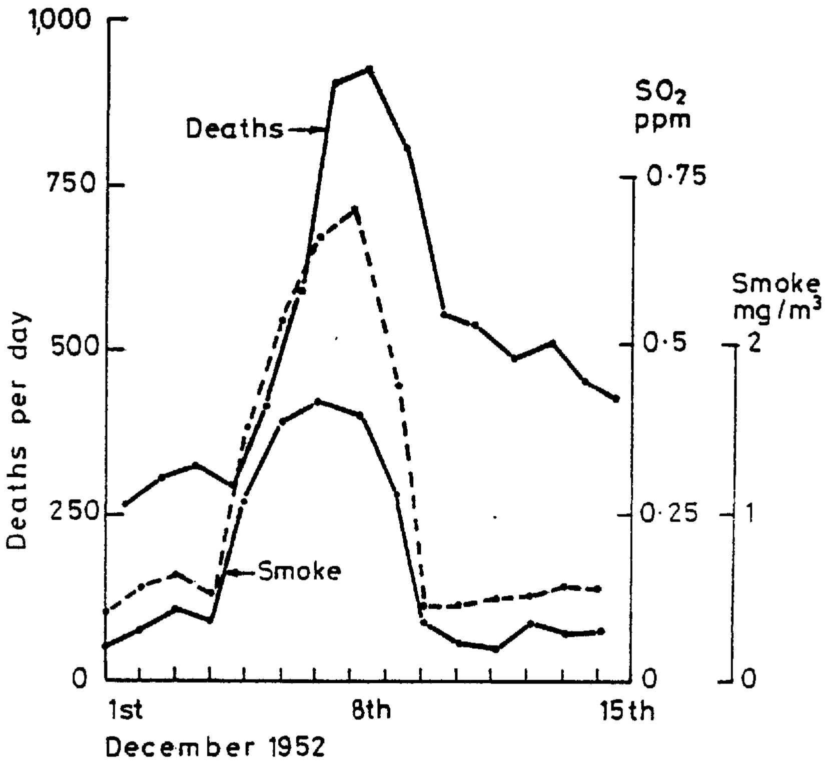


Fig 1·1 Death and pollution levels in the fog of December 1952.
after Lowther et al

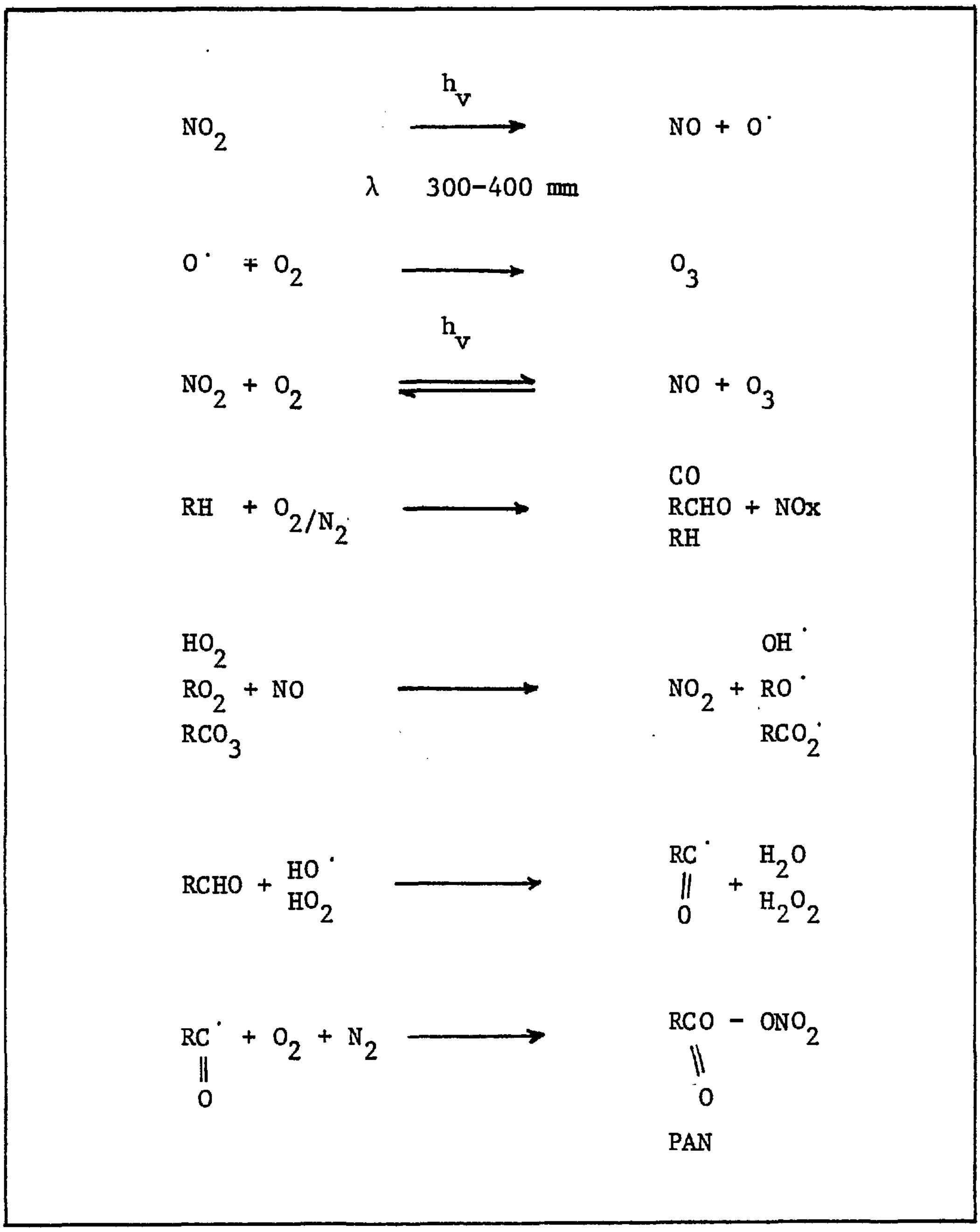
Materials emitted into the atmosphere are designated as primary pollutants. These, as they disperse, can react among themselves or with other substances already present in the atmosphere to produce secondary pollutants and as such the toxicity of the secondary materials need to be taken into account.

Most pollutants, whether primary or secondary find their way to a sink such as the ocean or to a receptor such as man. If dispersion is limited increased concentrations find their way directly to the receptor. Clearly in this type of smog formation, meteorological and topographical considerations are important and the London type smog is therefore characterized by a chemically reducing atmosphere accompanied by a build up of smoke and sulphur dioxide under temperature inversion conditions. As such they occur predominantly at night and give rise to problems with people who suffer from bronchial irritation.

Smog situations in the United States and other countries enjoying (4) high levels of sunshine are largely photochemical in nature. The pollutants of concern are secondary materials produced by chemical reaction in the sunlight and largely give rise to eye irritation and damage to vegetation. Clearly problems are exacerbated by limited dispersion caused by inversion conditions. In many ways the atmospheric situation is opposite to that present in the London type smog in that the atmosphere is chemically oxidizing and the major problems occur after midday rather than at night.

Photochemical smog is therefore caused by a complex series of chemical reactions involving oxides of nitrogen (NOx) and hydrocarbons (HC) as primary materials leading to the formation of such secondary pollutants as aldehydes, ketones and peroxyacylnitrates (Fig. 1.2). The complexity of this chain of reactions which is of course influenced by a vast number of individual hydrocarbons, illustrates the importance of understanding far more about the composition of the atmosphere and in particular of knowing the relative contribution to total hydrocarbon levels of the individual species involved.

Although photochemical smog formation has been predominantly associated with hot climates it has recently been demonstrated that limited activity takes place even in climates such as those of the UK (Fig. 1.3). Relatively, the concentrations of secondary materials produced are of little significance compared with the threshold levels at which health effects occur (5).



$$NO_2 \xrightarrow[\lambda \quad 300\text{-}400\ \mathrm{mm}]{h_v} NO + O^{\cdot}$$

$$O^{\cdot} + O_2 \longrightarrow O_3$$

$$NO_2 + O_2 \overset{h_v}{\rightleftharpoons} NO + O_3$$

$$RH + O_2/N_2 \longrightarrow \begin{matrix} CO \\ RCHO + NOx \\ RH \end{matrix}$$

$$\begin{matrix} HO_2 \\ RO_2 \\ RCO_3 \end{matrix} + NO \longrightarrow NO_2 + \begin{matrix} OH^{\cdot} \\ RO^{\cdot} \\ RCO_2^{\cdot} \end{matrix}$$

$$RCHO + \begin{matrix} HO^{\cdot} \\ HO_2 \end{matrix} \longrightarrow \underset{O}{\underset{\|}{RC^{\cdot}}} + \begin{matrix} H_2O \\ H_2O_2 \end{matrix}$$

$$\underset{O}{\underset{\|}{RC^{\cdot}}} + O_2 + N_2 \longrightarrow \underset{O}{\underset{\|}{RCO}} - ONO_2$$

PAN

Figure 1.2 Simplified mechanisms for the formation of photochemical smog

1.2 Pollutants and Sources

The most common air pollutants are associated with combustion processes of one form or another and many of them are products of incomplete combustion. These include:

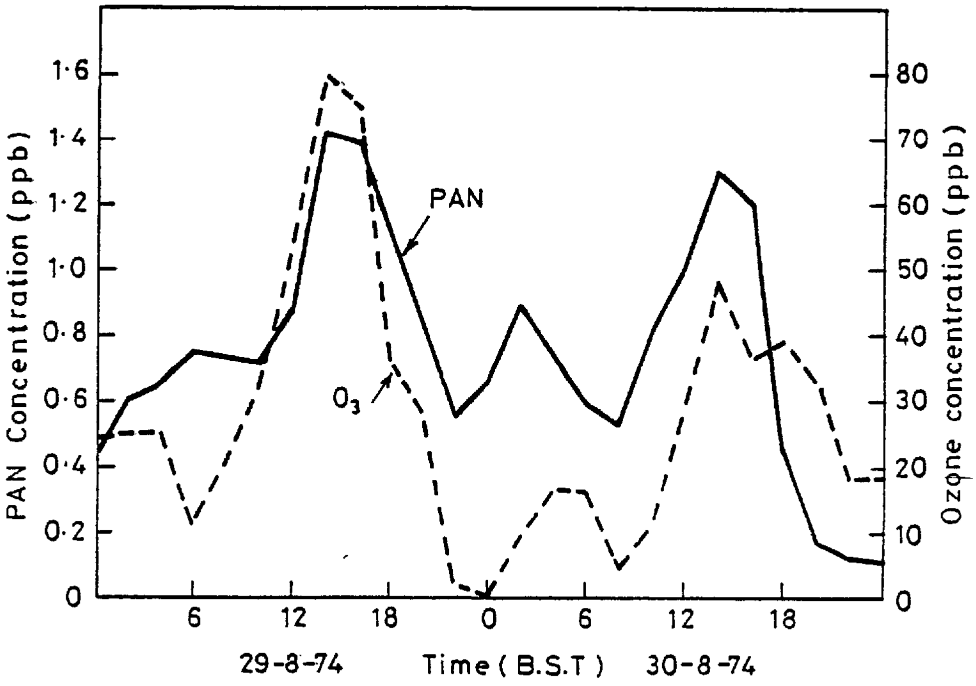


Fig 1·3 Variation of ground level concentrations of PAN and ozone at Harwell during two days in August 1974

(a) oxides of sulphur
(b) carbon monoxide
(c) carbon dioxide
(d) oxides of nitrogen
(e) hydrocarbons
(f) particulates

In considering the total burden of these materials being discharged to the atmosphere it is important to recognise the significant contribution made on a world basis by natural processes. Thus for instance 80% of the total sulphur dioxide compounds arise from the initial discharge of sulphur dioxide originating from anaerobic processes. Similarly, significant discharges of hydrocarbons occur from plants and trees and natural processes giving rise to hydrocarbon levels equivalent to approximately 1.5 ppm total hydrocarbons (THC) expressed as methane.

Apart from the above six major pollutants there are other materials of concern being discharged into the atmosphere normally associated with specific industries (6).

Table 1.1 Specific pollutants and their sources

	Pollutant	Sources
(a)	Ammonia	Ammonia works
(b)	Sulphur trioxide	Sulphuric acid works, brickworks
(c)	Sulphides, sulphur	Generating stations, metal smelting, rubber vulcanizing, coke ovens
(d)	Chlorine and hydrogen chloride	Chlorine works, aluminium works, metal recovery plants, refuse incinerators
(e)	Chlorinated hydrocarbons	Dry cleaning establishments
(f)	Bromides	Motor vehicle emissions
(g)	Fluorine and fluorides	Brickworks, glassworks, aluminium smelting, iron works
(h)	Mercaptans	Oil refineries, coke ovens
(i)	Metals	Specific to appropriate works

Many such materials exhibit well documented health effects at higher concentrations and as such are rigorously controlled in industrial atmospheres (7). The health related effects of the same materials at atmospheric concentrations are however, less certain and considerable controversy still exists in defining appropriate air quality standards. At the concentration levels encountered in an urban atmosphere with many of these minor industrially generated materials, significant analytical problems still exist in monitoring them and in studying their dispersion and chemical reactivity in the atmosphere. These problems are illustrated by the activities of the United States Environmental Protection Agency in attempting to define air quality standards for some one hundred and twenty nine different compounds (8,9).

Of the two major categories of air pollution source that exists, namely combustion processes and industrial processes, combustion sources include the major forms of transportation which utilize hydrocarbon fuels of different types. Gas chromatographic analyses of petrol, diesel and aircraft levels, show these distinct characteristics related to the boiling point range of the hydrocarbon materials involved (10). Clearly these influence dramatically the characteristics of the emissions from the source.

Other combustion processes include those associated with power generation and again a variety of hydrocarbon based fuels are involved. Emission factors vary according to the nature of the fuel and the stringency of control of the process involved (11).

1.2.1 Stationary Sources

Evaluation of emissions including dispersion calculations that can be related to ground level concentrations, can be far more readily carried out for stationary sources than for mobile ones.

The major stationary sources of emissions are industrial processes including power generation and refuse incineration. Domestic contributions vary significantly with the climate of the country concerned, according to the need for either domestic heating or air conditioning.

The last few years have seen significant improvement in air pollution controls in the UK. These have been brought about by change in the living standards and attitudes together with and by the enactment of the Clean Air Act following the smog problems of the 1950's (table 1.2) (12).

Table 1.2 UK emissions of sulphur dioxide and smoke from coal used by stationary sources in tonnes.10^6

	Smoke		Sulphur dioxide				
Year	Domestic	Industry	Domestic	Industry	Power Station	Gas Works	Coke Ovens
1969	0.70	0.08	0.42	0.70	2.12	0.08	0.13
1970	0.64	0.08	0.38	0.64	2.13	0.06	0.13
1971	0.55	0.06	0.33	0.52	2.01	0.04	0.13
1972	0.42	0.05	0.26	0.39	1.84	0.04	0.13
1973	0.44	0.05	0.25	0.39	2.07	0.03	0.15
1974	0.42	0.04	0.24	0.36	1.81	0.03	0.12
1975	0.35	0.04	0.20	0.28	2.15	0.03	0.13
1976	0.33	0.04	0.19	0.27	2.10	0.02	0.13

Typical emission factors for the various fuels used are summarized in table 1.3 and rely heavily upon UK and USA practice (11).

Table 1.3 Emission factors for various fuels and various sources in:
g Kg^{-1} fuel for solids and liquids
Kg $(10^6 \text{ therm})^{-1}$, for gas

Sources	NOx	CO	HC
(a) Transportation emission factors			
Gasoline eng.	16.5	401.4	19.5
Diesel eng.	30.0	41.0	6.6
(b) Domestic appliances emission factors			
Coal:bituminus	1.04	45	10
Coal:anthracite	1.5	45	1.25
SSF	1.6	45	1.25
Oil	2.9	0.79	0.15
Gas	3452	863	345
(c) Commerical and industrial emission factors			
Coal and SSF	7.5	1.0	0.5
Oil (distillate)	5.3	0.71	0.13
Oil fuel	6.7	0.68	0.13
Refinery oil	7.8	0.65	0.13
Gas (commercial)	5178	863	345
Gas (industrial)	9978	728	129
(d) Power generation emission factors			
Coal	9	0.5	0.15
Oil	6.5	0.65	0.12
Gas	12945	728	43
Coke + breeze	9	0.5	Neg.

Emission factors used are heavily dependent upon the source of fuel used and the control factors instituted in a particular country (13).

1.2.2 Mobile Sources

In any urbanized society, transportation sources make a major contribution to atmospheric pollution levels. Over the last two decades the balance between the alternative modes of transport have been moderated by the necessity of controlling vehicle emissions. This process will undoubtedly continue to be influenced in addition by the problems of energy conservation.

On the domestic front spark-ignition engines are the most significant. The need to control total emission levels was clearly demonstrated by predictions made by the Environmental Protection Agency (6), at the beginning of the last decade (Fig. 1.4).

Although downward modifications to the predicted increase in car population have resulted from the energy crisis (estimated as 304 million for 1980), there have been more recent indications of record levels of new vehicle registrations (14).

There are clear indications that over the first decade of vehicle controls in the United States, emission limitations were only accomplished at the cost of significant energy utilization (Fig. 1.5). During that period a registration increase of 45% related to an increased gasoline consumption of 60% whilst total mileage travelled only increased by 51% (15). Clearly the average fuel consumption per mile over that period increased significantly.

Although the total car populations in the US and in Europe are approximately the same (14) (125 million for the US, 113 million for Europe), the total emissions and fuel usage varies significantly owing to the relative size and efficiencies of the vehicles involved.

As with other combustion sources the major air pollutants arising from vehicles are carbon monoxide, hydrocarbons and oxides of nitrogen (16,17,18,19). Minor emissions include lead compounds, halogenated materials and certain carcinogenic hydrocarbons which are frequently adsorbed onto the particulate matter emitted (20).

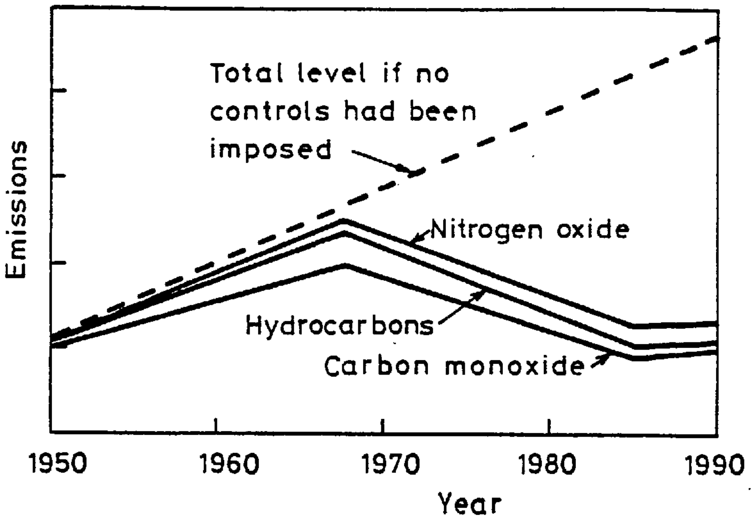


Fig 1·4 Predicted trends in vehicle emissions following introduction of controls

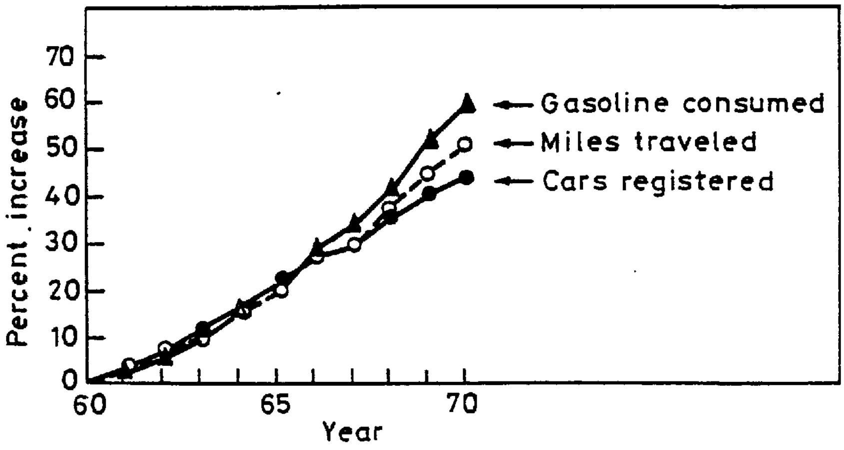


Fig 1·5 Passenger car trends, 1960 – 1970

Table 1.4 Hydrocarbons found in automotive exhaust

Polynuclear aromatics

anthracene
phenanthrene
fluoranthene
alkylfluoranthene
pyrene
alkylpyrene
triphenylene
chrysene*
alkylchrysene
benz[a]anthracene*
alkylbenz[a]anthracene
naphthacene
11H-benzo[b]fluorene
benzo[a]pyrene*
benzo[e]pyrene*
benzo[k]fluoranthene

perylene
benzo[j]fluoranthene*
alkylbenzo[a]pyrene
11 H-benzo[b]fluoranthene*
dibenz[a,h]anthracene*
benzo[ghi]fluoranthene
dibenz[b,h]phenanthrene
benzo[ghi]perylene
anthanthrene
indeno[1,2,3-cd]fluoranthene
indeno[1,2,3-cd]pyrene
dibenzo[a,l]naphthacene
dibenzo[a,e]pyrene*
dibenzo[a,l]pyrene*
coronene
dibenzo[b,pqr]perylene

Aliphatic hydrocarbons

hexadecane
heptadecane
octadecane
nonadecane

eicosane
docosane
tetracosane

* indicates that compound is known to be carcinogenic

Unfortunately, maximum emissions of nitrogen oxides occur under the most efficient combustion conditions (Fig. 1.6) and simple control procedures are therefore frequently related to an optimization of the air to fuel ratio involved (6).

The emission of lead compounds from vehicle exhausts has been a controversial issue with respect to potential control. The uncertainties stem from the interpretation of health effects data related to the concentration at which lead occurs in urban air (21-28).

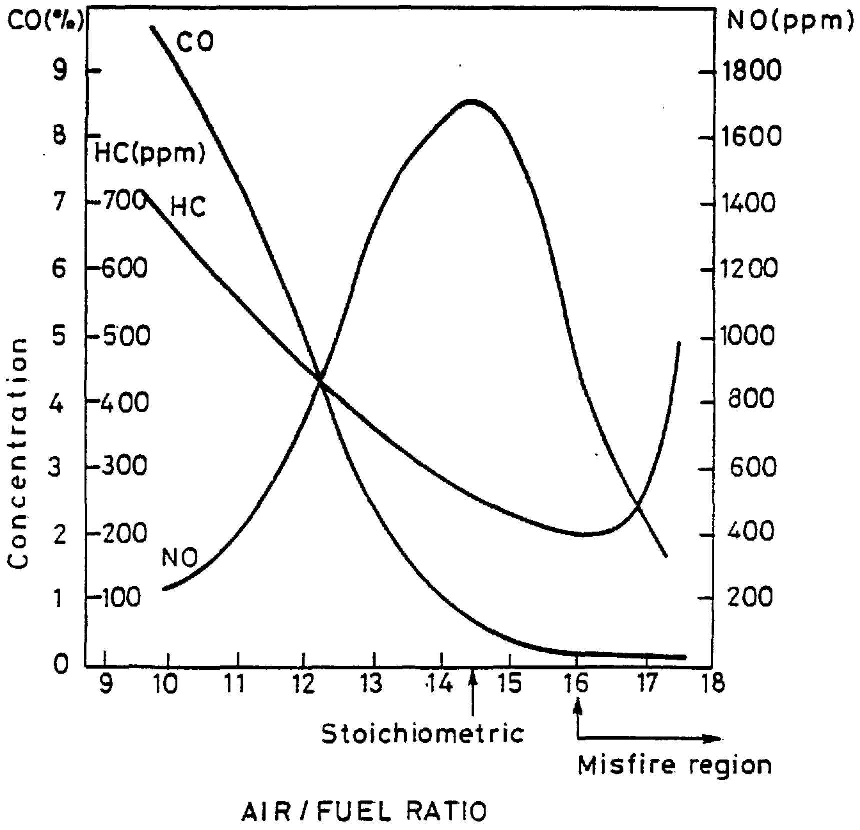


Fig 1·6 HC, CO, NO emissions relative to mixture strength

As with many similar environmental issues it is impossible to assess such a problem in isolation. With lead the emissions from motor vehicles need to be related to the total body burden to man including that contained in air, water and food.

The use of lead alkyls in petrol have contributed to the production of high octane fuels which have allowed the use of higher compression engines with their advantages in performance and efficiency. In considering various alternatives for emission controls involving either the removal of lead or the reduction in the level of its use, the energy factor in terms of the fuel consumption per mile is assuming a greater importance in any cost benefit study.

Ethylene dibromide and ethylene dichloride are two additional petrol additives used predominantly as scavengers for the lead compounds produced in the combustion system (29). The particulate lead compounds emitted from the exhaust are therefore predominantly lead bromochloride, although clearly many other compounds are also involved (30).

In addition to the products of combustion emitted from the tail pipe evaporative losses occur and unburnt materials can pass through an inefficient or inoperative combustion system and be discharged. Emissions here include the scavengers and lead compounds themselves in addition to the obvious hydrocarbons (31).

Subsequent transfer of many of the minor vehicle emissions including both polynuclear aromatic hydrocarbons and halogenated materials to surface waters have recently been shown to be of concern (Table 1.5) and has provided one of the motivations for the current research work undertaken (32,33).

Although exhaust emissions from petrol engines depend heavily upon the mode of activity of the engine (Fig. 1.7) losses on the form of crankcase blow by, depend greatly upon the fact that an air fuel mixture is involved at the compression stage. In the case of diesel engines major advantages in emission controls arise from the fact that only air is compressed and fuel injection follows the compression stage. If operating efficiently (34), emissions from diesel engines can therefore be significantly lower than those from gasoline engines (Table 1.6).

Table 1.5 Concentrations of polynuclear aromatic hydrocarbons found in runoff

ng l^{-1}

Traffic in thousands →	825	179	319	209	223	1043	641	80	240
Pyrene	0.6	0.7	0.3	0.6	0.4	0.1	0.8	0.3	1
Fluoranthene	3	7	12	33	13	18	28	6	20
Benzo(a)pyrene	2	1.8	6	23	13	6	8	2	5
Benzo(b)fluoranthene	1.8	4.5	8	33	17	6	9	4	8
Benzo(k)fluoranthene	1.5	0.7	6	15	13	9	4	3	5
Perylene	-	-	-	-	-	-	-	-	6
Indeno(123cd)pyrene	1.5	3	0.8	23	10	3	1.5	1	1.8
Benzo(ghi)perylene	1.8	0.7	0.8	14	17	2	6	1.2	4
Benzo(a)anthracene	-	-	-	-	-	-	-	-	7

Table 1.6 Representative composition of exhaust gases in ppm by volume

From Peiki and Ramsden

	Pollutant	Idling	Accelerating	Cruising	Decelerating
Petrol engines	Carbon Monoxide	69000	29000	27000	39000
	Hydrocarbons	5300	1600	1000	10000
	Nitrogen Oxides	30	1020	650	20
	Aldehydes	30	20	10	290
Diesel engines	Carbon Monoxide	Trace	1000	Trace	Trace
	Hydrocarbons	400	200	100	300
	Nitrogen Oxides	60	350	240	30
	Aldehydes	10	20	10	30

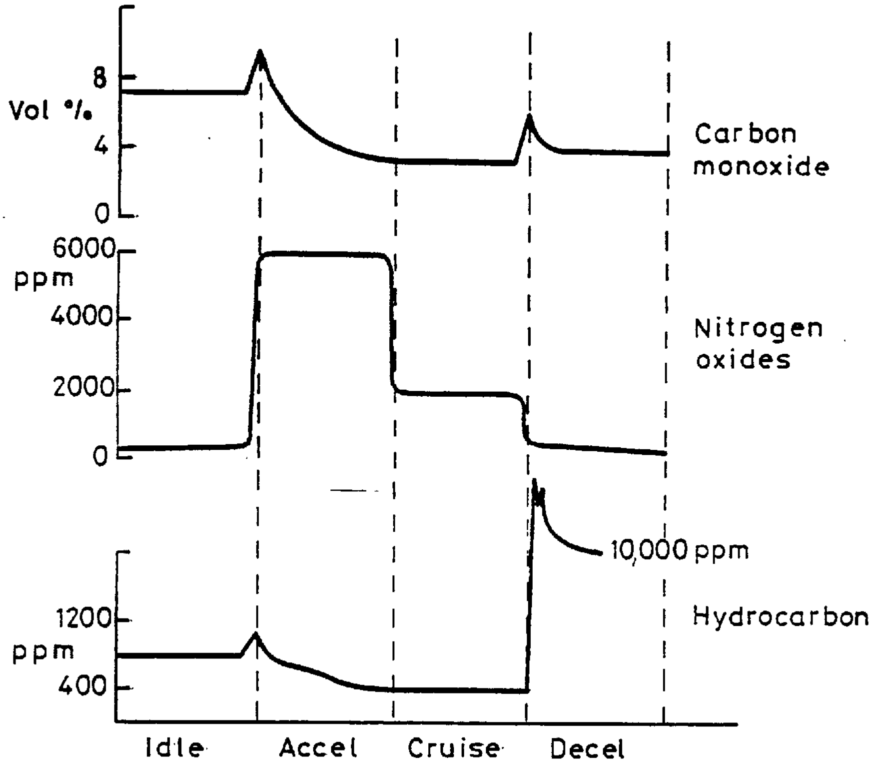


Fig 1·7 Exhaust emissions and driving mode

Many of the problems associated with diesel engines in relation to the control of the particulate matter can be ascertained from fig. 1.8. From this it can be seen that smoke emissions can be minimized if operation is limited to development of 90% of the possible power rating. Such a system together with careful maintenance would eliminate many of the characteristic problems associated with heavy goods vehicles. Certain additives including barium sulphonate, are used in diesel fuel and it would be expected that the formation of characteristic oxygen and sulphur compounds could account for some of the characteristic odorous materials produced in a diesel exhaust. A significant amount of work has been undertaken in this area (35), but the chemical changes involved are extremely complex and no definitive conclusions have been reached as to the structure of the materials causing the problems.

The anomalous control problems associated with road vehicles also apply to the control of emissions from aircraft although differences do occur with engine design.

Figure 1.9 illustrates the situation for gas turbine engines (36) and emphasizes the relationship between oxides of nitrogen and the other major pollutants in the various operating modes.

1.3 The Contribution of Individual Sources to Air Pollution

As a prerequisite to any control implementation by legislation it is necessary to know the contributions made by individual sources to the total atmospheric burden. Inventories of this type, involving the major combustion sources have been carried out in many developed countries. Table 1.7 gives a summary of the UK emissions for both stationary and mobile sources as a percentage of the total atmospheric burden (11,37).

The relative contributions of the sources involved have changed significantly over the last decade following implementation of the Clean Air Act. It must be borne in mind, however, that motor vehicles can contribute proportionally substantially more than the table below might imply in the vicinity of the busy street itself.

Work undertaken in the UK (11,38) has attempted to evaluate precisely the contribution made by motor vehicle pollution to the

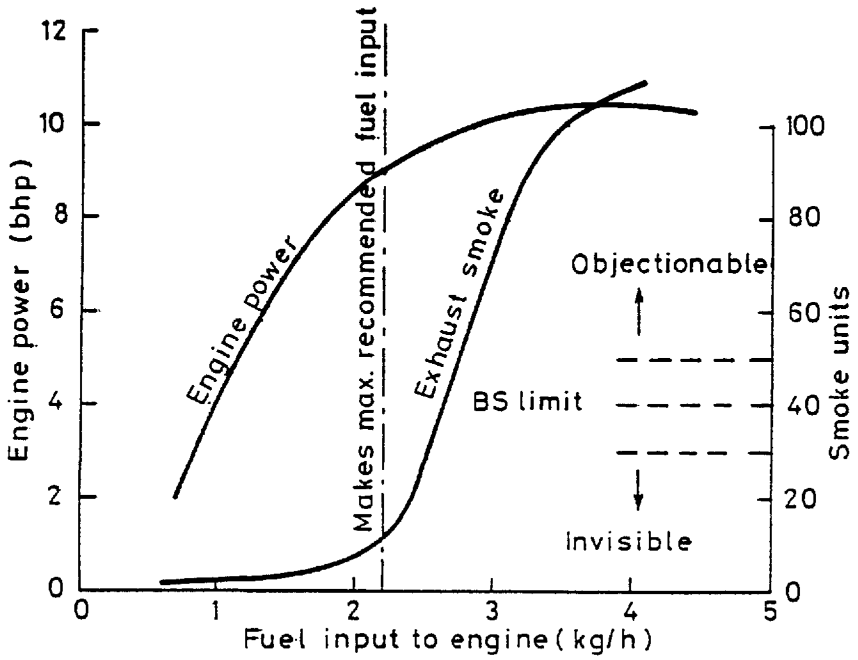


Fig 1·8 Effect of fuel input on power and exhaust smoke of diesel engines

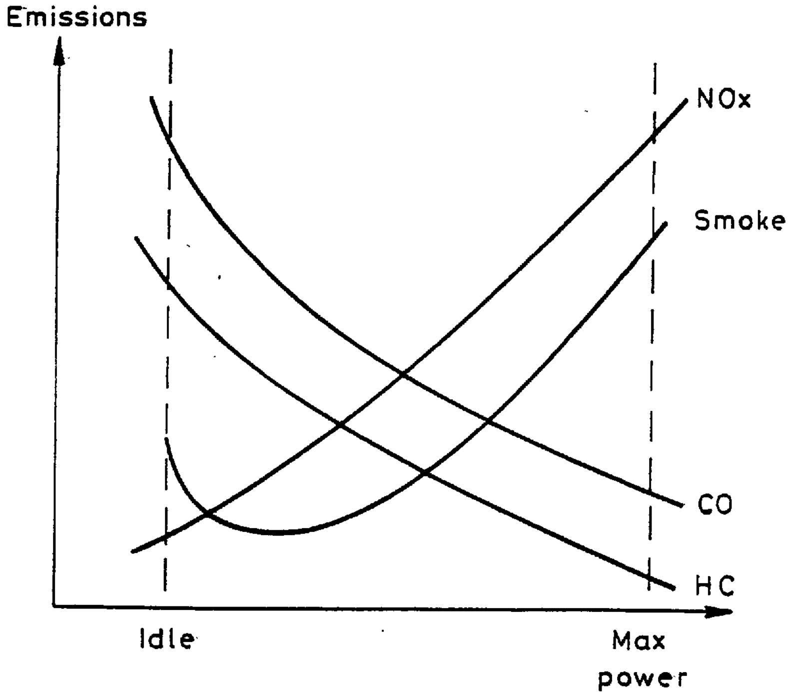


Fig 1·9 Emission characteristics of gas turbine engines

Table 1.7 Summary of estimated UK emissions of selected pollutants for 1976 per cent

Source	SO_2	NOx (as NO_2)	CO	HC	Smoke
Mobile (road)	1.0	25.8	87.5	31.6	23.9
" (rail)	0.4	2.5	0.2	0.9	
Power stations	54.0	44.9	0.6	1.1	-
Commercial + Industrial	39.0	23.5	0.6	1.2	7.6
Domestic	5.6	2.8	8.4	1.6	68.5
Incineration	-	0.2	0.6	0.2	-
Agricultural burning	-	0.2	2.2	3.0	-
Evaporation etc.	-	-	-	60.3	-

air quality of busy streets. The long term character of the survey undertaken gives a good indication of the concentration of air pollutants experienced in a busy street over a wide range of meteorological conditions. Table 1.8 presents these data and it can be seen that

Table 1.8 Hourly mean concentrations measured during the working week (Monday-Friday, 0700-1900) from 1974-5

	Percentiles of the cumulative frequency distribution					
	50th		90th		99th	
Pollutant	Kerbside*	Urban** Background	Kerbside*	Urban** Background	Kerbside*	Urban** Background
THC† (ppm)	4.0-5.5	3	8.5-11	6	14-18	10
CO (ppm)	4-6.5	3	9-16	5	15-30	8
NO (pphm)	5.5	3	23	8	54	18

* THC and CO values cover 5 cities; NO values for London only

** Inner-London off-street value

† Expressed as equivalent ppm methane and includes natural methane background (∿1.5 ppm median value)

the variations between pollutants in the daily and longer term pollution pattern give some indication of the relative responsibility of mobile and stationary sources to pollution levels. Sulphur dioxide measurements in London have indicated that motor vehicles make only minor contributions to kerbside SO_2 levels.

On the other hand table 1.9 indicates the substantial contribution made by vehicle to kerbside levels of smoke and lead. In areas where smoke control is rigidly enforced motor vehicles also contribute the major part of the urban background concentrations and it has been demonstrated by other studies (39,40) that motor vehicles are contributing between 40-50% of measured smoke depending on location and meteorological conditions.

Table 1.9 Ranges in measured annual mean smoke and Pb concentrations ($\mu g\ m^{-3}$)

Pollutant	Kerbside	Urban Background
Smoke	70-100	25-35
Pb	2-5	0.5-1.0

It is difficult to determine the proportional contribution from motor vehicles of NO_2 but it seems likely that motor vehicle emissions of NOx make a smaller proportionate contribution of NO_2 at the kerbside than to NO.

1.4 Air Pollution Control Trends in Legislation

Concern about air pollution in relation to industrial growth is now widespread. International bodies such as the World Health Organization (WHO) and the European Community (EEC) have actively encouraged even the poorer developing countries to give consideration to it in industrial planning and urbanization. Priorities however vary from country to country and in evaluation of the controls to be adopted the relative economic considerations influence policies adopted (41,42).

The degree and nature of industrial development together with climate and topography have all influenced the mode of approach (43,71).

1.4.1 Fixed Sources

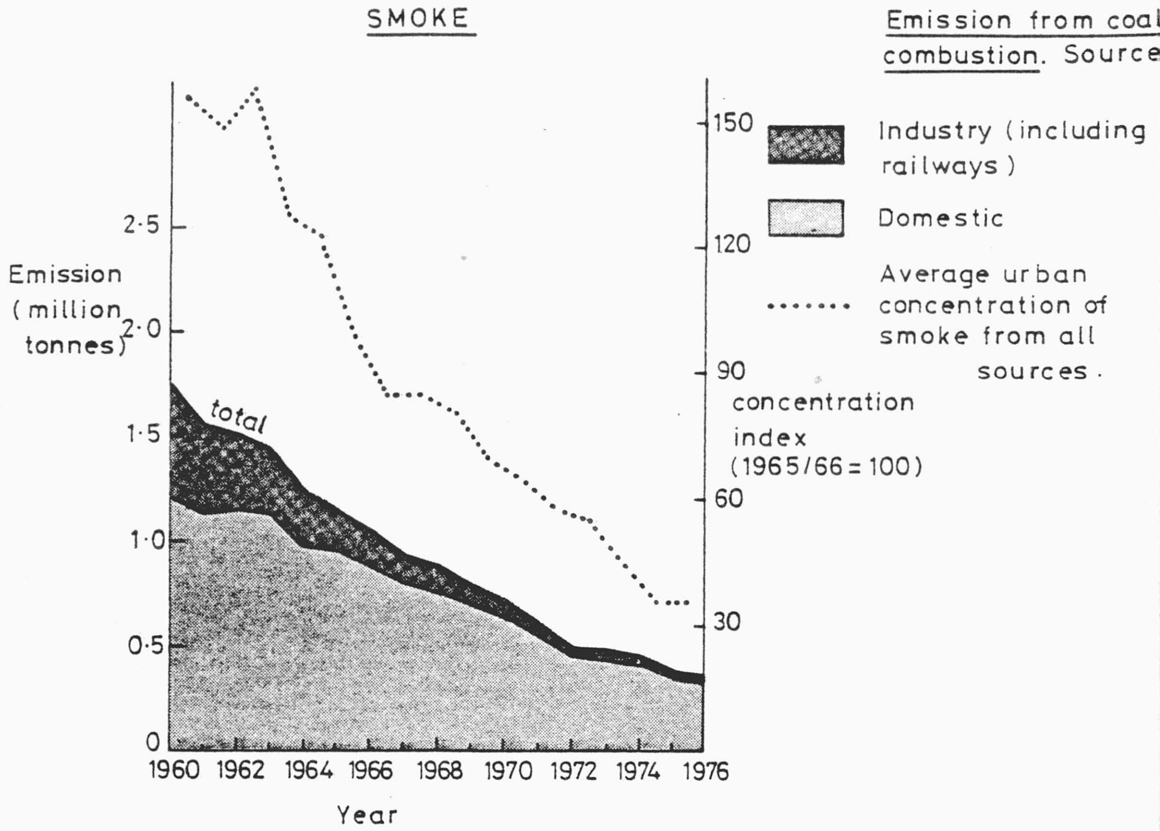
Approaches to control in the United States and the United Kingdom differ significantly in that the former centres its legislation around the definition of air quality standards (44) whilst the latter adopts a policy of variable emissions dependent upon the location and type of plant involved and the best practicable means available for control.

Such an approach developed from the 1863 Alkali Act which was subsequently extended to include a whole series of major scheduled industries.

Enactment of the Clean Air Act in 1956 (45) lead to greater emission controls with emphasis being given to sulphur dioxide and smoke reduction.

Although fixed air quality standards have never been adopted in the UK, the last 20 years have seen a dramatic improvement (Fig. 1.10) in air quality and in the main the development of a responsible attitude by major industry in dealing with these problems (12).

The difference of approach in the UK has been well justified as demonstrated by the result achieved, and the costs involved have been very considerably lower than those in the USA. The problems in that country however are completely different and relate predominantly to the formation and persistence of photochemically produced materials. It has been demonstrated for instance (46) that under favourable meteorological conditions levels of photochemical oxidants exceeding the USA National Air Quality Standards of 0.08 ppm for one hour can occur in such diverse regions as Alaska, Russia, Holland, Japan and Australia. This type of data and the emphasis given to it in the literature, illustrates the tremendous impact that the US Environmental Protection Agency have had in setting the trend for similar approaches to legislation in other countries. It must be emphasized however that photochemical reactions can vary greatly according to the types of organic materials present in the atmosphere and the influence of such factors as humidity and dust upon the photochemical chain of



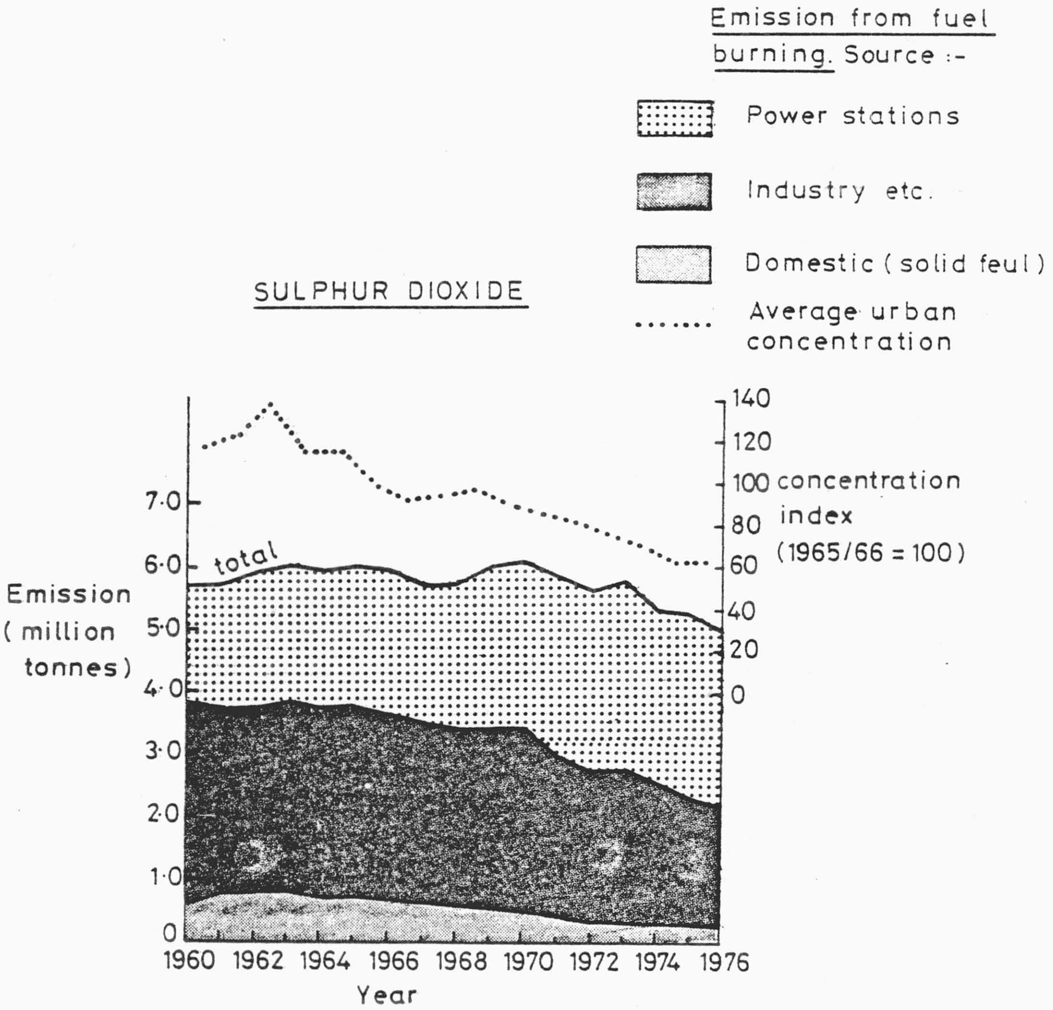


Fig 1·10 Smoke and sulphur dioxide trends in emissions and average urban concentrations reactions. Further, the relative contribution made by stationary and mobile sources varies immensely and in no way can California be considered typical of other world situation.

The importance of considering individual photochemically active materials was demonstrated as early as 1950 when the Los Angeles Air Pollution Control District implemented controls in the emission of butadiene which, in 1966,were subsequently responsible for the now well known rule which restricted severely the use of highly photochemically reactive organic materials as solvents.

Federal activity through the auspices of EPA have been responsible for air quality standards based upon air quality criteria summarized in table 1.10 (47).

Table 1.10 Federal ambient air quality standards

Pollutant	Time Concentration	Primary	Secondary
Carbon monoxide	maximum 8-hr " 1-hr	10 $\mu g/m^3$ 40 $\mu g/m^3$	10 $\mu g/m^3$ 40 $\mu g/m^3$
Non-methane hydrocarbons - as methane	maximum 3-hr (6-9 am)	160 $\mu g/m^3$	160 $\mu g/m^3$
Nitrogen dioxide	annual arith.mean	100 $\mu g/m^3$	100 $\mu g/m^3$
Sulphur dioxide	" " " maximum 24-hr " 3-hr	80 $\mu g/m^3$ 365 $\mu g/m^3$	60 $\mu g/m^3$ 260 $\mu g/m^3$ 1300 $\mu g/m^3$
Particulates	annual geom.mean maximum 24-hr	75 $\mu g/m^3$ 260 $\mu g/m^3$	60 $\mu g/m^3$ 150 $\mu g/m^3$

Similar trends are prevailing in almost every developed and industrialized country and has been reported by the Organization of Economic Cooperation and Development (OECD) that 11 of the 24 incorporated nations have air pollution control legislation (48).

1.4.2 Mobile Sources

1.4.2.1 Legislation

Control of gaseous exhaust emissions from motor vehicles was first intorudced in the USA in 1966 owing to the persistent problems of photochemical smog in California.

A schedule of the proposed reduction in emission is presented in Table 1.11.

Table 1.11 Trends in US Federal Legislation governing automobile emissions

	CO	HC	NO_2	Particulate emissions	Evap. g/test
	grams per mile				
1970	23	2.2			6
1971	23	2.2			2
1972	39	3.4			2
1973	39	3.4	3.6		2
1974	39	3.4	3.0		
1975	15.0	1.5	3.1	0.1	2
1976	3.4	0.41	3.1	0.03	2
1977	3.4	0.41	0.4-1.5		

The comparative ease of control for hydrocarbons (HC) and carbon monoxide (CO) in relation to oxides of nitrogen (NOx) is demonstrated in this table and it can be seen that when NOx controls were introduced in 1973 it was only done by a relaxation of the HC and CO limits.

The US Clean Air Act of 1970 had required the automobile to achieve a 90% reduction in pollutant levels by 1975, which lead to a dramatic series of optimizations prior to the introduction of major new innovations such as the catalytic converter and the thermal reactor.

In those earlier days, owing to environmental pressures being imposed, little attention was paid to the fuel utilization consequences of achieving environmental controls. Further considerable controversy existed in calculating at each stage of control contribution made by vehicles in relation to the total emissions from other sources (49,50). This applied particularly to controls of NOx from 1977 onwards.

Whilst the USA was undoubtedly the leader in controlling vehicle exhaust emissions, other countries including Canada, Japan and Australia soon followed. Indeed, Japan formulated her own test procedures somewhat along the lines of that developed by the EPA for the USA.

The European nations under the auspices of the Economic Commission for Europe (ECE) developed its own test cycle, sampling and measurement procedures. These were quite substantially different from those which evolved in the USA but they represented more closely the European situation.

Although no specific legislation was introduced in the UK, directives issued by the ECE are now complied with.

There are thus three main test procedures being employed for vehicle certification which include:

(a) U.S. Federal test cycle (both the 1973 and the 1975 modified one)

(b) European test cycle (ECE-15)

(c) Japanese test cycle

The US Federal test driving cycle is based on a nonrepetitive cycle, typical of a US urban driving pattern (fig. 1.11). This cycle was modified in 1975 by incorporating a hot start and repeating the first 505 seconds of the cycle after an interval of 10 minutes. A sample of the diluted exhaust is taken at a constant rate throughout the test (CVS), collected in an inert bag and analyzed for HC, CO and NOx (flame ionization-FID-for HC, non dispersive intra red-NDIR-for CO and chemiluminescence for NOx).

The ECE-15 Type I test, is based on an iterative model drive cycle (fig. 1.12). All raw exhaust gas emitted is collected in a large inert bag and analyzed for HC, CO and NOx. (HC with NDIR, CO with NDIR and NOx with a chemiluminescence technique). In new proposals for the ECE-15 04 test, where lower emission standards are included, it is expected that NDIR will be replaced by FID for HC monitoring.

The Japanese test procedure is based on a CVS (constant volume sampling) technique, with exhaust emission levels measured over two different cycles:

I A cold start 11-mode cycle
II A hot start 10-mode cycle

This is illustrated in fig. 1.13. In the cold start the cycle is iterated four times with gas collection and subsequent analysis as in the US Federal test. For the hot start the vehicle is pre-conditioned by running at a nominal 40 Kmph for a minimum of 15 min. Then one 10-mode cycle is driven with gas collection and analysis as before. In the Japanese certification procedure there are also separate evaluations of idle test hydrocarbons and carbon monoxide emissions.

In considering the trends in vehicle emission controls from an international standpoint, many countries have adopted one of the above test procedures but with a definition of emission limits that lag behind the US standards by several years. Sweden and Australia for instance, have adopted the 1973 US Federal standards representing at least a five years delay in relation to the US. On the other hand in the US individual states have the right to decide more stringent standards than those applying federally and table 1.12 illustrates the difference between California and the other 49 states as projected over the next three years.

Table 1.12 US 49 states and California standards

g/mile

Model Year	49 States			California		
	HC	CO	NOx	HC	CO	NOx
1979	1.5	15.0	2.0	0.41	9.0	1.5
1980	0.41	7.0	2.0	0.41	9.0	1.0
1981	0.41	3.4	1.0	0.41	3.4	1.0 or
1982/1983	0.41	3.4	1.0	0.39-0.41	7.0	0.7
				0.39-0.41	7.0	0.4 or
				0.39-0.41	7.0	0.7

Influenced by very different climatic conditions, Canada, although using the US Federal testing procedure,has suggested emission limits for vehicles manufactured between 1975-1985 as the HC - 2g/mile, CO - 25 g/mile and NOx - 3.1 g/mile, a situation that relates approximately to 1974 US Federal standards.

The fundamental difference of approach exists with the ECE

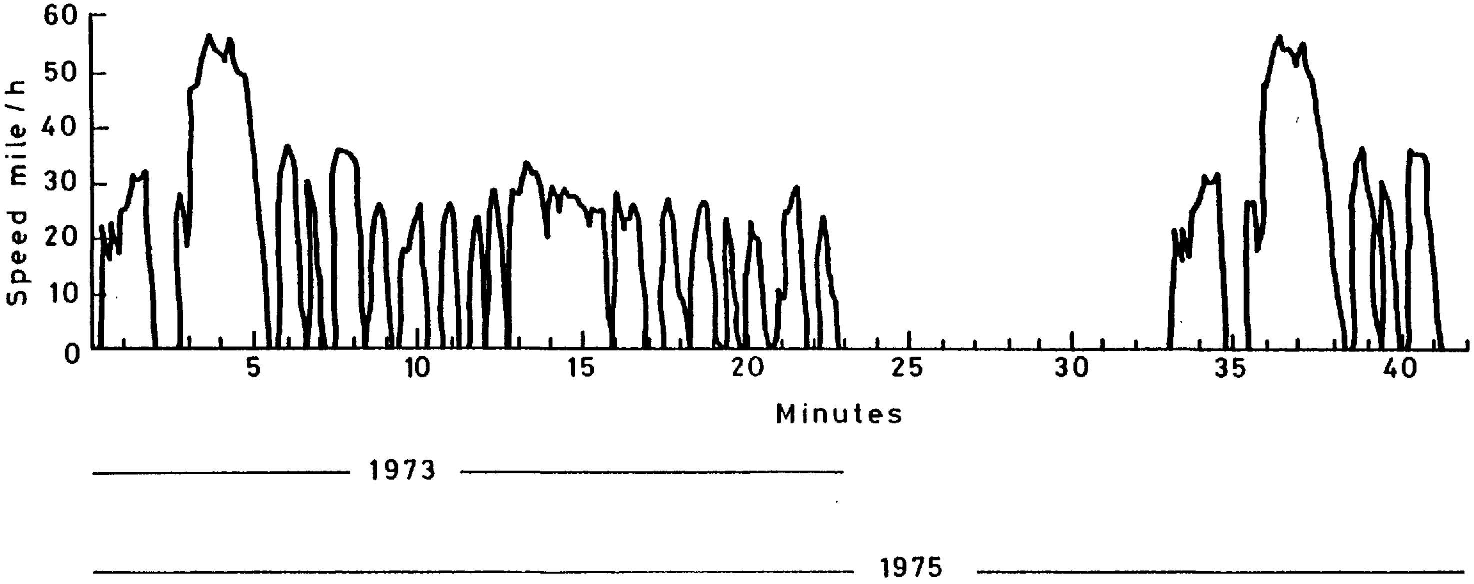


Fig 1·11 The 1973 and 1975 U.S. Federal test cycle

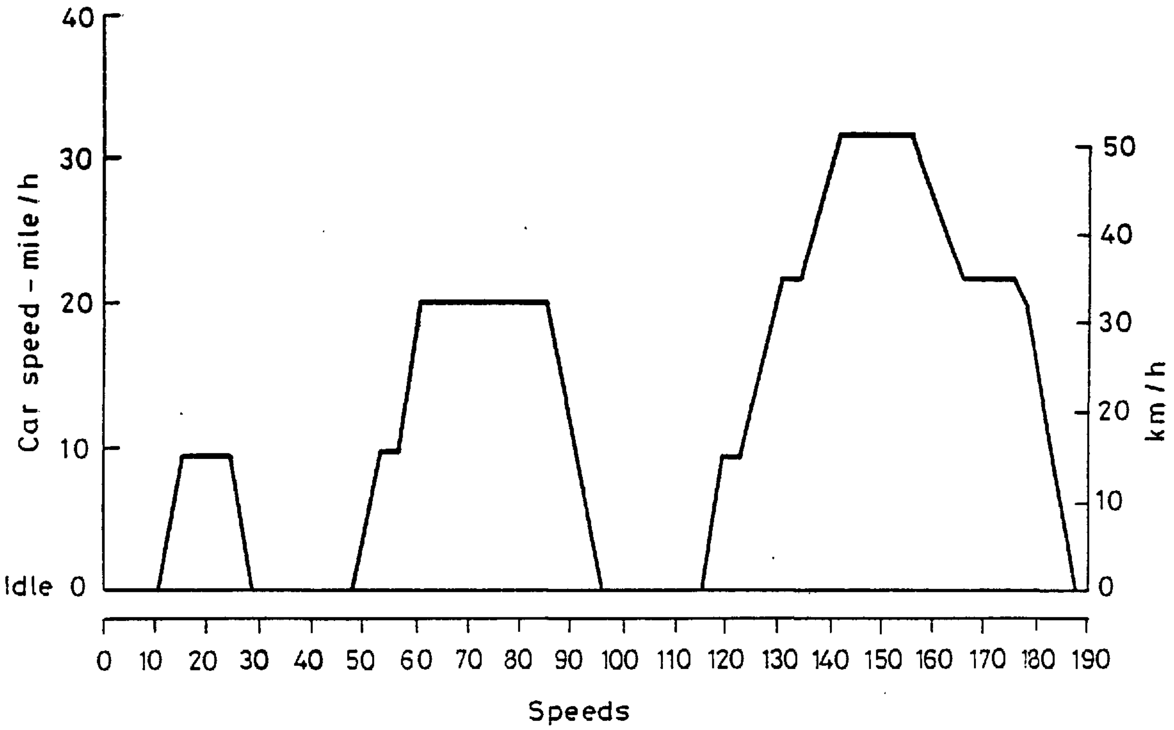
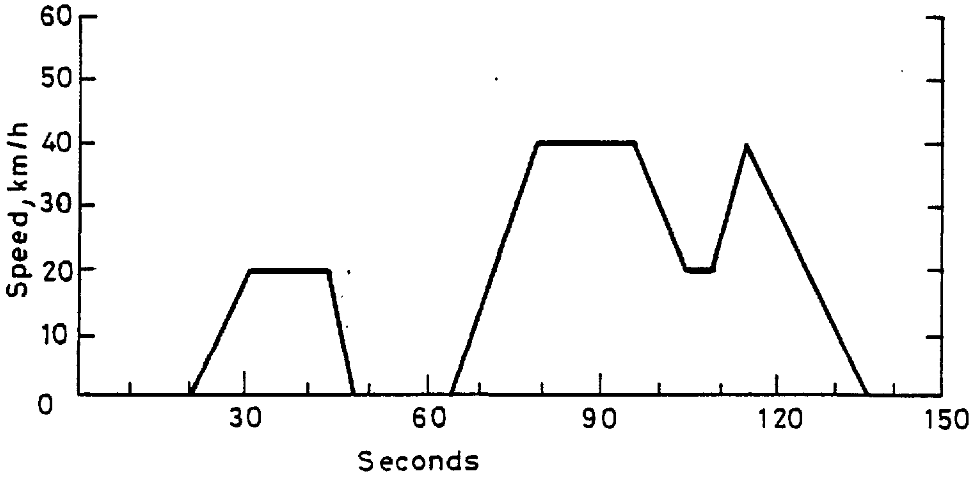
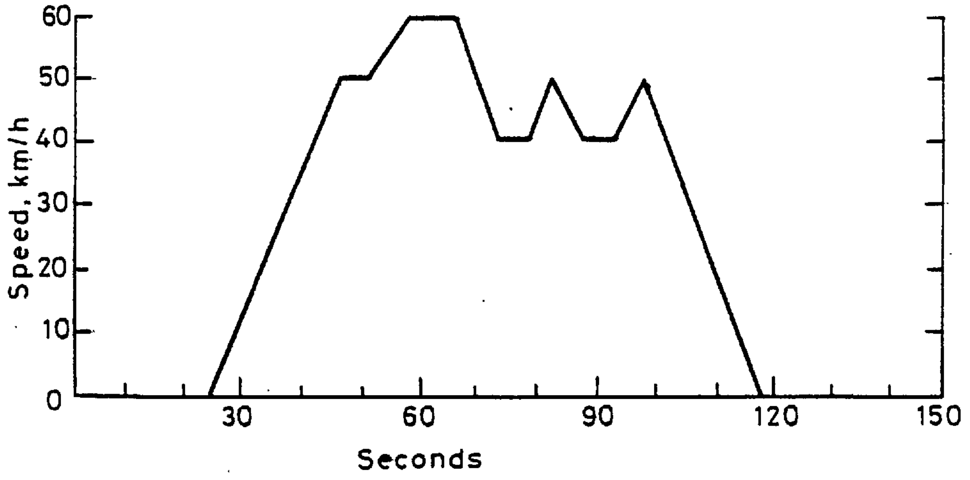


Fig 1·12 The European test cycle



10-MODE CYCLE



11-MODE CYCLE

Fig 1·13 The Japanese test cycle

countries, in that emission limits defined for the ECE-15 cycle are related in addition to the weight of the vehicle (table 1.13). This table also illustrates the proposed difference in test procedure described above.

Table 1.13 ECE - 15 standards

g/test

Reference weight (Kg)	ECE-15 03a from 1.10.1979			ECE-15 04b proposed	
	HC	NOx	CO	HC+NOx	CO
< 750	6.0	8.5	65	19.0	58
750 - 850	6.3	8.5	71	19.0	58
850 - 1020	6.5	8.5	76	19.0	58
1020 - 1250	7.1	10.2	87	20.5	67
1250 - 1470	7.6	11.9	99	22.0	76
1470 - 1700	8.1	12.3	110	23.5	86
1700 - 1930	8.6	12.8	121	25.0	93
1930 - 2150	9.1	13.2	132	26.5	101
> 2150	9.6	13.6	143	28.0	110

a : Big bag test - HC by NDIR
b : CVS testing - HC by FID
Combined HC+NOx standards

Many other countries are adopting the ECE limits including Austria, Switzerland, Spain, Czechoslovakia, East Germany, Finland, Hungary, Yugoslavia, Romania and USSR. The stringency of the proposed emission limits is inversely related to the size of the car and as such is giving rise to controversy at present owing to the energy implication.

The Japanese situation is presented in table 1.14 and the comparative trends in the control of the vehicle exhaust emissions are shown in fig. 1.14 which emphasizes in particular the difference between the US and European situation (51).

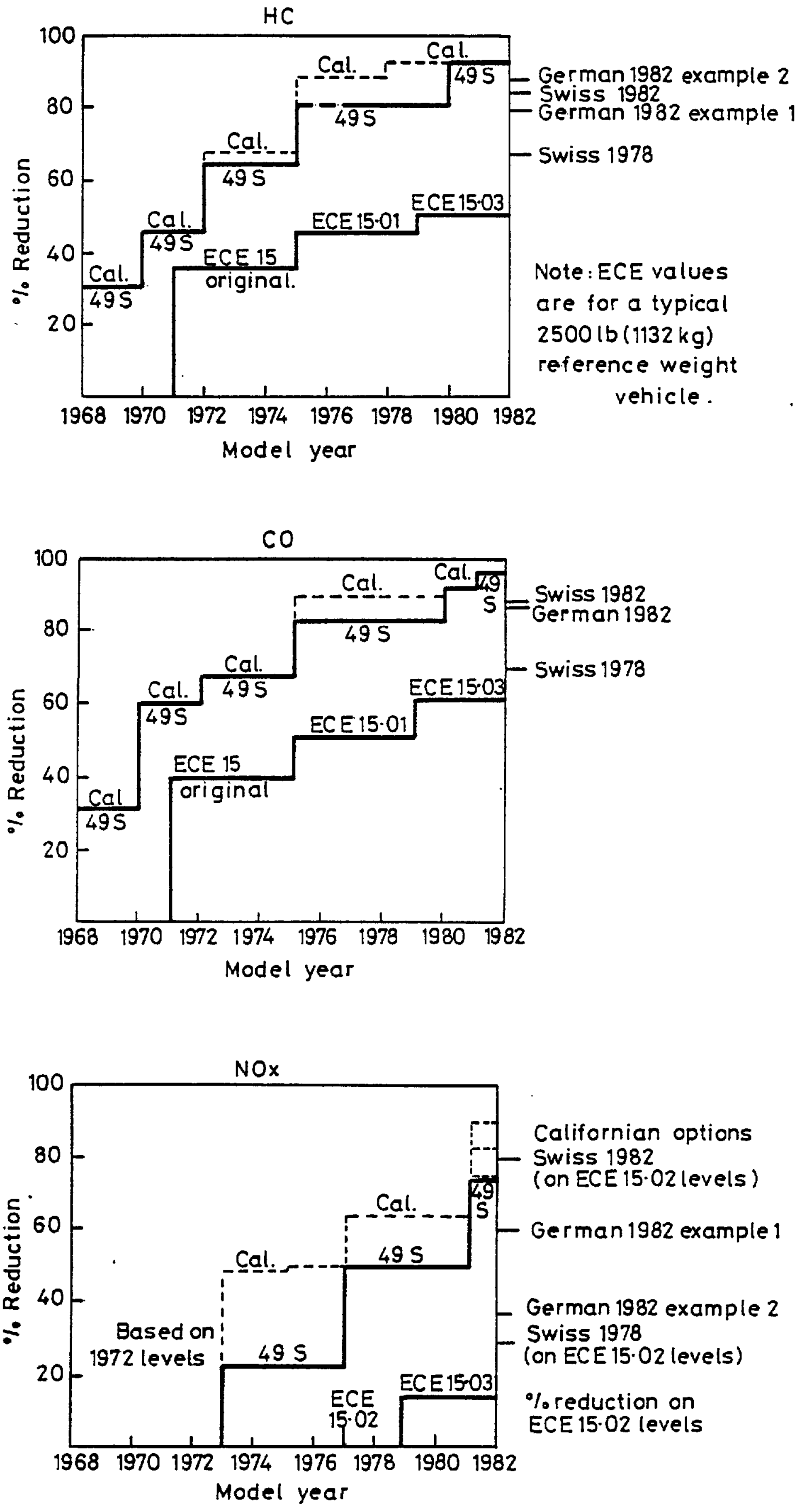


Fig 1·14 Comparative trends on HC, CO and NOx for Europe, U.S. 49 States and California standards

Table 1.14 Japanese standards

	$g\ Km^{-1}$			g/test		
Model Year	10 mode hot start test			11-mode cold start test		
1978-1980	HC	CO	NOx	HC	CO	NOx
maximum	0.39	2.7	0.48	9.5	85	6.0
average	0.25	2.1	0.25	7.0	60	4.4

1.4.2.2 Controls

The major emissions from an uncontrolled vehicle are illustrated in Fig. 1.15.

Techniques for control of emissions can be divided into two categories. The first of these includes the simple optimization procedures typical of those introduced in the US in the early 1970's. In the main, the costs involved are minimum in relation to the percentage reduction achieved. Figure 1.16 illustrates several of these controls including:- optimization of air to fuel (A/F) ratios, crankcase blow-by controls (CC), exhaust gas recirculations (EGR), evaporative controls, combustion modification (52,53,67).

These controls could be defined as preventative techniques.

To achieve the reductions to the emission levels required for the late 1970's in the USA additional control techniques are necessary and these are taking the form of hang-on devices such as the Thermal Reactor or the Catalytic Converter. These more sophisticated techniques ensure more complete oxidation of the exhaust gases, aided by additional air injection, prior to the secondary reaction zone (59).

The choice between these two alternative techniques has proved to be a controversial issue and depends much upon the ultimate reduction required. Of great significance to the European situation particularly is the lead related issue because of the larger numbers of small cars utilizing high compression ratio engines that are involved. Until recently use of a catalytic converter automatically precluded use of lead alkyls in petrol owing to the poisoning of a catalytic system involved (2, 54). Thus in the USA it was considered necessary to introduce catalytic converters in order to achieve the

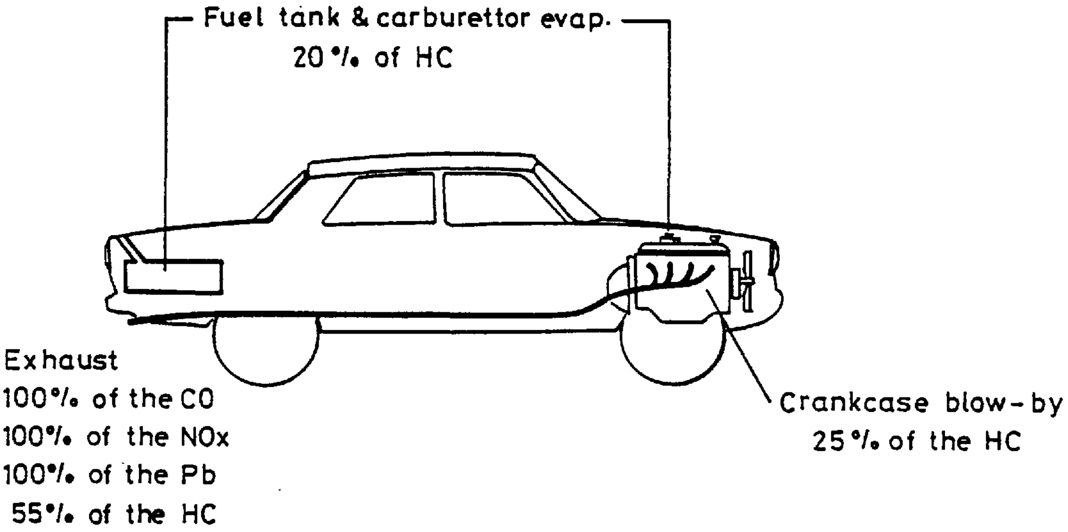


Fig 1·15 Approximate distribution of automobile emissions by source

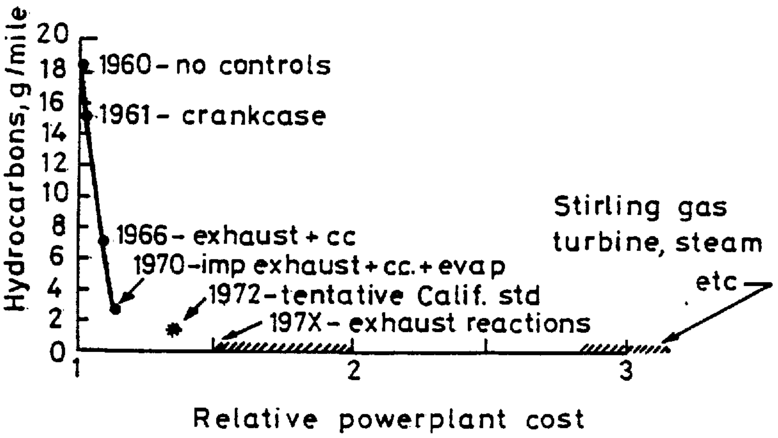


Fig 1·16 Hydrocarbon reduction economics California vehicles extremely stringent standards projected for the late 1970's and early 1980's (55, 56, 57).

Figure 1.17 illustrates the typical thermal reactor system incorporating air injection into the manifold (58).

Following initial design problems use of this system incorporating a lead trap or filter was demonstrated as a viable alternative to the catalyst system in all but the most stringent requirements for NOx removal (52) and use of these reactors will undoubtedly continue in many countries. However with the much larger engines frequently at lower compression ratio than those used in Europe the need to retain lead was not so critical.

Catalytic converters on the other hand operate most effectively under conditions of constant gas flow and temperature (fig. 1.18). The initial ones used on vehicles were the oxidation type and usually consisted of an active metal (Pt, Rd, Rh) on an inert substrate of high surface area (gamma alumina). Clearly these catalysts can only be used in new vehicles as they are readily poisoned by traces of such materials as Pb, S, P and as such critical control of the fuel input to the vehicle is necessary (55). For catalytic decrease of the primary pollutants (HC, CO, NOx) from vehicles, oxidation is required for HC and CO whereas reduction is required for NOx (Fig. 1.19).

This dual purpose function caused great technical problems in controlling vehicle emissions and it is only more recently that an effective three-way catalyst operating under a carefully controlled A/F ratio has been produced (57).

Initial introduction of catalytic systems lead to problems of sulphur trioxide (SO_3) formation and acid mist (60). This serves to emphasize the complexity of evaluating alternatives which must be clearly related to the conditions of a particular country and a clear definition of the air quality standards required.

A similar issue in control is related to the use of lead alkyls in petrol. These materials can be used to increase the octane value of a particular fuel whilst allowing for the use of more efficient high compression ratio engines (61,65). In addition to lead alkyls (TML, TEL) additives 1,2 dichloroethylene (EDC) and 1,2 dibromoethylene (EDB) are used as scavengers for the lead. Thus a

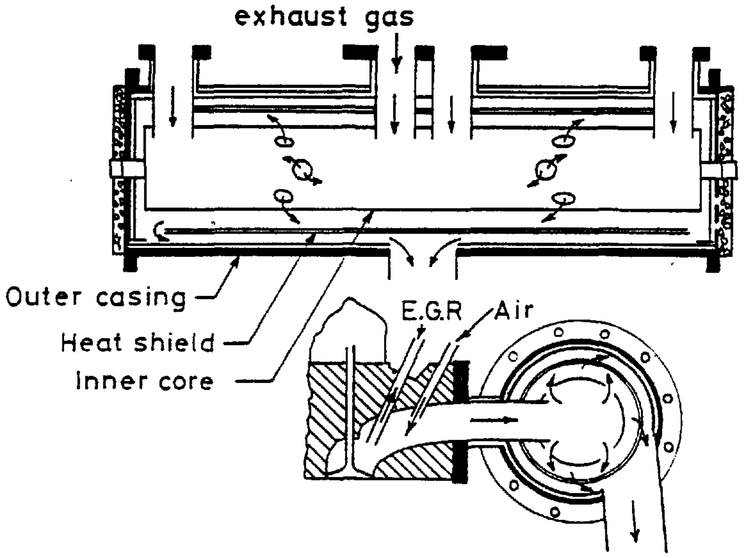


Fig 1·17 Typical thermal reactor incorporating air injection into the manifold

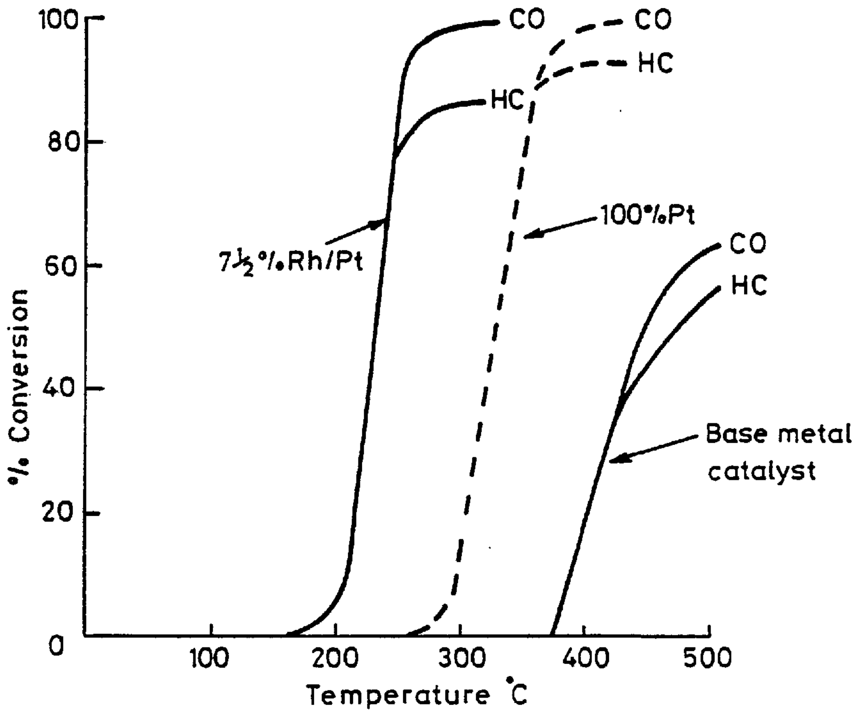


Fig 1·18 Effect of gas temperature on a catalyst performance

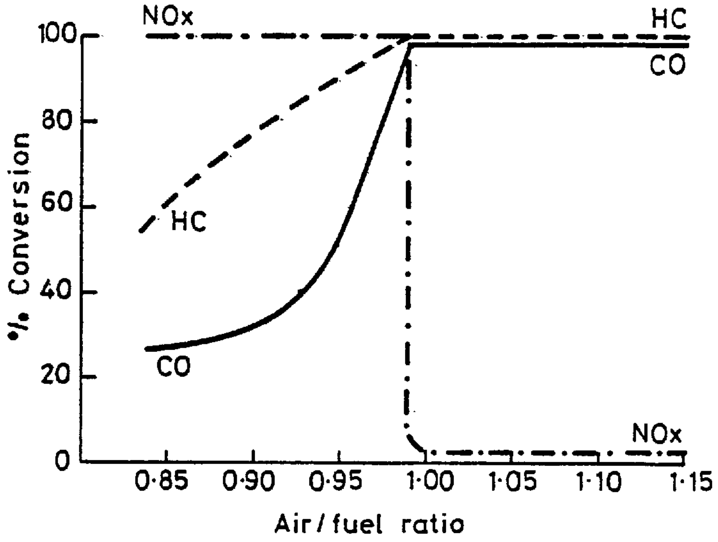


Fig 1·19 The effect of A/F ratio on the CO, HC, NOx concentration efficiency of a catalyst typical additive composition used in high octane petrol would be Pb:Cl:Br in a mole ratio of 1:1:0.5.

Emission from lead compounds from the exhaust will occur with lead being mainly in the form of its halides and oxide (30) although other forms of the compounds are possible (22,62,63).

Much has been written on the health effects of lead although controversy still exists as to the part lead emissions from vehicles play in relation to the health of an urban community (64). Most countries are however attempting to ensure that the total levels of lead emitted do not increase and this has resulted in a successive decrease in the use of lead alkyls in such countries as Sweden.

Control of emitted lead has been demonstrated by the use of a lead trap instead of a conventional silencer. Figure 1.20 demonstrates such a device which contains a bed of alumina pellets inducing agglomeration and growth of lead particulate to larger particles although different types have been demonstrated (52).

More recently, a further combination of exhaust controls has become viable with the development of lead resistant catalyst (15,66). These have been evaluated on the dynamometer studies with cycles of operation extending to an equivalent of 25,000 miles.

1.4.2.3 Energy Considerations with Respect to Emission Controls

Much of the work of the early 1970's took little account of the energy implications related to environmental controls and it is a matter of conjecture as to whether the USA would adopt the same control policies again if making the decisions now (51,68).

Even in the mid 1970's the economics of utilizing leaded fuel with high compression ratio engines and thermoreactors was compared to that of using catalytic converters with low compression ratio vehicles and unleaded fuel (fig. 1.21).

Although view points on this subject could be biased according to the source of the information it is clear that the earlier controls imposed resulted in a considerable loss in fuel economy (fig. 1.22) (69).

The overall energy implications have now, however, become

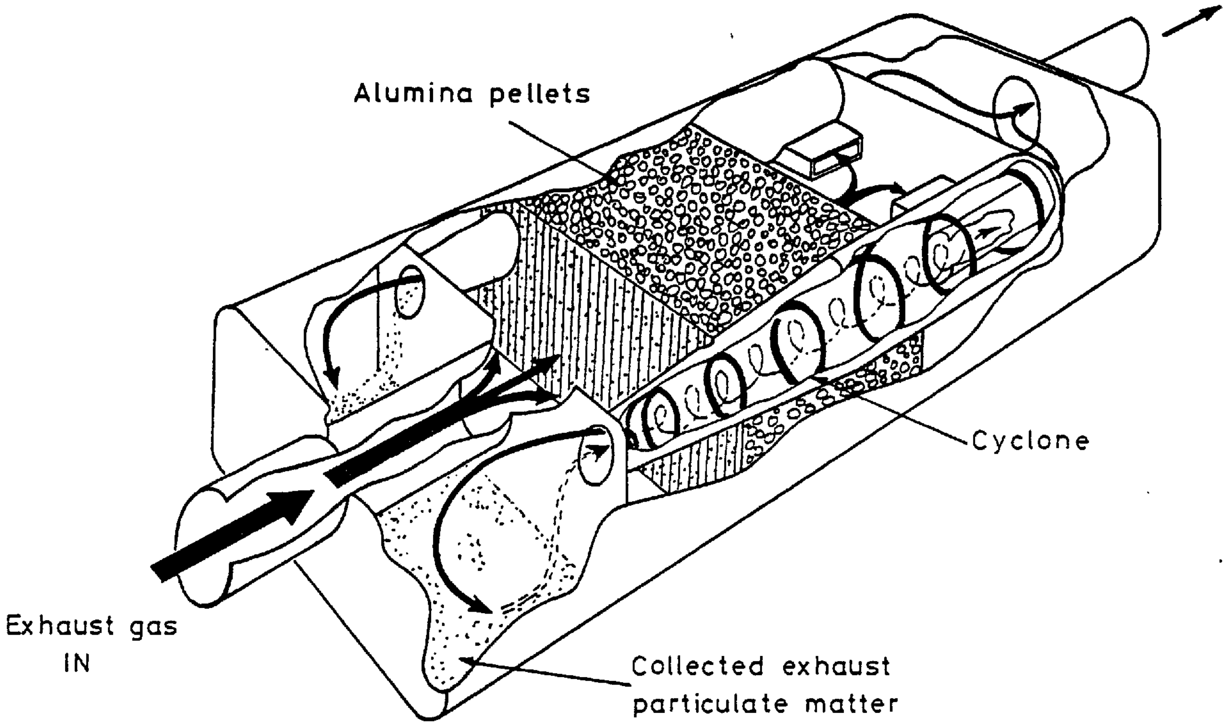


Fig 1·20 A lead trap (Du Pont)

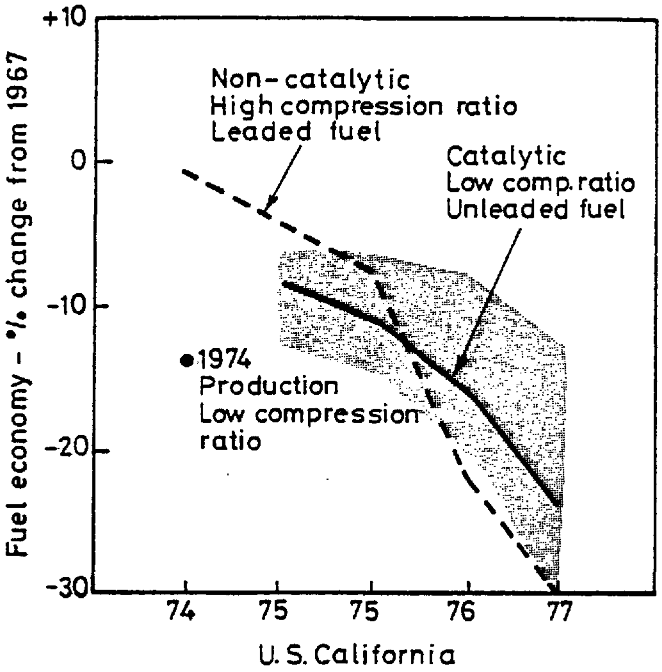
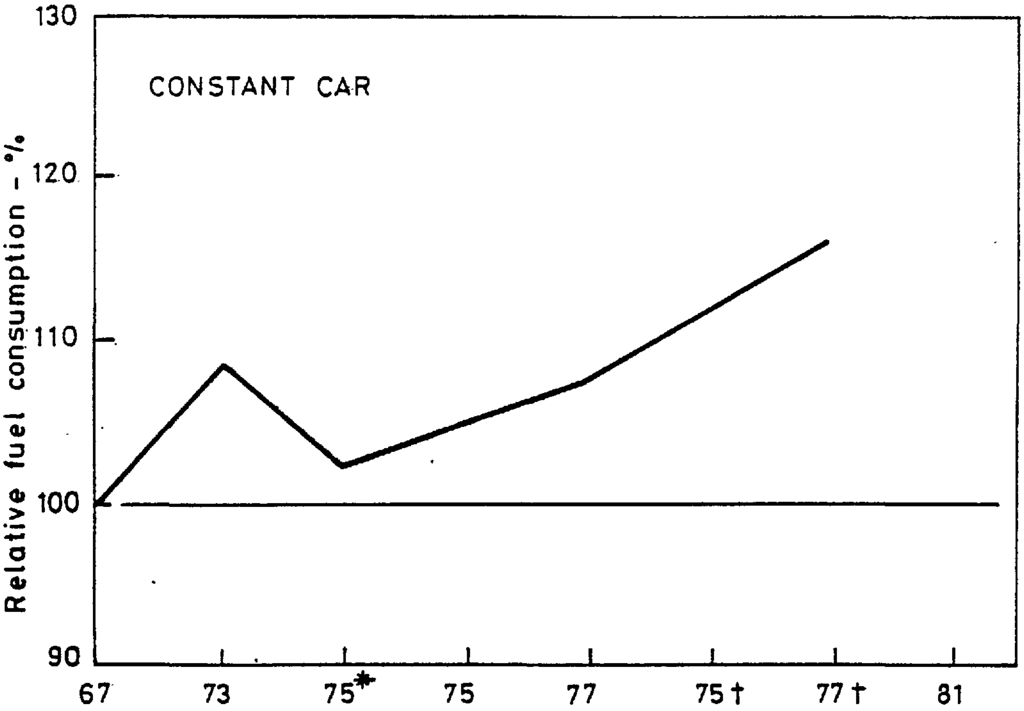


Fig 1·21 Comparison of the effect of catalytic & thermal emission control systems on fuel economy



	67	73	75*	75	77	75†	77†	81
CO	87	28	25	15	15	9·0	9·0	3·4
HC	7·6	3·1	2·0	1·5	1·5	0·9	0·4	0·4
NOx	3·4	3·1	3·1	3·1	2·0	2·0	1·5	1·0

*CAN †Cal.

Fig 1·22 Effect of emission standards on fuel consumption more apparent and in looking at projected controls in the next two to three years, clearly these energy factors will play an increasing role (51,68,69,70).

1.5 Objectives of the Research Programme

Many of the problems of air pollution control relate to a detailed knowledge of the materials present in the atmosphere and to an understanding of the mode of generation and subsequent reaction.

The setting of air quality standards together with a definition of emission limits for both stationary and mobile sources relies heavily upon the ability to specifically relate a particular pollutant concentration to its source or sources of emission. In this context many of the analytical procedures in routine use are deficient.

As such, research objectives are defined as follows:-

(a) Development of specific and sensitive analytical techniques for the determination of individual hydrocarbons (HC) and halogenated hydrocarbons (HCXn) in ambient air.

(b) Evaluation of the contribution made by these HC and HCXn to total hydrocarbon levels in various air pollution situations.

(c) Utilization of the analytical techniques developed in (a) in order to determine relative source contributions to total atmospheric loadings.

(d) Evaluation of techniques for determining the levels of the concentrations of both individual HC and HCXn materials in vehicle exhaust under varying conditions of engine operation and loading.

(e) Utilization of the same techniques to estimate the relevance of the concentration of the halogenated compounds in street air and to assess the possibility of utilizing the ratios of HC to HCX concentrations in identifying source contributions.

(f) To examine in detail a major airport as a multiple combustion source with the intension of attempting to identify the contribution made by the aircraft to the total atmospheric concentrations involved.

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CHAPTER 2 : ANALYTICAL TECHNIQUES

2.1 Introduction

Hydrocarbons and halocarbons of concern occur in the atmosphere at low concentrations, in the range of parts per million (ppm) to parts per trillion (ppt).

Accordingly, accuracy and precision in the analytical techniques used are essential. In much of the work that has been carried out and is reviewed here, insufficient attention has been paid to the concepts of repeatability and reproducibility as exhibited in both the laboratory and the field.

Many complex procedures for both sample collection and final evaluation have been proposed and used for isolated studies. Unfortunately however their very complexity has precluded their use for extensive data acquisition.

The variation throughout the year of such factors as humidity and temperature, has been inadequately catered for in many of the procedures cited, particularly where adsorption procedures are being used as a precollection method for pollutants at low concentrations.

Much of the recent published work relating to hydrocarbon and halocarbon analysis emphasizes the care that is necessary in setting up and proving the procedure adopted. This extends in particular to the selection of inert materials for use in the air sampling train and to the adoption of low blank reagents for use in the analytical procedures.

The development of such analytical instrumentation as Gas Chromatography (GC) and Mass Spectrometry (M/S) has provided means for the separation, identification and determination of trace materials with great sensitivity.

In environmental analysis the major problems of assessment relate to the sampling procedure used for pollutants and in particular to the storage and transfer of the samples in a suitable form into the analytical instrument.

In addition artifacts on repetitive analysis can be caused by deficient sampling techniques.

Many of the procedures adopted by other workers illustrate these problems and these are reviewed chronologically over the period of the mid 1960's to the present.

As early as 1962, Stephens and Scott (1) in a study of the relative reactivity of various hydrocarbons in polluted atmospheres, suggested three viable instrumental methods for the final evaluation. These included long path infrared spectrometry, gas chromatography and mass spectrometry. Although the concentration procedure used involved a cold trap, these workers were unable to provide definitive identification at atmospheric concentrations of less than 20 ppm.

In a later study, Lonneman et al. measured aromatic hydrocarbons in the atmosphere of the Los Angeles basin and reported concentrations of 0.033 ppm for benzene, 0.071 ppm for toluene and 0.012 for ethylbenzene (2). The pollutants were trapped on either 40-50 mesh Analabs (Tee-Six) Teflon, or glass beads and desorbed into an open tubular chromatographic column and identified by Flame Ionization techniques (FID).

Long path spectrophotometry was used by Glasson et al. in an investigation of the reactivity of airborne hydrocarbons which contribute to photochemical smog (3). A routine procedure for chromatographic analysis of Automotive hydrocarbon emissions, has been described by Dimitriades and Seizinger (4), who identified 165 components, whereas qualitative and quantitative investigations involving C_6-C_{20} volatile organic substances in the air of Zürich were undertaken by Grob and Grob (5). To trap the organic materials a specially designed filter was used containing 25 mg of charcoal. High resolution gas chromatrophay coupled with mass spectrometry was used for the analysis of the extract from the charcoal filters using carbon disulphide.

Altshuller et al. (6) advanced the earlier adsorption techniques by the use of 10% Carbowax 1540 on gas Chrom Z instead of glass beads (2). Support bonded silicones on various types of chromosorb were then used by Aue and Teli (7).

High speed collection of organic vapours from the atmosphere on chromosorb 102 and transfer to a gas chromatograph through a special injector needle was developed by Dravnieks et al. (8) with a reported reproducibility of ±3%.

Examination of toluene to benzene ratios for over one thousand air samples was first undertaken by Pilar and Graydon (9), who reported ratios of 2.4:1. The samples were transferred into a conventional packed chromatographic column by heating specially designed cold traps.

An evaluation of Porapak P, carbosieve, Tenax GC for the adsorption of organic volatiles from the air was undertaken by Zlatkis et al. (10) and a modified injection port with a valve for the insertion of the sample into the GC was described. Sampling on a porous polymer in ambient temperature, followed by direct heating desorption into a packed column has been described in detail by Mieure and Dietrich (11). Ambient concentrations for more than 30 compounds were reported. Preconcentration of volatiles from the air on Tenax GC and transfer to the analytical column of a GC coupled with M/S has been reported by both Novotny (12) and Berget (13).

Raymond and Guichon (14) compared hydrocarbons C_8-C_{18} found in Paris air to those found previously by Grob (5) in Zürich. These workers used graphitized carbon black to trap the pollutants and the analysis was carried out by a gas chromatograph coupled to a mass spectrometer.

For the separation of the less volatile C_6-C_{12} hydrocarbons the use of a gas chromatograph fitted with a SCOT column was suggested by Rasmussen et al. (15), after an evaluation of a wide range of columns.

Lonnerman et al. also, carried out a study of the diurnal patterns of hydrocarbons in urban air (16). For the individual aromatic hydrocarbons a trap packed with glass beads was used and a three valve injection to the chromatographic column system was described.

A rigorous evaluation of existing techniques for sampling and analysis was undertaken by Bertsch et al. (17) who concluded that aromatic hydrocarbons should be trapped on a porous polymer, preferably Tenax GC and transferred to a GC column through a condensation trap. An alternative approach involved the development of a programmable cryogenic gas chromatograph and this has been described by Giannovario et al. (18). This approach compared with the cryogenic separation was described by Cooper et al. (19).

Pellizzari et al.,based on their previous work (20,21) on resolving a sampling technique, used Tenax GC to collect organic vapours in the ambient air of Houston and Los Angeles. The vapours were thermally desorbed into a capillary column and analyzed by gas chromatography - mass spectrometry with an on line computer. More than one hundred species were identified but levels of these pollutants are not reported (22).

The application of thin-layer chromatography to the detection and analysis of trace amounts of aromatic hydrocarbons has been investigated by Hunter (23) and has been shown to have very limited application.

Sampling tubes packed with different packings were used by Russel (24) for concentrating organic pollutants from air. The collected pollutants were thermally desorbed into a conventional packed column of a GC with an FID. The suitability of various packings - Tenax GC, Porapak N, Carbosieve B, Porapak R and 20% DC-200 silicone oil on CWHP support - for collecting and concentrating specific compounds was shown by determination of breakthrough volumes and recovery values. A chromatographic system was described by Black et al. (25) permiting direct determination of hydrocarbons in a system employing four packed columns and a single FID.

A cryogenic preconcentration of volatile trace components in air samples was used by Wang et al. (26). Known environmental air samples were drawn through a trap at $-78^{o}C$ for 1 min. As the trap was warmed, the contents were swept into the mass spectrometry with methane for analysis in the chemical ionization (CI) mode.

A method has been employed by Louw and Richards (27), involving the use of gas chromatography combined with selective subtraction, infrared spectrometry and mass spectrometry. Selective subtraction involved the selective removal of certain types of compounds from a given air sample with suitable subtractor materials prior to gas chromatographic analysis. Samples were collected either on chromosorb pre-column or on charcoal sampler and extraction was following with carbon disulphide. Quantitative determinations showed that the concentrations obtained for a number of the C_1-C_{13} volatile compounds in the air of three large South African cities, were very similar to those reported elsewhere in the world.

A novel approach, the whisker-walled open tubular columns, involving deactivated silica whiskers, has been suggested by Schieke and Pretorius (28) for the separation of hydrocarbon mixtures, whereas properties and limitations of a highly efficient aluminium oxide coated column was described for analysis of hydrocarbon emissions (C_1-C_9) in ppb range of concentrations (29).

In 1978 Lonneman et al. carried out a three day study to investigate natural contributions to the overall hydrocarbon burden in Florida (30). Air samples were collected in Tedlar bags and analyzed by gas chromatography (16). Despite former assumptions, no significant natural hydrocarbon contribution was observed from samples collected within inches of citrus type trees.

The importance of changes in molecular structure following adsorption was emphasized in a study involving six porous polymers of chromosorb and Porapak types (31).

Mitchel and Deveraux (32), have suggested the simultaneous use of an FID, ECD and thermionic detector for a reliable air quality monitoring which requires selective sensitive detection of the traces of specific compounds, usually in complex mixtures in the atmosphere. Responses of these detectors to different types of chemical structure were discussed and evaluated.

An automated gas chromatographic technique has been reported by Hester and Meyer (33), to monitor benzene and alkylbenzene concentrations in ambient air, in sub-parts per billion. Multi-day benzene and toluene measurements have been made and typical concentrations in the range of 0.4 to 13 ppb have been reported.

Joffe et al. (34), reported a detailed comparative analysis of organic pollutants in the atmosphere of six large cities in the U.S.S.R. The qualitative composition of the hydrocarbons collected was relatively constant. Atmospheric C_4-C_{13} hydrocarbons were comprised of paraffins ($\sim$50%), aromatic compounds ($\sim$30%) and alkenes ($\sim$10-20%). The pollutants were adsorbed in a stainless steel tube packed with Carbochrome K-5 and PSKT - a material developed by depositing pyrocarbon on activated charcoal. Analysis was carried out by direct heating desorption into a copper capillary column linked to a mass spectrometer. Surprisingly high levels were reported up to 0.7 mg m^{-3}.

A novel technique utilizing two columns in parallel was used by Lukac (35) for the separation of C_1-C_{10} hydrocarbons from the ambient air whilst Sieck developed a technique for the partial quantification of aromatic and olefinic sample components of the air by a modification of chemical ionization mass spectrometry (36).

Denyazyn et al. (37) described a technique for the determination of C_6-C_{10} aromatic hydrocarbons which involved separation by a 60 m SCOT capillary column. Injection of the air sample occurred through a sample loop following cryogenic concentration on a trap packed with 60-80 mesh silanized glass beads.

A unique air sampling system has been developed by Freed (38), in which gaseous pentane is introduced into the air stream during sample collection. The mixed gases then pass through a cold trap maintained in liquid nitrogen, during which time the pentane vapour solidifies. Trace organic constituents of the air are trapped into the matrix thus ensuring efficient collection. The method was developed in particular to deal with problems of irreversibly adsorption on reaction on the surface of the solid sorbent when dealing with pollutants of high reactivity.

An organic vapour dosimeter was proposed by Bamberger et al. (39) as a means of sampling specific organic materials from industrial atmospheres. This technique which consists of a membrane mounted over a small container of activated charcoal relies upon the diffusion rate of the organic material concerned through the membrane. Quantification of the analytical data however proved to be somewhat problematical.

Comparatively little work has been undertaken on the analysis of halocarbons at ambient levels. It is only recently that the significance of the occurrence of these materials has been appreciated and now despite the apparently low levels that are involved it is important to understand far more about the nature of these materials and the way in which they disperse and react in the atmosphere.

The incorporation of the halogen material into the halocarbon matrix with its increased electron capturing capability renders these materials suitable to analyses by electron capture detection chromatotraphy. Murray and Riley (40) utilized this method.

The Du Pont de Nemours and Company have also described a method for the determination of ethylene dibromide in ambient air based upon adsorption into a charcoal sampling tube, desorption by dilution in carbon disulphide and quantitative analysis in an FID gas chromatograph (41).

Bertsch et al. (17), identified several halogenated compounds whilst Pellizzari et al. (22) detected 21 halocarbons by GC/MS technique. These include 1,2 dichlroethane and vinyl chloride but unfortunately quantitative data were not reported.

McConnel et al. (42) considered the problems associated with C_1 and C_2 chloroderivatives, with respect to estimated world production. Despite the millions of tonnes of each produced halocarbon, they concluded that these compounds only exist in the atmosphere at a background level in that they are rapidly degraded in the environment to carbon dioxide, water and the chloride ion. Subsequent gas chromatographic-mass spectrometric work by Grimsrud and Rasmussen (43) in a determination of 19 halogenated hydrocarbons in ambient air showed levels of 1,1 and 1,2-dichloroethane to be lower than 5 ppt.

The importance of vinyl chloride was emphasized by the development of the EPA of a tentative method for its determination in the atmosphere. The method proposed consists of an adsorption onto charcoal tubes followed by extraction with carbon disulphide and gas chromatographic analysis (44).

Preliminary studies undertaken by the same organization in 1975, attempted to quantify the levels of 1,2-dibromoethane (EDB) in urban air, in the vicinity of petrol stations and manufacturing plants. The reported concentrations were respectively 0.07-0.11 $\mu g.m^{-3}$, 0.2-1.7 $\mu g\ m^{-3}$ and 90-115 $\mu g.m^{-3}$, which suggested that EDB is present in ambient air at very low concentrations (45). Tenax GC was used in this work as a solid sorbent at subambient temperature and samples were analyzed after extraction with hexane by gas chromatography, using an analytical column packed with Carbowax 20 M. Two more extensive reports by EPA followed (46,47) which concluded that:

> "The principal use of EDB is consumptive and amounts entering the environment cannot be readily estimated. Very limited and preliminary air monitoring data suggest EDB is present in ambient air at very low concentrations. A significant environmental hazard does not appear to be present in regard to EDB; however, due to lack of available data documenting long term low level exposure in humans, the component cannot be considered environmentally innocuous".

The adsorption characteristics of airborne vinyl chloride on activated charcoal was examined by Guddeback et al. (48). The effluent from the charcoal tube was sampled by means of a stainless steel seven-port valve and analysis was carried out by a GC equipped with FID. McClenny et al. (49) also found great difficulty in determining vinyl chloride below 0.05 ppm. Even at this level these workers proposed a two stage analytical procedure involving initial separation from other components by gas chromatography, followed by detection of vinyl chloride utilizing its chemiluminescence reaction with ozone.

Hammarstrand (50) used gas chromatography with either an EC detector or an FID, for the determination of the same compound. The sampling procedures varied depending upon the concentration involved and included either direct injection using gas tight syringe or preconcentration on carbon, chromosorb 102 or Porapak Q followed by extraction with carbon disulphide.

Gas chromatography coupled with mass spectrometry was used by Bellar et al. (51), for detection of vinyl chloride in a range of concentrations 4-40 $\mu g.l^{-1}$. The compound was concentrated on silica gel or Carbosieve-B under non-cryogenic conditions.

In order to measure the exposure of personnell to vinyl chloride, Nelms et al. (52) utilized the permeation technique for sampling. The vinyl chloride was trapped onto charcoal having passed through a membrane. This procedure was subsequently developed to cope with ambient concentrations above 1 ppb.

An alternative approach utilizes the hydrogenation of vinyl chloride to ethyl chloride using different catalyst (53), whereas a selective GC column for the determination of the same compound in air, was developed by Krockenberger et al. (54), who verified their work in the presence of 21 possible pollutants.

The importance of halogenated materials in a photochemical chain was demonstrated by Gay et al. (55) who showed the range of reactivity of chlorinated ethylenes to be as: 1,1-dichloroethane > 1,2-dichloroethane > vinyl chloride.

Modifications in detector design allowed for the reevaluation of direct injection techniques (56). Subsequently Singh et al. (57) carried out a study to determine 11 anthropogenic and natural halocarbons in relation to the distribution, sources and sinks of these compounds in the atmosphere. Using gas chromatography with two independent frequency-modulated electron capture detectors, they analysed a great number of samples. Their conclusion was that the troposphere is contaminated with a number of halogenated compounds of predominantly anthropogenic origin in concentrations 0.1 to 1000 ppt.

Concentrations of halocarbons in rural air have been determined by Russell and Shadoff (58), using a sampling procedure employing preconcentration on a porous polymer. The samples were analyzed by a GC with ECD. Both quantitative and qualitative confirmation of the results (10-130 ppt) were achieved by GC/MS.

A simple method has been developed by Rasmussen et al. (59) for routine use in the analysis of atmospheric samples for halogenated compounds by GC/MS. In conjunction with sample concentration by freeze-out techniques determination of 11 halocarbons in a single analysis was feasible. Reported detection limits varied between 0.2 and 200 ppt.

A comparison of the performances of various adsorbents - Porapak Q, Porapak T, Tenax GC - and graphitized carbon black-Carbosieve C-HT - has been undertaken in respect of their retention capabilities towards chlorinated hydrocarbons (60). The conclusion reached was that carbopack is preferred as a stationary phase for the analytical column whereas Porapak Q and Tenax GC have the highest trapping capacity and they can be operated easily from very low to very high temperatures.

The separation of chloroethanes was further studied by Zilka and Matucha (61) using a temperature programmed GC with FID. Different stationary phases - OV-101, OV-17, SE-30 - were tested in a conventionally packed column.

Both atmospheric and vehicle emission work involving ethylene dibromide measurements, have been reported by Leinster et al. (62). Their techniques involved sampling on chromosorb 102 and direct heated desorption into a column packed with Carbowax 20 M using a GC equipped with an ECD.

The problems connected with the analysis of ultra-trace amounts of halocarbons in air were discussed in terms of trapping procedures, interferences and chromatographic columns, by Bruner et al. (63), who suggested an electron capture detector and carbopack B as a packing material for the analytical column. They concluded that thermal desorption procedures from porous polymers has several advantages over solvent extraction.

Batjer et al. (64) evaluated the relative merits of a split and splitless injection technique when using capillary columns for quantitative halocarbon analysis. They clearly demonstrated the reduction in error achieved with splitless injections.

Five different chromatographic columns were presented and evaluated for the separation of C_1-C_2 halocarbons by Knoll et al. (65). An investigation for the stability of four aliphatic halocarbons sampled in Tedlar bags showed that ethylene dichloride remained stable for one day whereas others including tetrachloroethylene and carbon tetrachloride remained stable for ten days.

Grimsrud and Miller (66), investigated the concept of oxygen doping which involves addition of this gas to the carrier involved in the chromatographic separation. Utilization of this procedure gave clear signal enhancement for many of the halocarbons of interest which is found to be reproducible and quantitative.

The necessity of avoiding contamination with laboratory air at the sampling and analytical stage was clearly demonstrated by Denyazyn et al. (37) who developed a sophisticated gas valve system to overcome the situation.

Very few correlation studies involving both halocarbons and hydrocarbons have been undertaken and only recently have one or two been reported.

Such a study was undertaken by Holzer et al. (67) who attempted to develop techniques for measurement of hydrocarbons, oxygenated materials and halocarbons in both rural and urban areas. A gas chromatograph was used with parallel flame ionization and electron capture detectors and coupling via a separator was also provided with mass spectrometry. Tenax GC, carbopack BHT and Ambesorb XE-340 were used as adsorbents in the sampling tubes allowing concentrations from the ppb to the ppt level to be determined.

A method for simultaneous analysis of 1,2 dichloroethane, 1,2-dibromoethane and benzene in air was reported by Jonsson and Berg(68) who used mass-fragmentography for ultimate detection and analysis.

Seifert and Ullrich (69) used a single column (10% OV-101 + 0.5% Carbowax 20 M on chromosorb 750) linked via a splitter to two detectors an FID and an ECD, for the determination of the two groups of compounds in the same samples. Tenax GC maintained at subambient temperatures was used at the sampling stage enabling even methane to be detected.

Simultaneous detection of hydrocarbons and halocarbons have been reported by Södergren (70), who used electron capture and flame ionization detectors linked in series. He concluded that a combination of ECD and FID could result in additional information to that obtained by a single detector.

Present and future trends in analyzing organic pollutants in ambient air, were discussed at the recent Conference on Sampling and Analysis of Toxic Organics in the Atmosphere, sponsored by the American Society of Testing and Materials (ASTM) and cosponsored by the Environmental Protection Agency (EPA) and other agencies (71). Ambient air is a complex mixture of hundreds of compounds mainly present in very low concentrations. The part of the analytical work which separates, identifies, verifies and quantifies these compounds is well understood but the same thing can not be said for the sampling which is still the weakest link of the analytical chain. It is fraught with problems of all kinds and in particular with the reactions of collected pollutants on adsorbents and the contamination of the sample during collection which produces artifacts of all types.

It is the demonstration of the occurrence of these artifacts that constitutes the main problem of many of the methods described above, particularly where little repetitive field work has been undertaken. It is this area of work therefore that is receiving greater attention at the present time and,for instance, as recently described, a method for collecting airborne nitrosamines in an artifact free technique, using a specially treated collection tube called Thermosorb/N™ (Thermal Electron Waltman, MA). Roumbehler (71) was able to show that these tubes collect and concentrate secondary pollutants in atmospheres containing precursors (primary pollutants) to these compounds. Unlike the other solid sorbents tested, there was not in situ artifact formation of the secondary amines. The collection tubes are now being field tested.

Jones (71) has also described another way to avoid artifacts during the sampling stage. This involves drawing the air directly into a gas chromatograph utilizing lasers as detectors. Additional work by the same man includes the development of a two-photon photoionization laser detector able to determine organics at the 1 ppt level without fluorescence, which,he claims, may eventually detect single molecules.

Sievers and Phillips (71,72) described an improvement in an electron capture detector that may eventually offer greatly increased sensitivities. It is called selective electron capture sensitization (SECS) and involves addition of nitrous oxide to the carrier gas.

This type of procedure plus the adoption of multiple techniques (73) illustrates the developments that are now taking place aimed at increased sensitivity and specificity in detection and the elimination of artifact occurrences in repetitive analyses.

2.2 Sampling Techniques

The process of sampling organic materials from the atmosphere is one of concentration with the requirement that the materials collected should not react further among themselves following collection. The two main techniques which are used for this purpose, utilize either cryogenic or adsorption preconcentration procedures.

Cryogenic trapping techniques have been widely adopted by many workers in air pollution analysis and have been frequently reported in the literature. The main problems encountered in adopting these techniques relate to the presence of water vapour in the atmosphere, which rapidly condenses prior to the cold trap, obstructing and altering the characteristics of the overall sampling operation.

The use of dessicants prior to the sampling tube reduces this problem but the choice of suitably inert materials for this purpose is limited (69). The use of liquid nitrogen as the cryogenic material has been shown to be essential for hydrocarbons of high volatility, mainly the ones in the C_1-C_6 range, although clearly the use of liquid nitrogen makes field work more difficult on a wide scale.

Adsorption techniques utilizing a solid sorbent is the preferred procedure for collection of higher molecular weight compounds (usually > C_6)(8,10,62,74,75), whereas their use for highly volatile compounds is severely limited.

The choice of adsorbent for use in a particular situation depends very much upon the chemical properties of the compounds to be sampled (76-80), and there is a range of different adsorbents in use including:

(a) Activated carbons

(b) Silica gel

(c) Support bonded chromatographic stationary phases

(d) Porous polymers

The parameters involved in assessing the performance of an adsorbent include those related to the sampling conditions, such as sampling time, air temperature and humidity and those related to the physicochemical properties of the adsorbent such as surface area, particle size, porosity, thermal stability and reactivity. Many of these properties are however interrelated.

Following adsorption, samples collected are removed either by extraction with an organic solvent or by direct thermal desorption.

The ideal situation would involve the use of an adsorption procedure, operating at ambient temperature, followed by rapid thermal desorption of the sample. This would allow for fast repetitive analytical evaluations.

Accordingly, development along these lines was accepted as the principle objective in the experimental preconcentration procedure and the following criteria were therefore evaluated in relation to the final choice of adsorbent:

(a) The flow rate achievable through comparably packed tubes

(b) The effect of water vapour upon adsorption and desorption processes

(c) The adsorption capacity

(d) The effect of sampling flow rate upon adsorption capacity

(e) The thermal desorption efficiency

(f) The thermal stability at high temperatures (up to 350^o)

(g) Desorption characteristics with respect to gas chromatographic resolution.

The range of solid sorbents used in this work included:

1. Activated carbon (ready purchased NIOSH tubes)
2. Carbopack C (0.2 Carbowax 1500 on 60/80 mesh Carbopack)
3. Supelkoport (1.5% OV_{17} + 1.95% QF-1 on 100/120 mesh Supelkoport)
4. Porapak Q, 80/100 mesh
5. Tenax GC, 60/80 mesh
6. Chromosorb 101, 80/100 mesh
7. Chromosorb 102, 80/100 mesh
8. Chromosorb 103, 80/100 mesh
9. Chromosorb 104, 60/80 mesh

All of these were used in extensive experimental work, but two, Tenax GC and chromosorb 102 were evaluated in detail.

2.2.1 Instrumentation

(a) Sampling Pumps

Three Du Pont constant flow pumps were used including: two P-4000, with a pumping range 20-4000 ml min^{-1} and one P-125 with a range 25-125 ml min^{-1}. These allowed known volumes of air to be sampled with confidence, in that sample collection rates were automatically regulated to constant preset flow rates (maintained to within 5%).

Additionally an M.D.A. Accuhaler sampling pump was used, with which the same volumes of air could be sampled over longer periods of time, in a non continuous mode (1.5 l in 1 hour).

Calibration and adjustment of the desired flow sampling rates were achieved by the use of a bubble flow meter and a flow rate indicator. Plate 1 illustrates the pumps and the calibration system used.

(b) Adsorption Tubes

Stainless steel tubes 4 × ¼ in o.d., were used for the solid sorbents and a number of sampling tubes were packed under identical

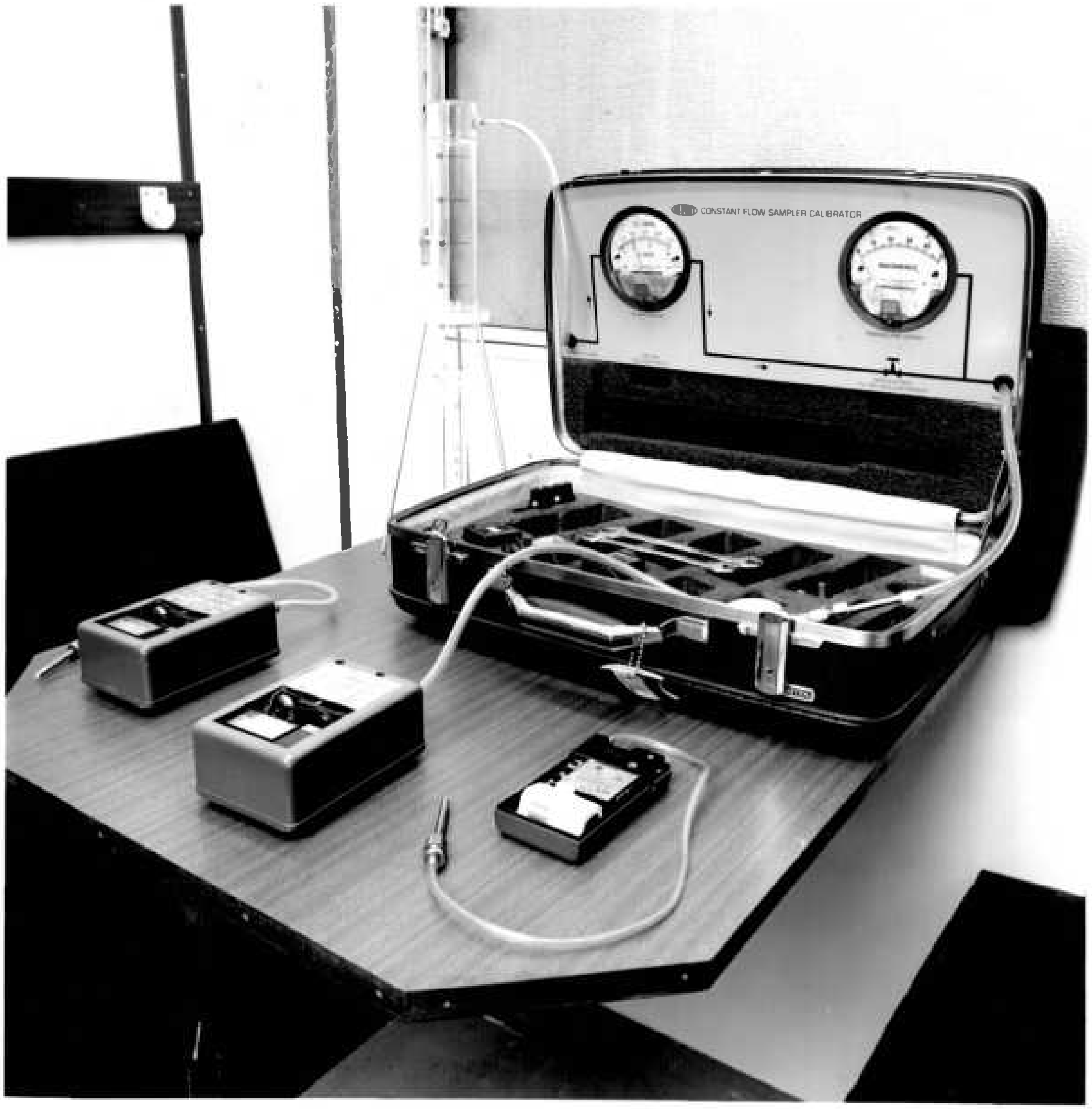


Plate 1 : Sampling pumps and calibration system

conditions of the above nine sorbents. Both ends were plugged with glass wool, and the tubes were conditioned with helium carrier gas at a flow rate of 20 ml min^{-1} at 230°-250°C. Prior to use, the tubes were repacked with the conditioned media in order to overcome problems of preferential gas channelling arising from the shrinkage of the polymers at the conditioning stage. They were then purged again for 30 min prior to use.

(c) Thermal Desorbers

Thermal desorption of the collected individual compounds was achieved by the use of two different types of ovens with their associated gas valve systems. The construction of these was based upon:

(i) The Carle oven

(ii) The Bendix Flasher

and are shown schematically in figure 2.1.

The Carle six port valve incorporated into the first system, allowed the carrier gas to be diverted either through the blank tube or through the sample tube. Temperatures achieved with this system were limited to 200-250°C.

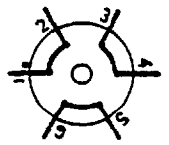
Higher and more constant temperatures, up to 350°C can be achieved by the second system which incorporated a more sophisticated gas sampling valve system.

In operation these systems were connected through the injection port to the analytical column of the gas chromatograph in such a way as to allow the smallest possible dead volume.

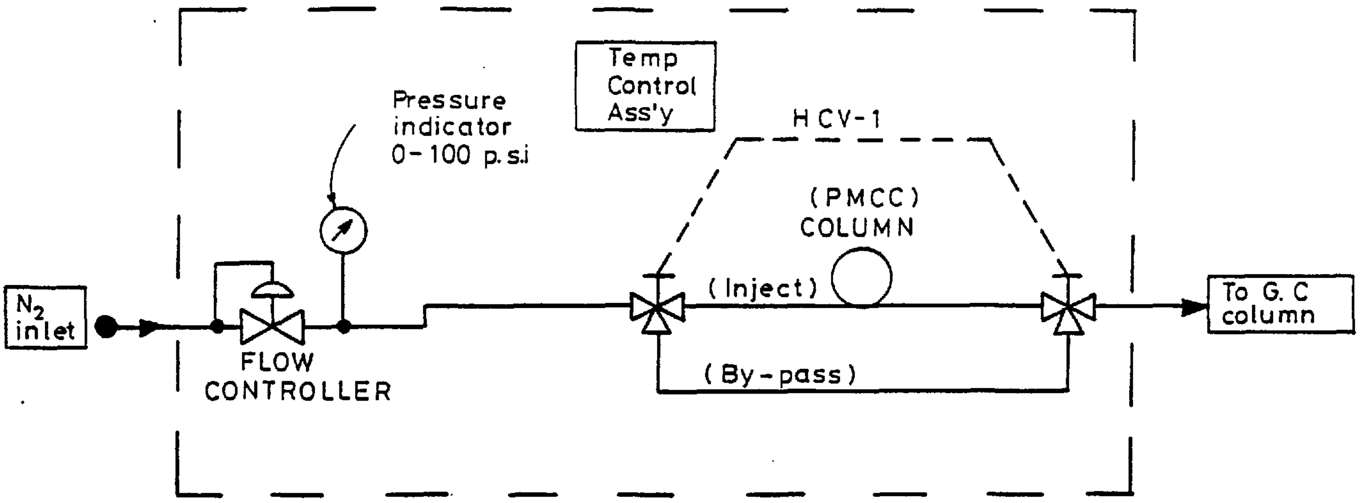
(d) Gas Chromatograph

A Hewlett Packard 5700 gas chromatograph equipped with a flame ionization detector (FID) was used for the analysis of the hydrocarbons. Separation of the compounds was achieved by a 20 ft × 1/8 in o.d. stainless steel column, packed with 3% OV_7 on chromosorb W (AW-DMCS). Helium was used as a carrier gas at a flow rate of 30 ml min^{-1}.

For the analysis of halocarbons the gas chromatograph was equipped with an electron capture detector (ECD) and the column used for separation was a 6 ft × 1/8 in o.d. stainless steel one, packed



THE SIX PORT
CARLE VALVE



BENDIX FLASHER

Fig 2·1 Thermal desorption systems

with 0.2% Carbowax 1500 on 60/80 mesh Carbopack C. Argon (95%) methane (5%) was used as carrier gas at the same flow rate as used above.

Chromatograms were recorded by use of either a Servoscribe recorder or a 3880 A Hewlett Packard integrator. Use of the integration facility allowed for the accurate recording of retention times for every eluted compound and integration of associated peak areas.

(e) Permeation Oven

An Analysis Automation 1901 permeation oven was used as a basis for calibration purposes. This allowed for variable temperature operation (up to 150°C) and appropriate dilution was achieved with the use of zero grade nitrogen.

The permeation oven together with other instruments already described is illustrated in plate 2.

(f) Mass Spectrometry

A Hewlett Packard 5930 A dodecapole Mass Spectrometer with an on line 5932 A data system was used for the definitive identification of the separated individual hydrocarbons and halocarbons studied. The chromatograph was interfaced to the mass spectrometer via a molecular separator (jet type).

Utilizing the standard software of the data system, normalized mass spectra of the individual compounds were obtained and in some instances improved analysis was obtained by reconstructing chromatograms with respect to characteristic ions derived from the compounds of interest.

2.2.2 Experimental Work

2.2.2.1 Preliminary Assessment of Adsorbents

A large number of analytical tests were carried out with the nine adsorbents, in order to select the two most promising adsorbents for further evaluation.

(a) Quantitative Adsorption/Desorption of Specific Compounds

Some six permeation tubes containing either hydrocarbons or

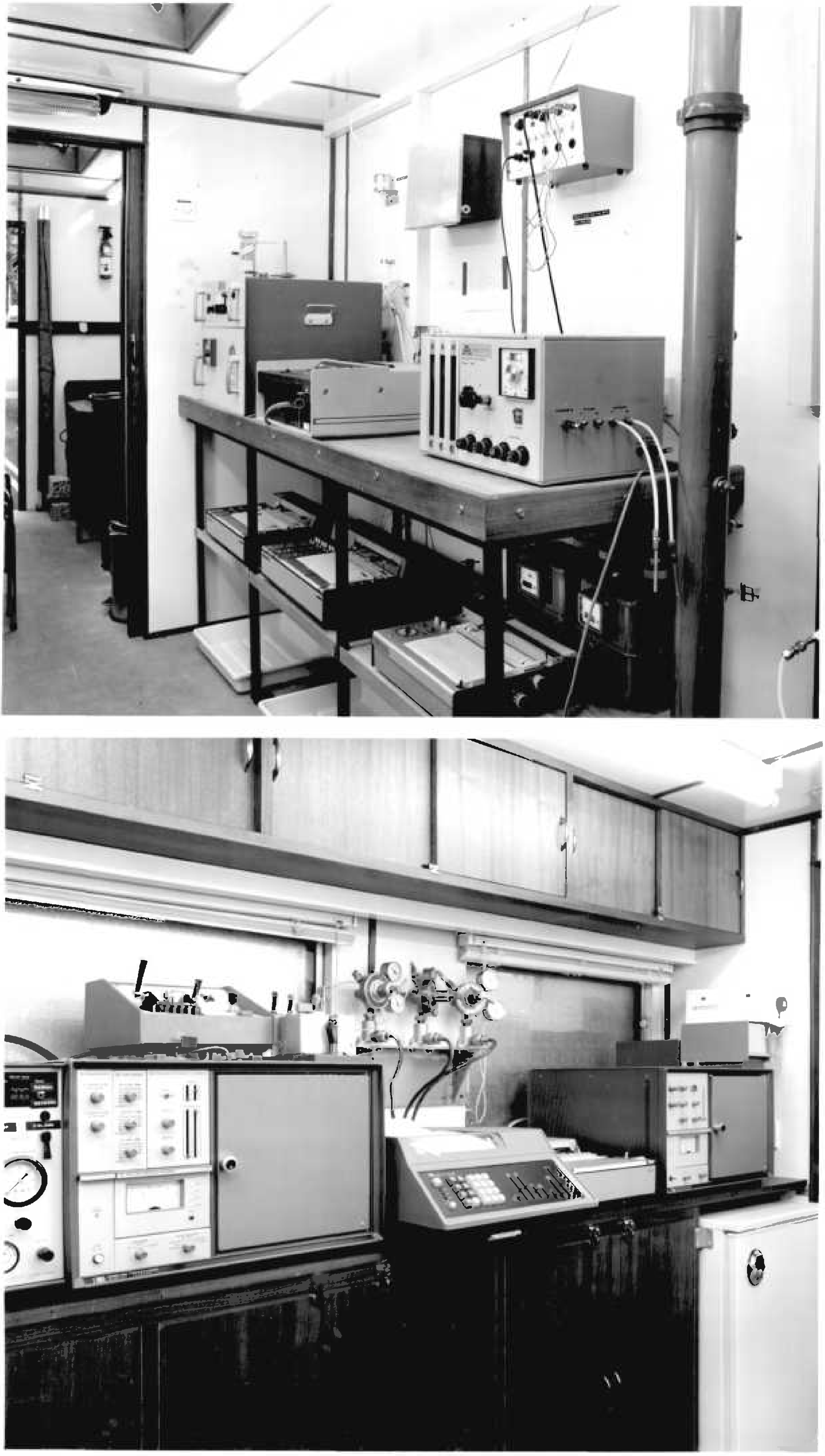


Plate 2 : Analytical instruments

halocarbons were used to produce concentrations of the materials up to an order of magnitude higher than that expected in urban atmospheres. These standard dilutions were passed through the sampling tubes at a rate of 150 ml $\min^{-1}$, the samples were thermally desorbed at a temperature 200°-230°C into the gas chromatograph and results were quantitatively recorded by the integrator. Duplicate analyses were carried out for time periods ranging from 1 min up to 30 min each.

(b) Quantitative Analyses of Injected Mixtures

The same tubes, after they were purged again, were spiked with aliquots of standard mixtures made up in spectroscopic hexane. Quantities of material used approximated to 100 ng μl^{-1} and injections ranged from 0.2 µl up to 5 µl. The desorbed materials were assessed by gas chromatographic separation and compared to direct injection into the gas chromatograph of the same quantities of materials.

(c) Assessment of Urban Air Samples

Street air, representing a much more complex mixture of compounds, was sampled onto each type of tube. Three l of air was sampled in each case at a flow rate of 100 ml $\min^{-1}$. The obtained chromatograms were compared in order to assess the efficiency of these adsorbents towards the organic pollutants encountered in the atmosphere.

(d) The Effect of Water Vapour

One l of ambient air, first saturated by passing through a Drechsel bottle containing water, was passed through each plug of adsorbent. Subsequent desorption and analysis was carried out as above and a comparative assessment was made.

(c) Flow Rate Variations

The compatibility of the pumping system associated with the different adsorption tubes was investigated for different preset flow rates namely: 100, 200 and 300 ml $\min^{-1}$.

Each tube was connected between the pump and a bubble flow meter and the observed fall off in flow rate was noted particularly at the higher values.

2.2.2.2 Detailed Evaluation of Two Principle Adsorbents (Chromosorb 102 and Tenax GC)

Permeation tubes containing benzene and toluene were independently used over a range of sampling periods (1-60 min) for each adsorption tube.

The tubes were thermally desorbed into the gas chromatograph and the recoveries quantitatively recorded.

In absolute quantities this involved up to 40 μg of benzene and 60 μg of toluene.

An assessment of maximum adsorbable concentrations was made by sequentially extending the sampling period up to twelve hours. In this way the equilibrium point was determined.

Similar experiments were carried out using double adsorption tubes linked in series by means of a piece of teflon tube.

Initially a benzene atmosphere was passed through the two tubes for one hour and the second tube only was analyzed for benzene. This tube was replaced with a similarly packed clean tube and the experiment was continued by passing a toluene atmosphere through the dual tube system for a further hour. Finally both the tubes were analyzed separately for benzene and toluene.

This experimental sequence was repeated for both adsorbents, Tenax and Chromosorb.

More detailed quantitative analyses of the compounds of urban air were carried out, utilizing each adsorbent. Simultaneous sampling of street air utilizing identical pumps (Du-Pont P-4000) was undertaken over 30 min periods at a flow rate of 100 ml min^{-1}. Of the compounds adsorbed, four compounds (benzene, toluene, m+p-xylene and o-xylene) were quantitatively analyzed utilizing direct chromatographic injections for reference calibration.

(b) The Effect of Flow Rate upon Adsorption Capacity

The head space of a petrol dilution in hexane in a closed 10 l container was used to assess the effect of flow rate upon adsorption capacity. Similar volumes (300 ml) were drawn through each tube under different flow rates (100, 150 and 250 ml min^{-1}), and were analyzed for five compounds (benzene, toluene, ethyl-benzene, m+p-xylene and o-xylene).

The safe sampling volumes, at the optimum flow rate, were then determined for each of the tubes, relating to a 100% retention of the same compounds. For this purpose, two similar tubes were linked in series with a teflon tube and pairs of samples were taken from street air under identical conditions.

Volumes of air ranging from 1 to 6 l at a flow rate of 100 ml min^{-1}, were sampled and the separate tubes analyzed.

(c) The Thermal Desorption Efficiency

Desorption efficiencies were evaluated by injecting standard quantities of hydrocarbons (0.2 µl to 5 µl) onto the adsorption tube and comparing the amounts obtained on desorption with those obtained by direct injections of the same aliquots.

This procedure was carried in triplicate and mean recoveries were compared.

Incomplete desorption was checked by desorbing a second time, following divertion of the carrier gas through a blank tube for 5 min period.

(d) Thermal Stability at High Temperatures (350°)

Following desorption at the temperature of 200°-220°C, the effect of increasing temperature in 30° increments, was evaluated for each of the adsorbents. Whilst adjusting the temperature and awaiting stabilization, the carrier gas was diverted through a blank tube and redirected through the adsorbent and into the chromatograph once stability had been reached.

Operation of the Carle Oven and associated gas sampling valves was limited to 250°C whereas the Bendix system was evaluated up to 350°C. In this way the thermal stability of the two adsorbents was compared up to this high temperature.

(e) Desorption Characteristics with Respect to Gas Chromatographic Resolution

Chromatograms obtained by desorbing spiked chromosorb and

Tenax tubes were compared to those obtained by direct injections of the same samples with regard to resolution. Petroleum mixtures were used for spiking and attention was paid in particular to the number of smaller peaks observed inbetween the main compounds.

2.2.2.3 Results and Discussion

Of the nine tested adsorbents only two, namely Chromosorb 102 and Tenax GC were found, from the initial experimental work, to be suitable for detailed evaluation.

In particular, activated carbon and Carbopack, despite their advantageous trapping efficiency, were very much affected by the presence of water vapour. Desorption under conditions of high humidity gave rise to chromatographic peaks that were ill defined and tailed badly being indicative of poor desorption characteristics as shown in fig. 2.2.

Of the other materials evaluated, Supelkoport exhibited low trapping efficiencies for the compounds of interest whereas Porapak Q was adversely affected in subsequent chromatographic resolution owing to its desorption characteristics.

Chromosorb 103 appeared to be unstable at temperatures about 180^{o}C and gave rise to the production of chromatographable breakdown products. Chromosorb 102, proved to be preferable to 101 and 104 in terms of the reproducibility of desorption and the subsequent chromatographic resolution obtained for the hydrocarbon mixtures studied.

Table 2.1 Flow rate variation for different adsorbents

packing sorbent	F.R. 100 ml min^{-1}	drop %	F.R. 200 ml min^{-1}	drop %	F.R. 300 ml min^{-1}	drop %
1. Activated carbon	100	0	196	2	290	3.3
2. Carbopack	100	0	195	2.5	290	3.3
3. Supelkoport	100	0	200	0	300	0
4. Porapak Q	100	0	200	0	300	0
5. Tenax GC	100	0	200	0	300	0
6. Chromosorb 101	70	30	148	26	212	29
7. Chromosorb 102	77	23	162	19	234	22
8. Chromosorb 103	95	5	186	7	270	10
9. Chromosorb 104	97	3	190	5	280	6.6

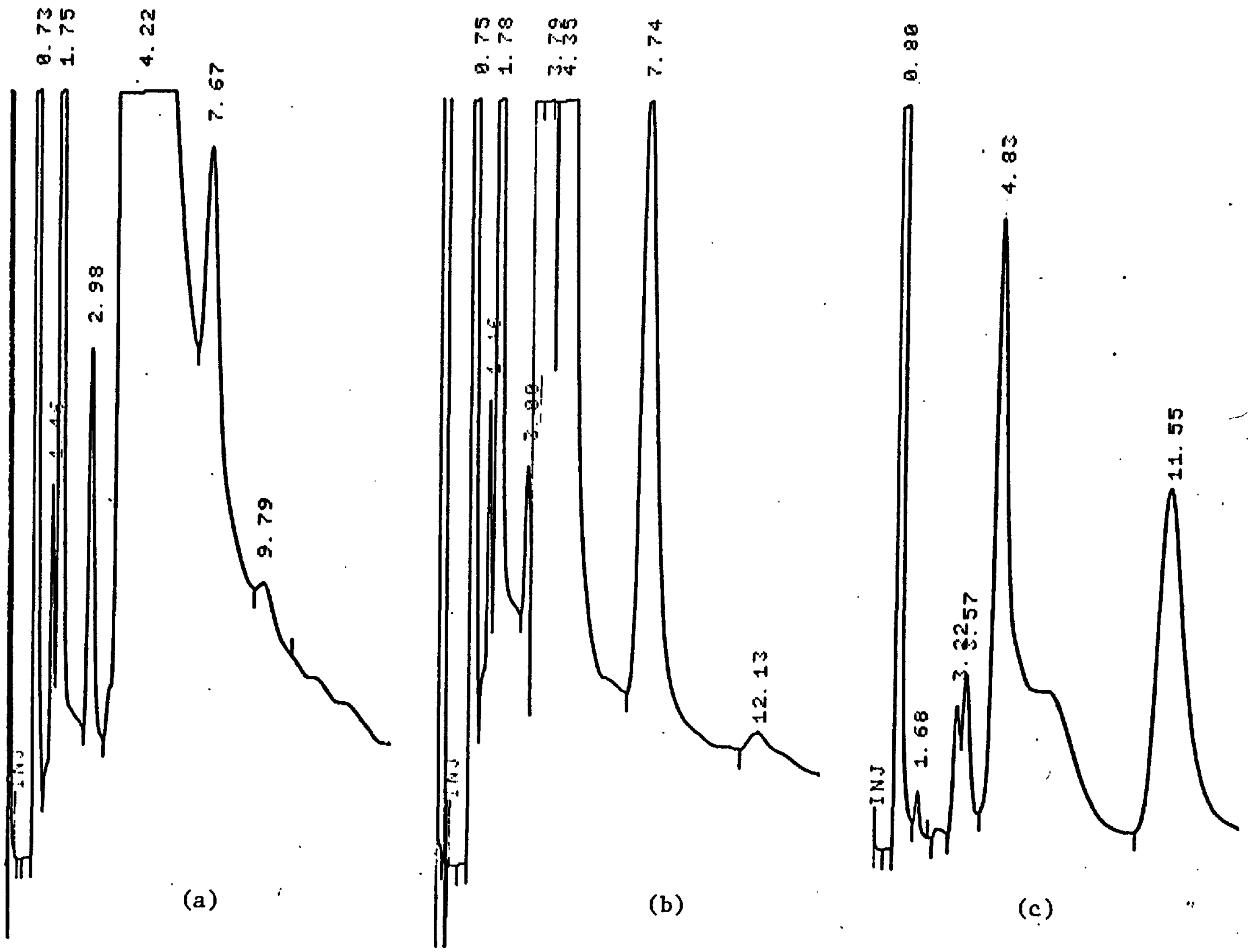


Fig. 2.2 Chromatograms obtained by thermal desorption from activated carbon (a), carbopack (b) and porapak Q (c)

The superiority of Tenax with regard to gas flow characteristics is shown in table 2.1, which indicates the drop in flow rate associated with standard changes in pumping rates (fig. 2.3). Clearly, the pressure drop experienced with the Chromosorb materials can be accounted for in the calibration procedure but the susceptibility to partial blocking of the tubes that would arise in sampling certain atmospheres is unacceptable.

Comparative trapping efficiencies of Chromosorb 102 and Tenax GC towards such substances as benzene and toluene are presented in table 2.2. Both demonstrated an extended linear capacity indicated in fig. 2.4 and 2.5.

Table 2.2. Comparative trapping of benzene and toluene onto Chromosorb 102 and Tenax GC

Sampling Period	Benzene in μg		Toluene in μg	
	Tenax	Chromosorb	Tenax	Chromosorb
1'	0.702	0.688	1.138	1.117
2'	1.362	1.360	2.237	2.176
3'	2.131	2.035	3.298	2.984
4'	2.772	2.760	4.426	4.050
5'	3.905	3.350	5.843	5.484
10'	7.264	6.726	11.868	10.749
20'	13.976	12.250	21.804	19.842
30'	20.836	18.349	31.985	28.519
45'	31.378	25.401	47.328	38.122
60'	39.918	32.802	60.380	44.904

The highest capacities for both adsorbents towards benzene and toluene are shown in table 2.3 in which the lower capacity of chromosorb is clearly demonstrated.

The equilibrium quantities achieved during these experiments for both adsorbents is shown in fig. 2.6. At the concentrations

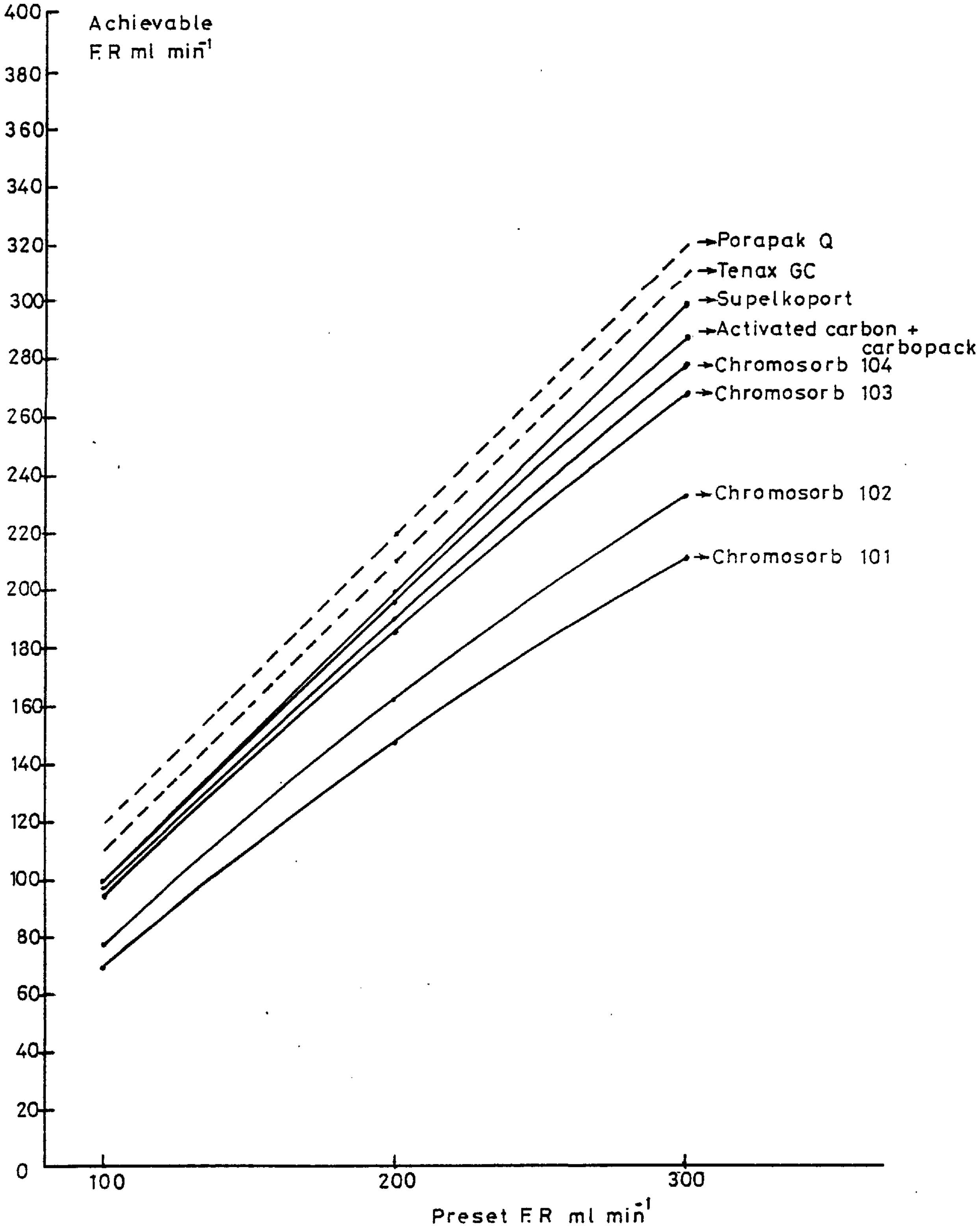


Fig 2·3 Flow rate variations for different adsorbents

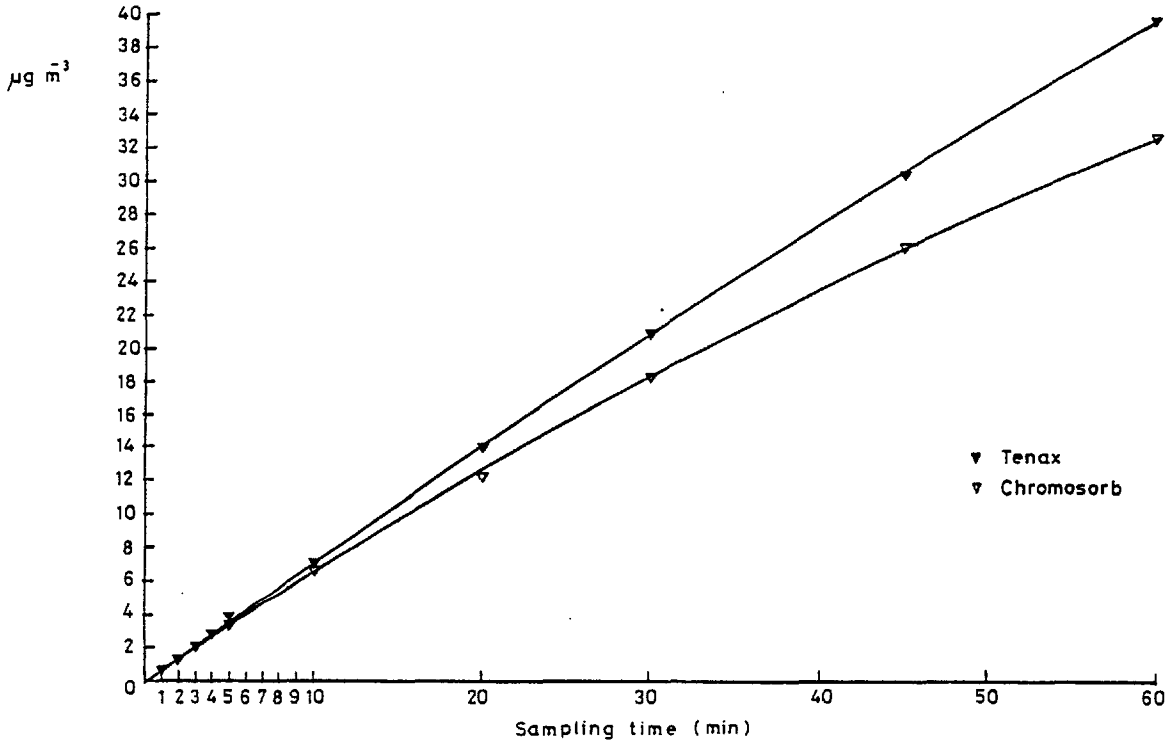


Fig 2·4 Sampling benzene on tenax and chromosorb 102

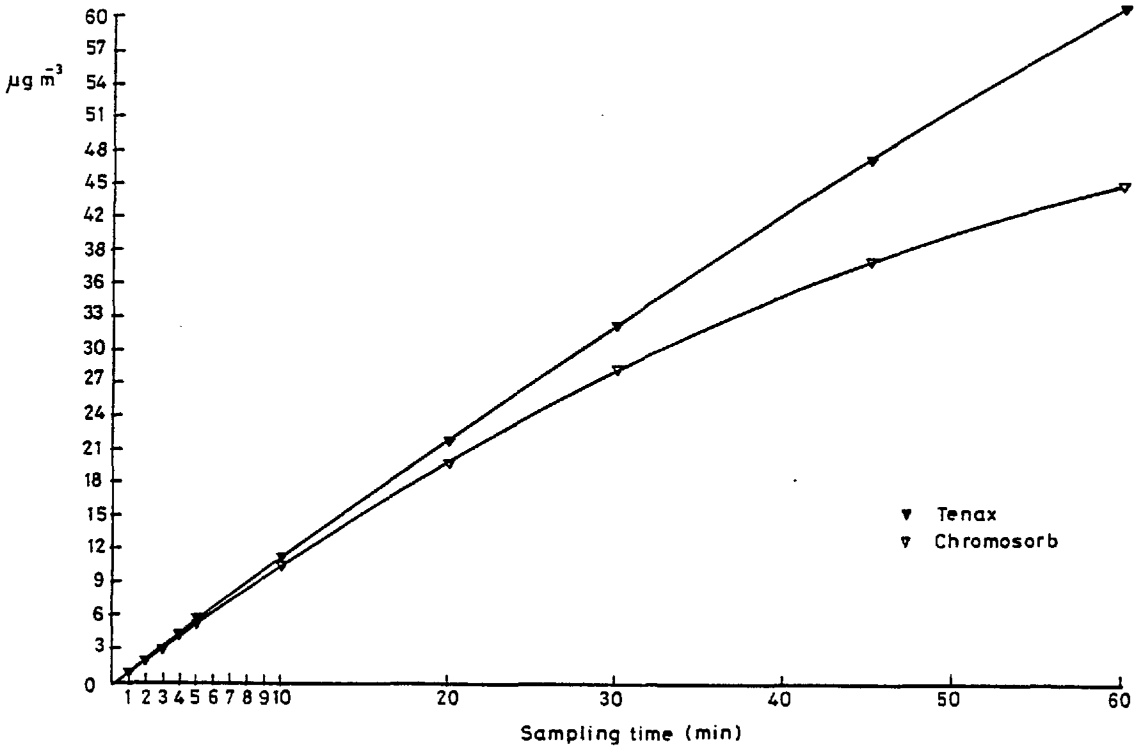


Fig 2·5 Sampling toluene on tenax and chromosorb 102

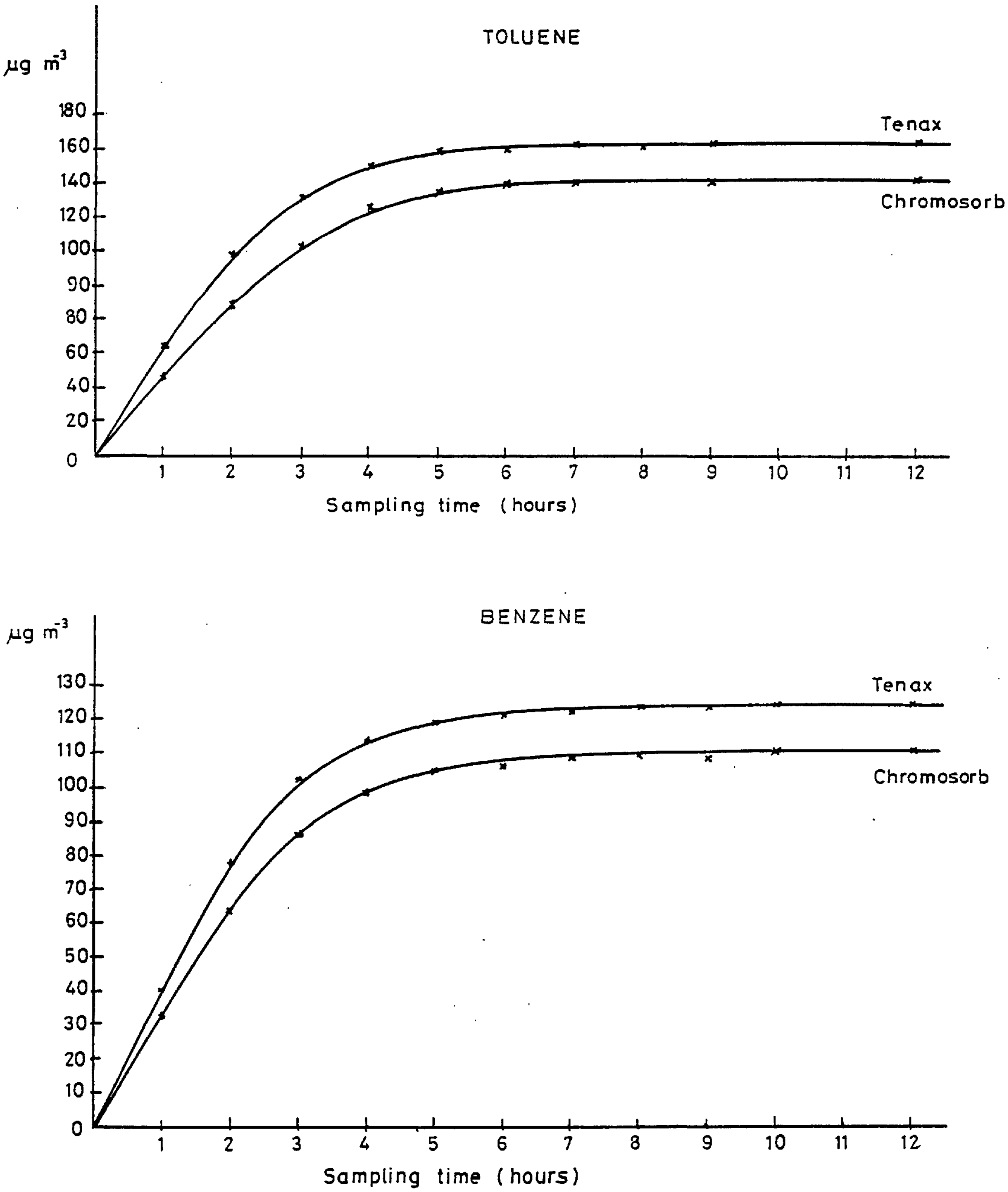


Fig 2·6 Extended sampling benzene and toluene onto tenax GC and chromosorb 102

Table 2.3 Higher trapping efficiencies of Tenax and Chromosorb for benzene and toluene

	Benzene in µg		Toluene in µg	
Hours	Tenax	Chromosorb	Tenax	Chromosorb
1	39.918	32.802	60.380	44.904
2	78.148	63.814	117.976	87.923
3	102.936	86.017	151.698	122.471
4	114.123	98.520	169.775	146.088
5	119.105	105.239	179.232	155.107
6	120.987	106.084	179.611	159.727
7	121.243	108.890	182.507	160.158
8	123.878	109.425	181.832	-
9	123.442	109.088	182.709	160.543
10	124.019	110.141	-	-
12	124.813	111.548	183.117	162.203

Table 2.4 Sequential sampling of benzene and toluene (dual tube system)

Sampling period on	Benzene in µg		Toluene in µg	
Tenax	1st tube	2nd tube	1st tube	2nd tube
60' benzene	40.096	0	-	-
60' toluene	35.871	4.225	59.165	0.227
Chromosorb				
60' benzene	32.870	0	-	-
60' toluene	28.724	4.146	44.805	0.112

used adsorption processes follow a similar pattern for the two adsorbents with equilibrium reached between the 5th and 6th hour of sampling for benzene and almost one hour later for toluene. After the second hour of sampling the adsorption process ceases to be linear moving towards the equilibrium point in the way shown. Linearity up to one hour is indicated further in table 2.4.

For sampling periods of up to one hour no problems were experienced in sampling either benzene or toluene, as indicated by the absence of these materials on the second analytical tube.

It is further shown by the data presented that once equilibrium is reached in an adsorption type sampling tube, preferential migration takes place of the more volatile materials. Thus in the table presented the rate of migration of benzene is greater than that of toluene.

Examples of duplicate street air analysis utilizing Tenax and Chromosorb as the adsorbents are recorded in table 2.5, with data presented for four individual compounds. The analytical data are in good general agreement for both adsorbents although the greater trapping efficiency of Tenax is clearly shown.

Table 2.5 Duplicate street air samples taken onto Tenax GC and Chromosorb 102

A Tenax ng l^{-1}

Date	Time	Benzene	Toluene	m+p xylene	o-xylene
16/11/78	9.30-10.00	22.5	35.7	37.9	13.2
	10.00-10.30	25.5	55.7	31.6	21.1
	10.30-11.00	21.6	43.7	26.7	9.6
	11.00-11.30	22.0	41.5	24.4	11.3
17/11/78	9.00- 9.30	48.0	62.4	62.8	24.1
	9.30-10.00	64.3	114.4	72.5	30.9
	10.00-10.30	57.4	96.9	64.2	24.5

B. Chromosorb ng l^{-1}

Date	Time	Benzene	Toluene	m+p xylene	o-xylene
16/11/78	9.30-10.00	19.9	28.3	37.6	13.4
	10.00-10.30	22.2	53.7	29.0	10.6
	10.30-11.00	18.9	41.9	22.5	7.2
	11.00-11.30	21.7	38.0	21.0	7.9
17/11/78	9.00- 9.30	42.3	52.8	51.7	16.3
	9.30-10.00	55.0	102.7	58.6	30.8
	10.00-10.30	45.8	91.7	51.5	17.4

Table 2.6 is a summary of data obtained for the collection of five different compounds under different flow rate conditions. It is clear, as also demonstrated in fig. 2.7, that higher flow rates have a negative effect on the trapping efficiency of both adsorbents, although the observed variations are rather small.

Table 2.6 The effect of flow rate upon trapping capacity of Tenax and Chromosorb

Tenax		AMU × 10^{-3}				
Time	F.R. ml min^{-1}	Benzene	Toluene	Ethyl- benzene	m+p- xylene	o- xylene
3'	100	605.774	654.977	173.839	465.167	237.788
2'	150	550.266	528.331	150.388	405.364	223.251
1.2'	250	472.331	490.526	139.725	339.132	219.769
Chromosorb						
3'	100	617.876	654.253	223.602	438.764	217.656
2'	150	515.249	565.543	188.971	390.254	154.124
1.2'	250	412.034	485.716	131.529	255.901	105.826

The above experimental work would indicate that a flow rate of 100 ml min^{-1} is optimum and that a sampling volume of 3 l is acceptable for street air samples. At volumes lower than this no transfer to a second tube of materials of concern has been demonstrated in the exhausted number of experiments undertaken.

It is clear from the chromatographic data presented that even for the more volatile compounds (boiling point < 70°C) a maximum of 35% migrates onto the second tube under the conditions described above.

The mean values obtained for triplicate injections and thermal desorptions for two different solutions, are included in table 2.7 together with the calculated recoveries in percentages. It is clear that recoveries from Tenax GC are superior to those from chromosorb 102 (100% ± 4.3 and 100% ± 20.4 respectively), presumably owing to the

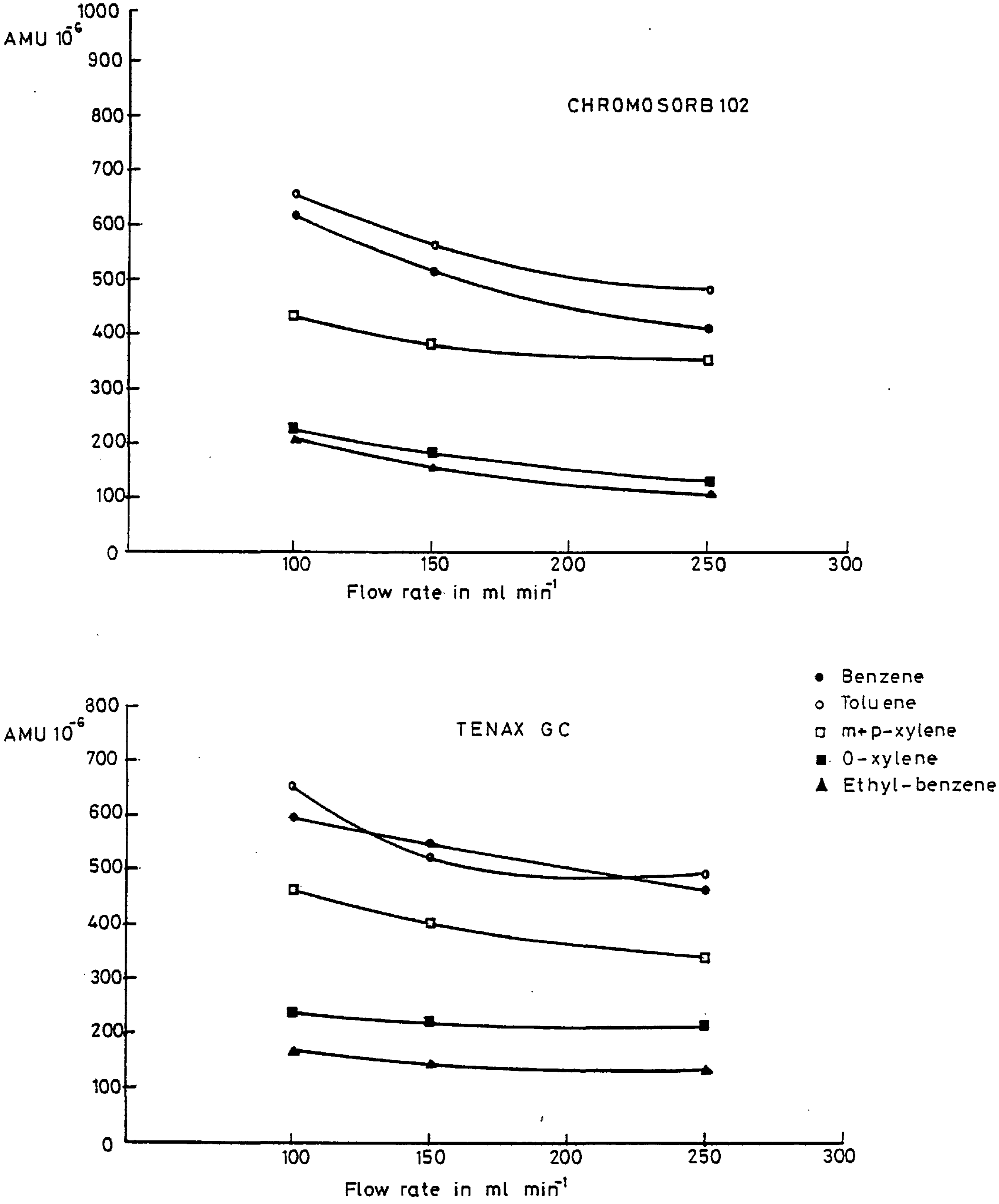


Fig 2·7 Effect of flow rate upon the adsorption capacities of Tenax GC and chromosorb 102

Table 2.7 Thermal desorption from Tenax and Chromosorb compared to direct injection (data in ng)

A. Petrol Solution 2 µl	Benzene	Toluene	Ethyl-benzene	m+p-xylene	o-xylene
Injection	746	2544	350	2418	740
Tenax	747	2532	339	2447	708
Chromosorb	594	2114	315	2324	523
B. Standard solution 2 µl					
Injection	235	682	192	305	18
Tenax	233	676	191	306	18
Chromosorb	228	613	180	288	19

Recoveries %

A.	Benzene	Toluene	Ethyl-benzene	m+p-xylene	o-xylene
Tenax	100.1	99.5	96.9	101.2	95.7
Chromosorb	79.6	83.1	90.0	96.1	70.7

B.

Tenax	99.1	99.1	99.5	100.3	100.0
Chromosorb	97.0	89.9	93.8	94.4	105.6

Tenax	100% ± 4.3
Chromosorb	100% ± 20.4

higher temperatures at which Tenax can be operated. Indeed, Tenax demonstrates very high stability up to 350°C which allows for complete thermal desorption, whereas Chromosorb is stable only up to a 200°C limit. Chromatographable breakdown products of Chromosorb 102 at temperatures above 200°C are shown in fig. 2.8.

Two chromatograms obtained under identical conditions of thermal desorption from Tenax GC and Chromosorb 102 are illustrated in fig. 2.9.

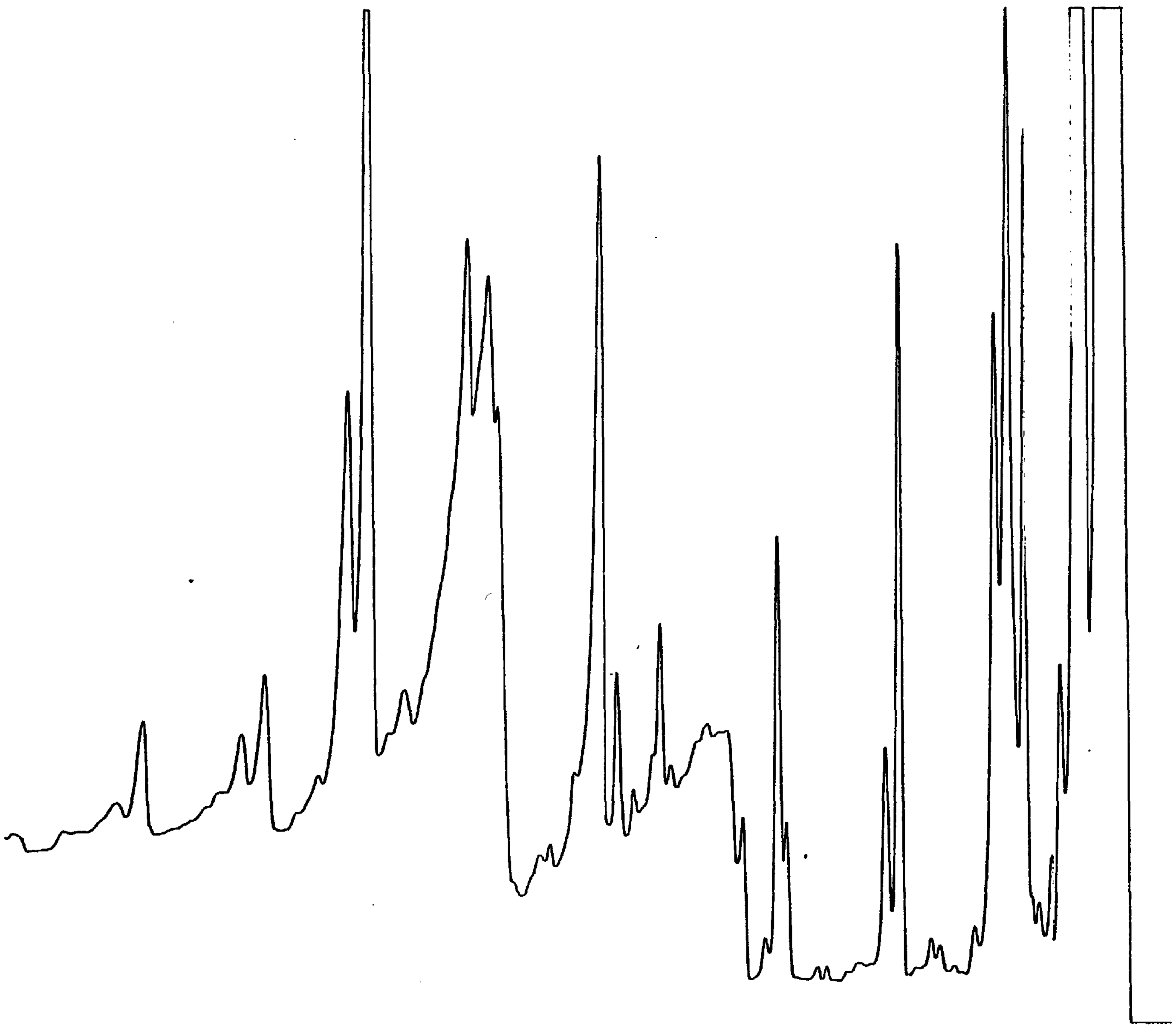


Fig. 2.8 Breakdown products of Chromosorb 102 at temperatures above 200°C

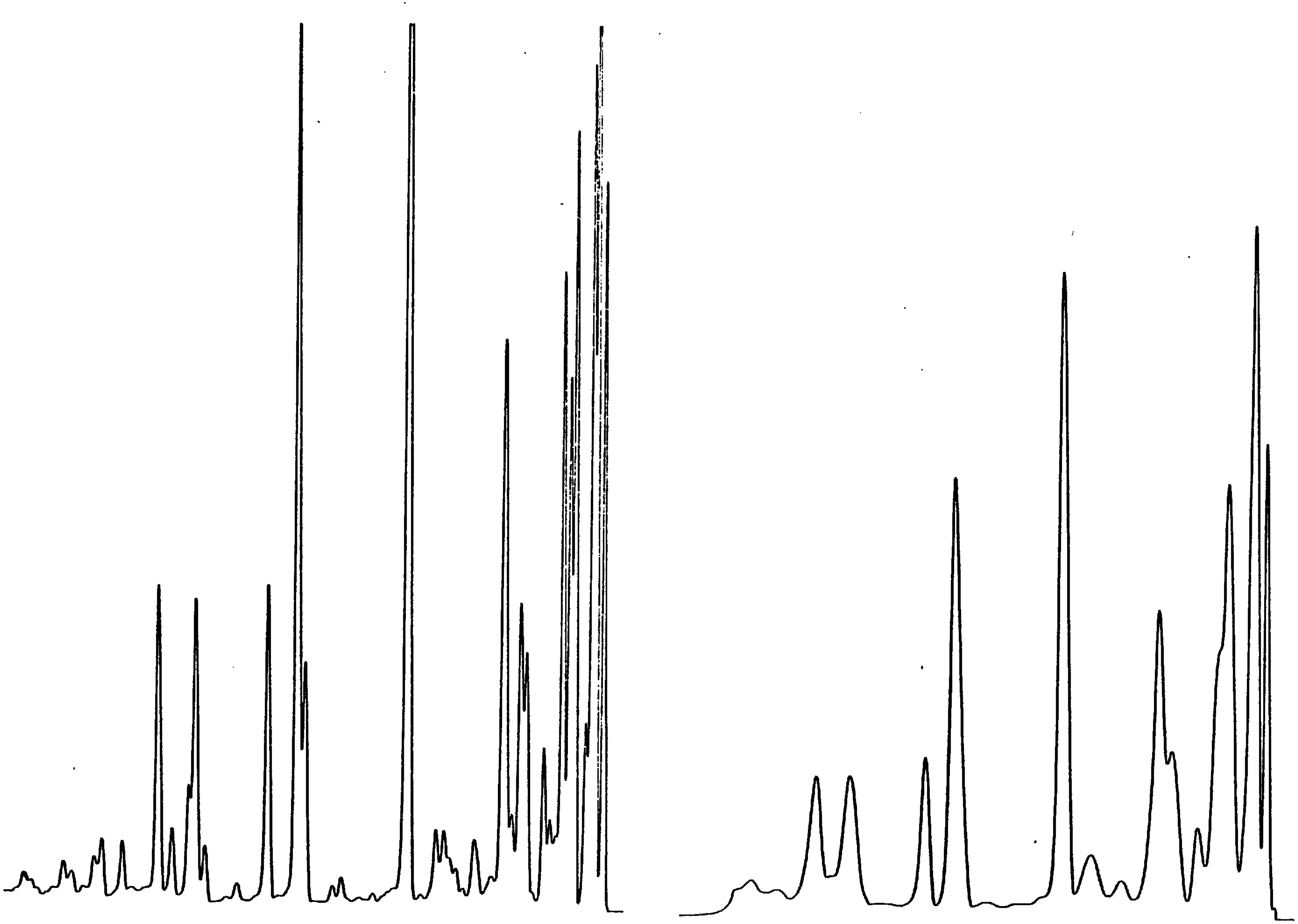


Fig. 2.9 Chromatograms of hydrocarbons obtained under identical conditions from Tenax GC and Chromosorb 102

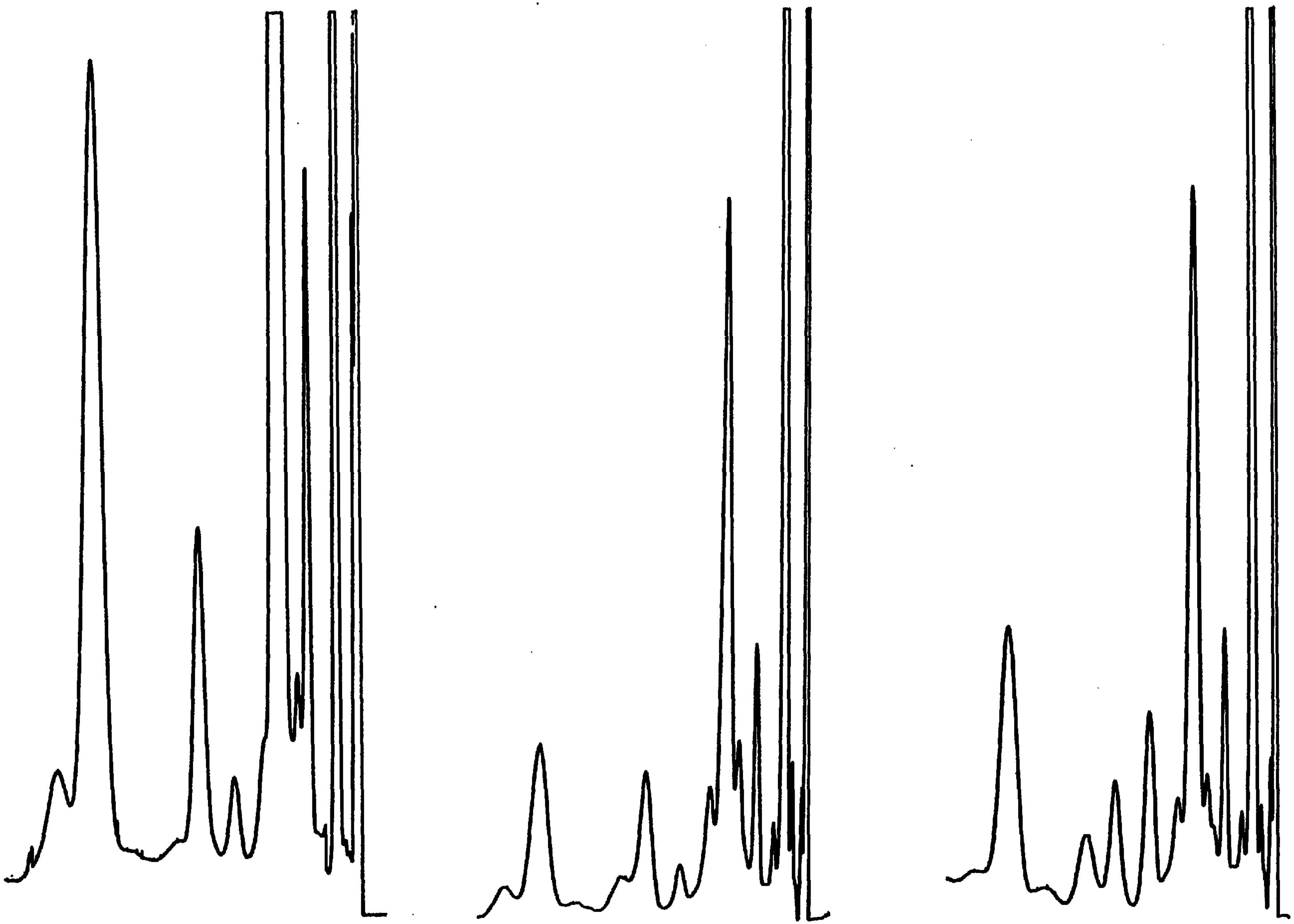


Fig. 2.10 Three chromatograms of halocarbons obtained by thermal desorption from Tenax GC

Similar tests using the halogenated materials of interest instead of hydrocarbons, gave results very similar to those for hydrocarbons, indicating that Tenax is the more suitable adsorbent for these species under the same mode of operation. In fig. 2.10 chromatograms of the halocarbons measured in three different locations are included.

2.2.3 Selected Analytical Procedures for Individual Compounds

2.2.3.1 Sampling Procedures

Sampling tubes of stainless steel, 4 × ¼ in o.d., carefully cleaned (boiled in a beaker with Decon 90), were packed with adsorbent (preconditioned Tenax GC at 300°). These were then purged with helium carrier gas at a flow rate of 20 ml min^{-1} for 5 hours whilst being maintained at temperature of 260°-280°C. Prepared sampling tubes were stored in an oven at 200°C until use.

2.2.3.2 Desorption Procedure

The sampling tube was connected gas-tight into the desorption oven, and the temperature allowed to stabilise (15 min for the Carle Oven and 5 min for the Bendix Flasher). Then the carrier gas was diverted through the sampling tube in order to remove the collected compounds into the analytical column. The tubes were purged until the end of chromatographic analysis (30 min for individual hydrocarbons and 15 min for halocarbons).

2.2.3.3 Gas Chromatographic Conditions for Separation of Eluted Materials

(i) Separation of hydrocarbons was achieved by a 20 ft × 1/8 in o.d. stainless steel column, packed with 3% OV_7 on Chromosorb W (AW-DMCS). The analysis was thermally programmed, starting initially from 40°C (maintained for 2 min) and increased up to 160°C at a rate of 4°C min^{-1}. The detector temperature was maintained at 300°C.

(ii) Separation of halocarbons was achieved by two columns linked in series: firstly, a 6 ft × 1/8 in o.d. stainless steel, packed with 0.2% Carbowax 1500 on 60/80 mesh Carbopack C, and secondly, a 6 ft × 1/8 in o.d. packed with Carbowax 20 M on Gas Chromosorb W(AW-DMCS). The analysis was isothermal at 105°C for ethylenedichloride and ethylenedibromide and at 50°C for vinyl chloride. The detector temperature was maintained at 350°C.

2.2.3.4 Calibration Procedure

Gravimetric calibration of each individual permeation tube was extended over a period of 2 to 3 weeks during which the permeation oven was maintained under constant conditions of temperature (selected between 30^{o} and $70^{o}C$) and flow rate of carrier gas (150 ml min^{-1}). Absolute amounts of pure compounds included within each tube at a selected temperature, removed by the carrier gas to the outlet of the permeation oven, were calculated over a period of 1 min from the absolute amount permeating the tube over a 24 hour period (measured gravimetrically).

2.3 Analytical Techniques Used for General Air Pollutants

2.3.1 Total and Non-Methane Hydrocarbons and Carbon Monoxide (up to 10 ppm)

Figure 2.11 shows diagrammatically a 6800 Beckman air quality chromatograph (AQC). A system of two gas sampling valves (A and B) allows the introduction of ambient air into the sampling loops (shown as A and B) at 5 min periods. The sample from loop B is flushed directly into the flame ionization detector (FID) for the measurement of total hydrocarbon content. The sample from the loop A is passed through a separation column (C_3). This allows methane to advance to the FID resulting in measurement of methane, whereas carbon monoxide (CO) is passed first through a CO methanator and next to the FID. The last peak is related to the amount of CO entering sampling loop A.

2.3.2 Oxides of Nitrogen

A Thermo Electron Model 14D Chemiluminescence Analyzer was used to obtain a continuous determination of nitric oxide (NO), nitrogen dioxide (NO_2) and total oxides of nitrogen (NOx), shown diagrammatically in fig. 2.12.

The phenomenon of chemiluminescence, which occurs when part of the energy of an exothermic chemical reaction is released as light, is basically utilized in such an analyzer. The fast reaction between NO and ozone (O_3) in the gas phase produces excited NO_2 molecules which lose energy by light emission, and the system gives a continuous signal proportional to the amount of NO entering the reaction cell. Read out of NO_2 is by difference of NOx and NO, also on continuous basis.

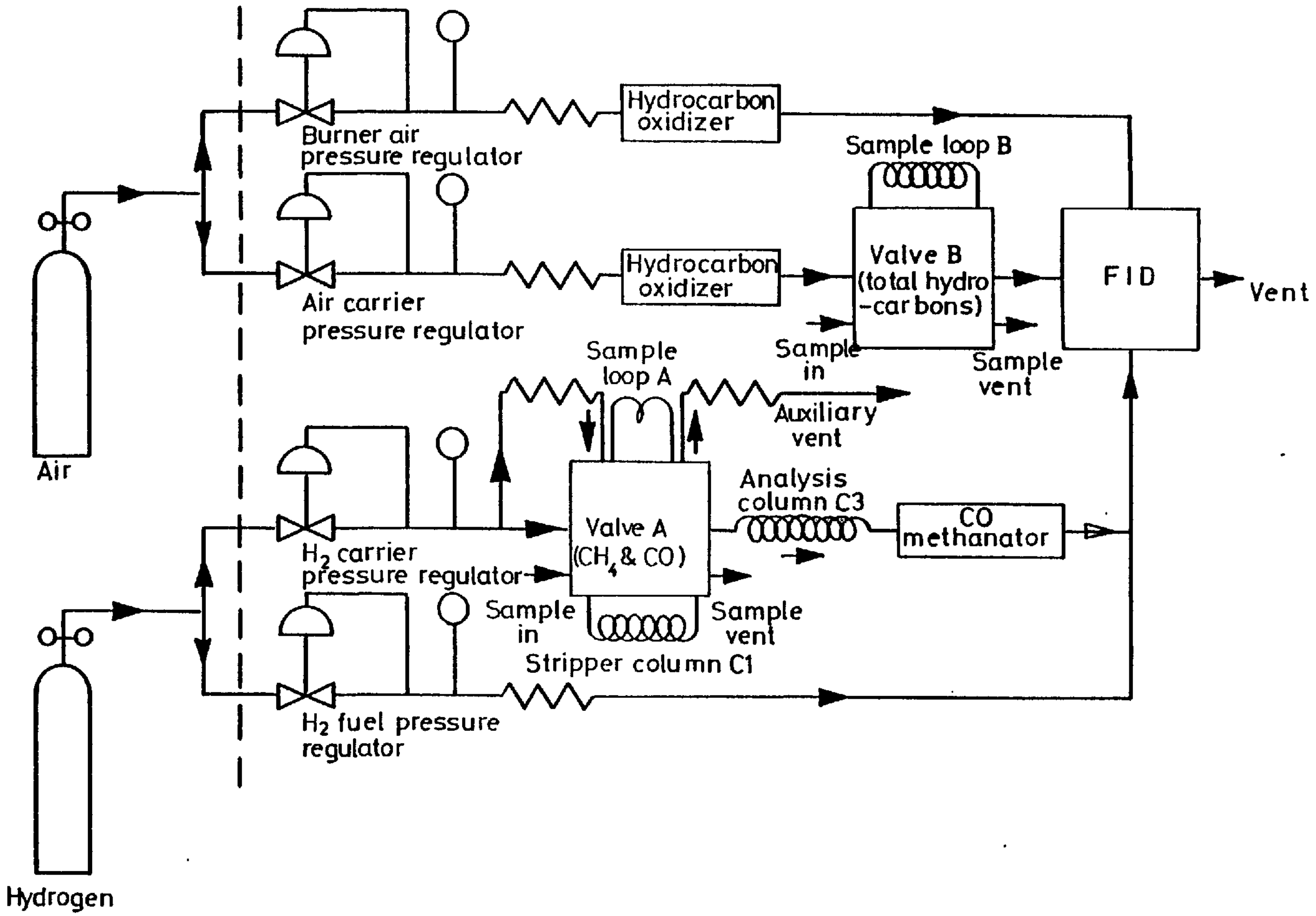


Fig 2·11 Bechman air quality chromatograph model 6800

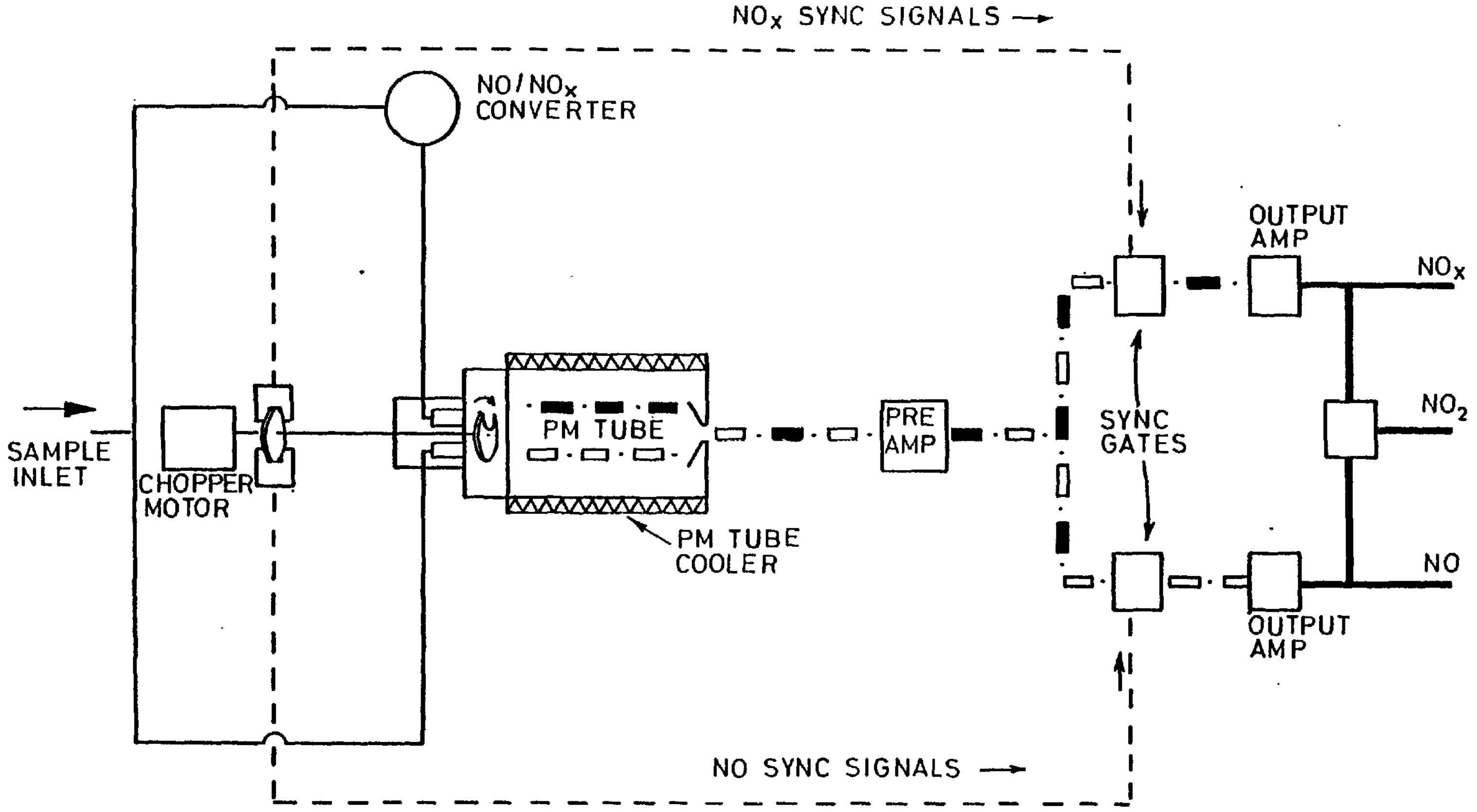


Fig 2·12 Chemiluminescence 14 D analyzer for oxides of nitrogen

2.3.3 Carbon Monoxide (concentrations above 10 ppm)

Concentrations of carbon monoxide less than 10 ppm, were readily measured by the AQC (fig. 2.11). For concentrations from 10 ppm up to 1000 ppm ecolyzers were used. The principle of measuring CO in such an instrument is based on catalytic oxidation of CO to carbon dioxide, which passes into a cell containing sulphuric acid, giving a response related to the amount of CO entering into the cell.

2.3.4 Lead Analysis

Air samples were isokinetically drawn through a 0.22 μ millipore filter, at a flow rate of approximately 1 l min^{-1}.

Filter papers were acid digested (Aristar grade nitric acid 20 ml) over a period of 30 min. Lead levels were measured by flameless atomic absorption spectrophotometry (absorption line 283.3 nm) using a Perkin Elmer 605/HGA76 system.

2.3.5 Calibration

All the instruments used during this study were calibrated on a regular basis, using standard gas mixtures of the required concentrations, prepared and supplied by the British Oxygen Company.

2.4 Summary and Conclusions

(a) Evaluation of nine adsorbents on an adsorption/thermal desorption mode of operation for hydrocarbon and halocarbon air analysis had proven two of them (Tenax GC and Chromosorb 102) to be the most suitable.

(b) The porous polymers did not appear to be significantly affected by the presence of water vapour whereas adverse effects due to such factors was clearly shown in the case of activated carbon and Carbopack.

(c) Flow rate variations were found to be higher for the group of Chromosorbs (up to 30%) and insignificant for the other adsorbents.

(d) The adsorption capacity of Tenax GC has proven superior to that of Chromosorb 102.

(e) Recoveries by thermal desorption were calculated as 100% ± 4.3 from Tenax GC and 100% ± 20.4 from Chromosorb 102.

(f) Tenax GC demonstrates a thermal stability up to 350°C whereas that of Chromosorb 102 is limited above 200°C, therefore Tenax is much more suitable.

(g) Desorption characteristics and Chromatographic resolution had proven Tenax GC to be superior to Chromosorb 102.

(h) Storage of the prepared sampling tubes (packed with Tenax GC) in an oven at 200°C and use of gas tight thermos flask for sample transportation (to the field) is very critical in avoiding contamination problems.

(i) The use of the second column for the separation of the halogenated species was necessary especially for good resolution of ethylenedichloride.

(j) One of the halogenated compounds of interest, vinyl chloride, could be traced more easily as a C_2 hydrocarbon, by the FID in a room-temperature oven. This produced a higher response than that of a single chlorine compound from an ECD.

(k) Calibration in the field could be readily carried out using gravimetrically prepared solutions of standards in spectroscopic hexane. This solution must be first cross-calibrated against the permeation tubes in the laboratory and were stored in gas-tight sealed glass containers. These were stable for at least a one-month period.

(l) The repeatability and reproducibility of the selected analytical procedure was well within ±5%.

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CHAPTER 3 : AMBIENT CONCENTRATIONS OF POLLUTANTS OF CONCERN

To fulfil the objectives of this research a programme of work was established, which by use of the previously described analytical techniques, would lead to the accumulation of a body of data amenable to statistical analysis. To this end a variety of sampling locations were selected in order to provide typical examples of a range of atmospheric qualities.

3.1 Hydrocarbon and Halocarbon Concentrations in an Urban Location

Exhibition Road, a dual carriage way in central London, typically carrying 1500-2000 vehicles per hour, was considered to be representative of a busy urban street. Over a period of 10 months - January to October 1979 - approximately two hundred individual samples were taken at this site and analyzed for hydrocarbon and halocarbon content.

Sixteen aromatic hydrocarbons, representing the main peaks in the range C_6-C_{10} on chromatograms of ambient air samples from repetitive analyses, were identified using the GC/MS system.

These sixteen compounds, consisting of benzene and benzene derivatives, are indicated in table 3.1, and were found to be present at various concentrations in the atmosphere at every location where work was carried out.

Similarly, three halocarbons (C_2) were encountered in ambient air, generated by internal combustion engines. The two saturated compounds were 1,2 dichloroethane or dichloroethylene (EDC) and 1,2 dibromoethane or dibromoethylene (EDB), which are added to petrol as lead scavengers. The third halocarbon was an unsaturated compound, Vinyl Chloride (VCL), which is suspected of being formed during internal combustion, a hypothesis which has not yet been proved.

3.1.1 Sampling Programme

The majority of samples were taken during the working day with a few collected during weekends and Bank Holidays. Sampling was concentrated on the rush hours, 08.00-10.00 and 16.00-19.00, but was extended in a few instances over a twelve-hour period of the day (08.00-20.00 h).

Table 3.1 Hydrocarbons and halocarbons determined in ambient air samples

Number	Compound
1	Benzene
2	Toluene
3	Ethyl-benzene
4	m+p-Xylene
5	o-Xylene
6	Iso-propyl-benzene
7	N-propyl-benzene
8	m+p-Ethyl-toluene
9	1,3,5 Trimethyl-benzene
10	o-Ethyl-toluene
11	1,2,4 Trimethyl-benzene
12	1,2,3 Trimethyl-benzene
13	m-Diethyl-benzene
14	p-Diethyl-benzene
15	o-Diethyl-benzene
16	Dimethyl-ethyl-benzene
17	1,2 Dibromomoethane
18	1,2 Dichloroethane

In such cases monitoring of general air pollutants (total hydrocarbons, carbon monoxide and oxides of nitrogen) was also carried out.

Additional work involved sampling over a period of 10 days at the same time (09.00-11.00) utilizing the M.D.A. accuhaler low flow rate pump.

The sampling point was at a distance of 5.0 m from the kerb at a height 1.5-2.0 m above ground level.

Duplicate samples were taken simultaneously using two identical Du Pont P-4000 constant flow automatic sampling pumps, when both hydrocarbons and halocarbons were investigated.

All the samples were analysed using the procedures described in Chapter 2.

3.1.2 Results and Discussion

3.1.2.1 Hydrocarbons

Appendix A includes all the raw data in $\mu g\ m^{-3}$ for the sixteen hydrocarbons (referred to as numbers 1-16) from the Exhibition Road samples, together with dates and times of sampling.

(a) Diurnal variation (0 8.00 to 20.00 h)

The diurnal variation in the concentrations of four aromatic hydrocarbons (benzene, toluene, m+p-xylene and o-xylene) which represent approximately 40-70% of the found aromatic constituent at this site, is shown in fig. 3.1.

The data clearly indicate an increase in the concentrations of the four hydrocarbons during the morning and afternoon rush hour periods, with a recession between 10.00 and 14.00, a phenomenon which was commonly observed during the weekdays.

Exceptions were observed during weekends and Bank Holidays, when the diurnal variation was completely different but always related to traffic flows.

General air pollutants showed very similar trends, with concentrations elevated during the rush hour period and decreased during the rest of a 24 hour period as indicated in fig. 3.2.

(b) Daily variation

The daily variation of the same four hydrocarbons for the period 22 February to 3 March is shown in fig. 3.3. The highest concentrations observed were on 23 February and 2 March, both Fridays. The lowest concentrations were found on Sunday 25 February.

All sixteen measured hydrocarbons in Exhibition Road gave for the 10 month period concentrations between 0.2 and 298 $\mu g\ m^{-3}$. The highest concentrations during the same period were observed on 25 October during the evening rush hour (16.00-18.00) which was almost certainly caused by increased vehicle activity due to a particular social function in the immediate vicinity.

An hourly distribution of benzene, toluene, m+p-xylene and o-xylene measurements over the 10 month period at this site, is shown in fig. 3.4 (a,b,c,d).

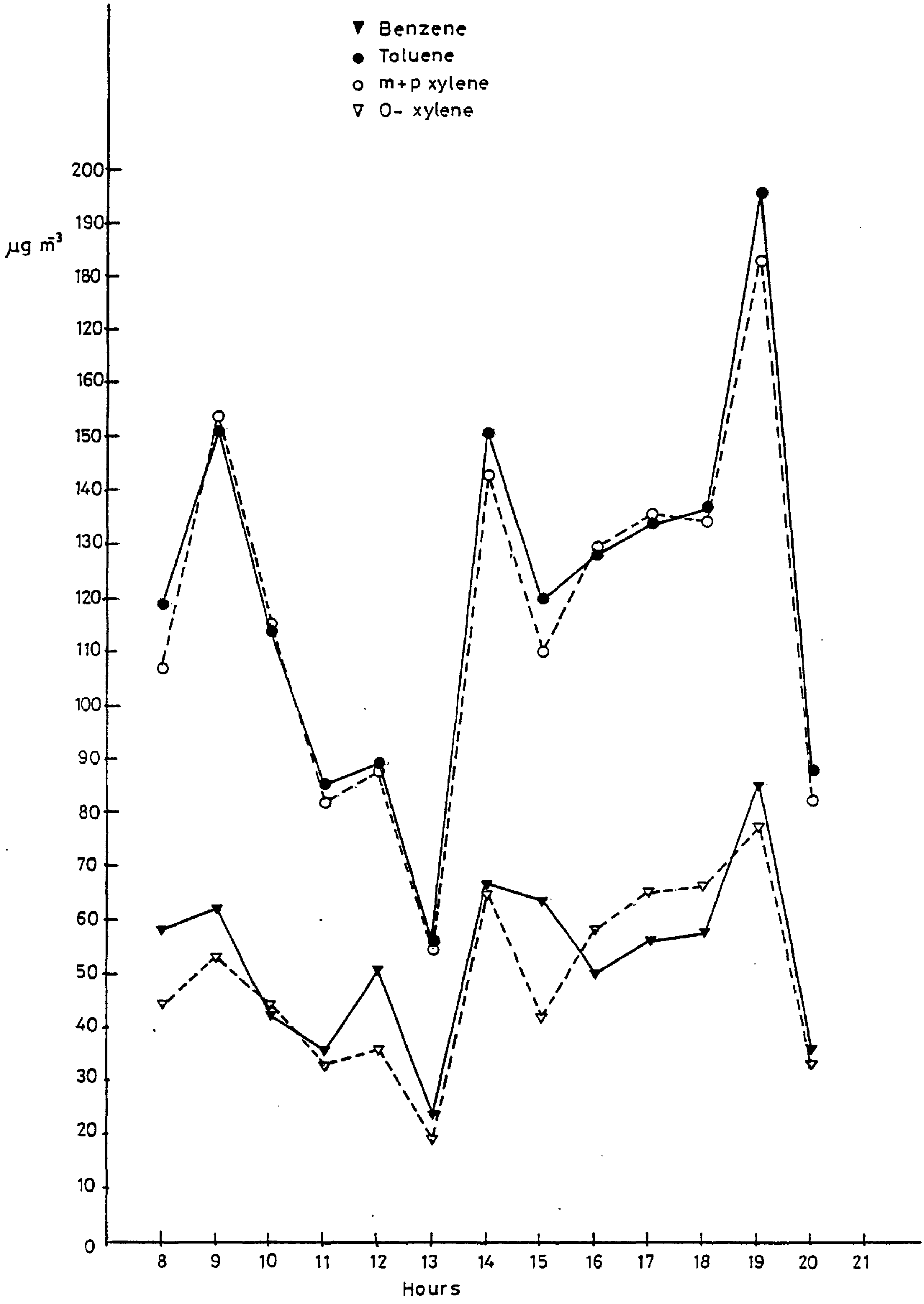


Fig. 3·1 Diurnal variation of four hydrocarbons at Exhibition Road site on the 31/1/79

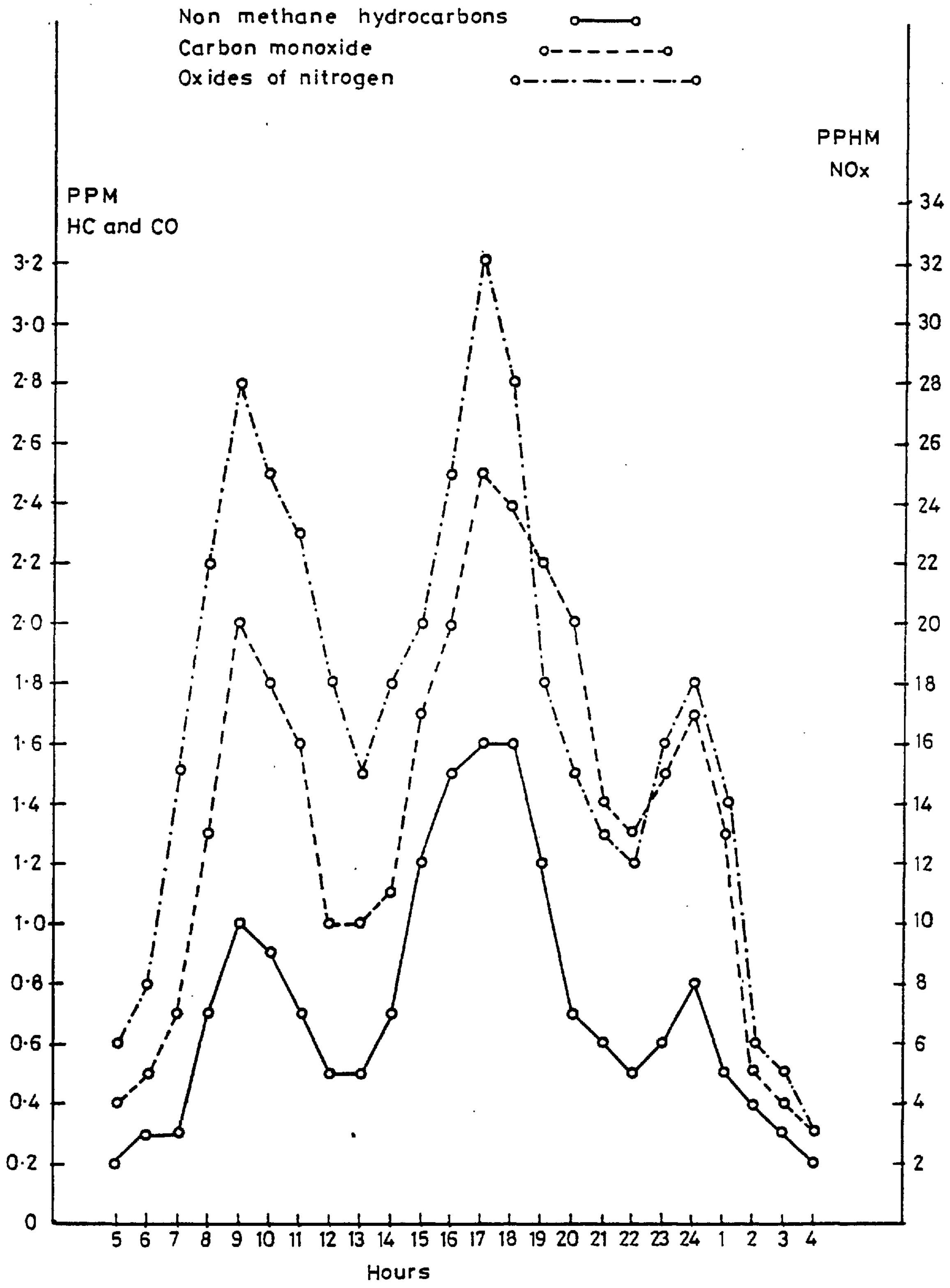


Fig 3·2 Diurnal variation of general air pollutants at Exhibition Rd site

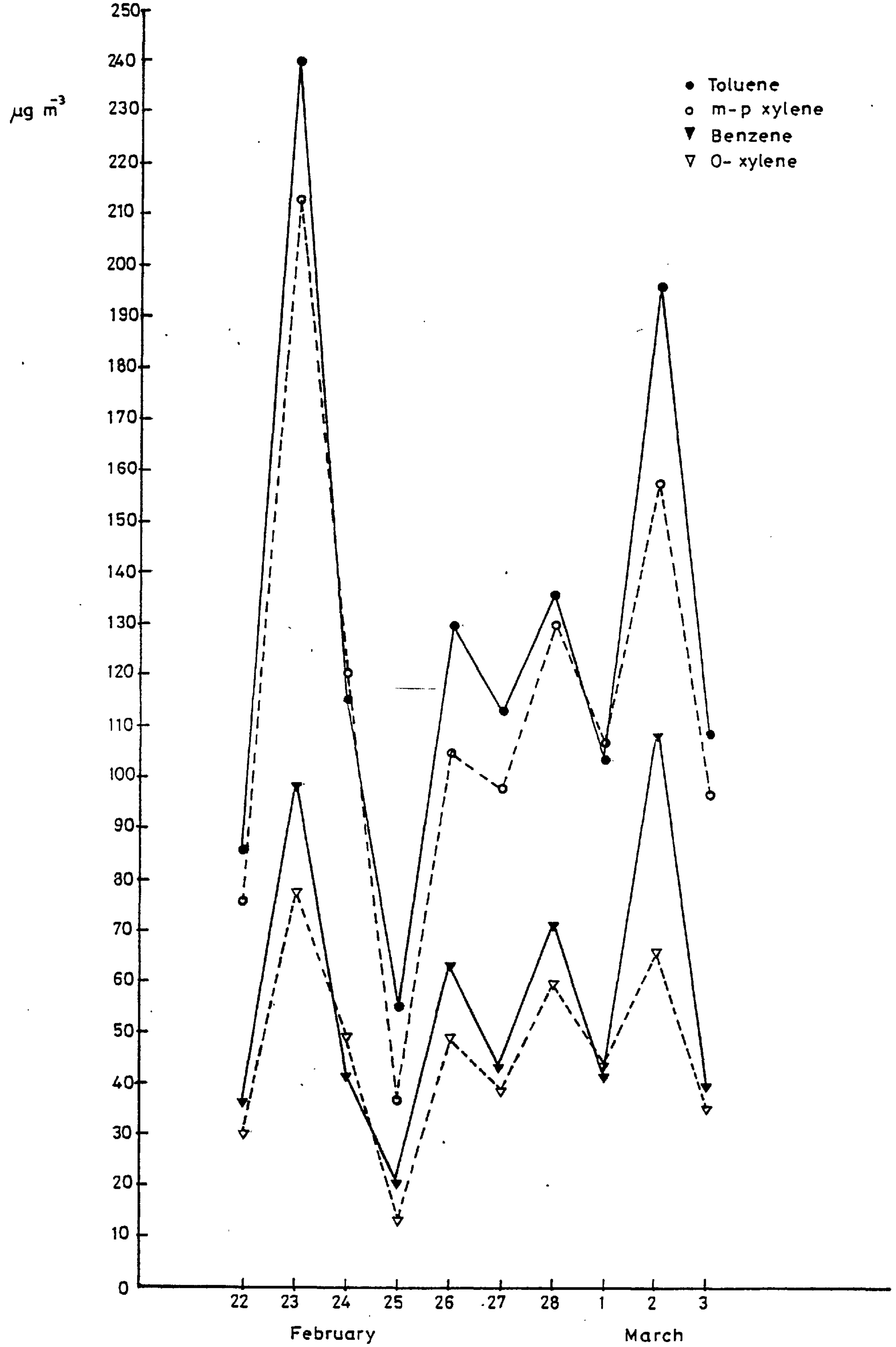


Fig 3·3 Daily variation of hydrocarbons over the period 22nd February to 3rd March

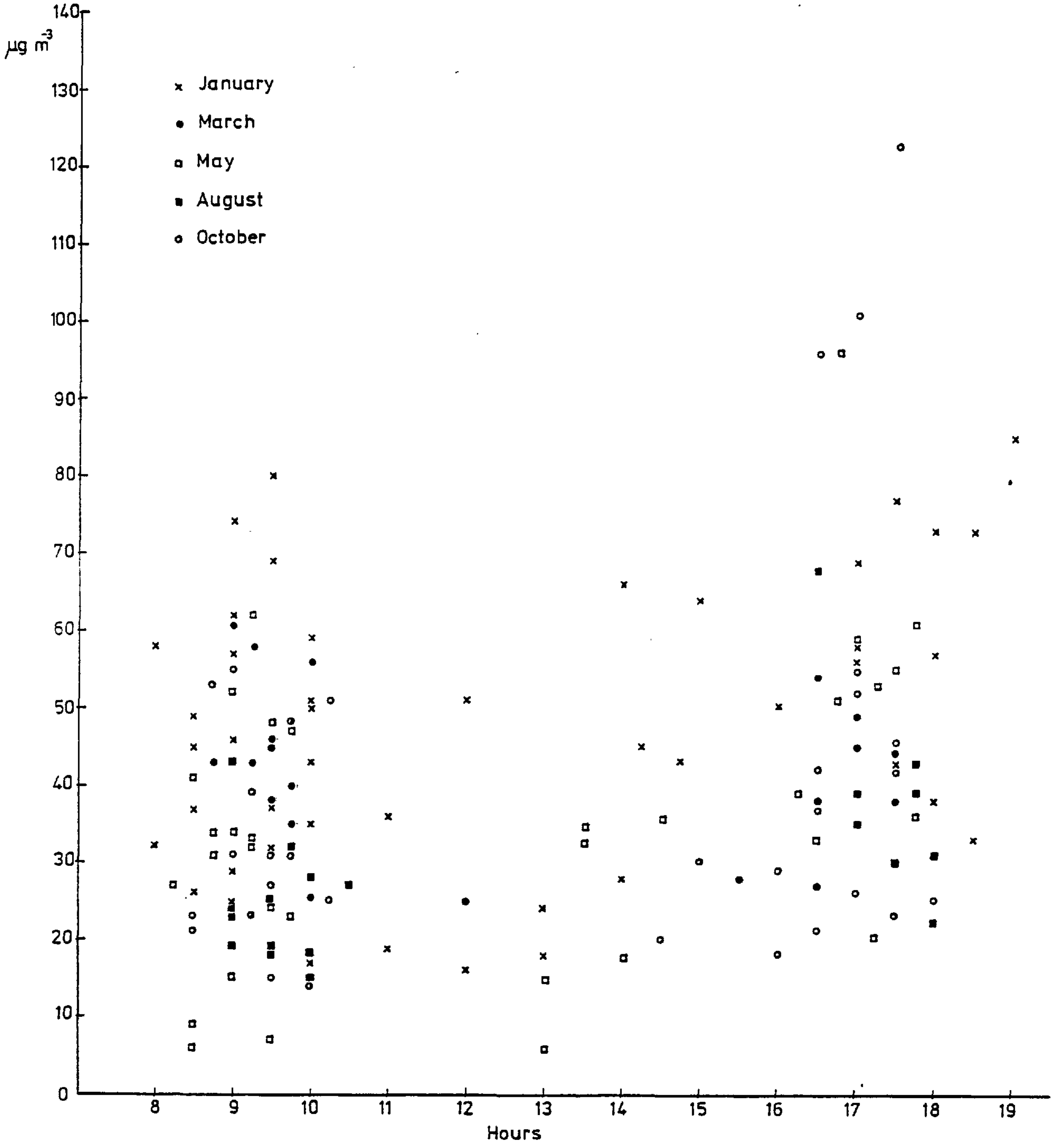


Fig 3·4 (a) Hourly distribution of benzene measurements in Exhibition Road (January - October 1979)

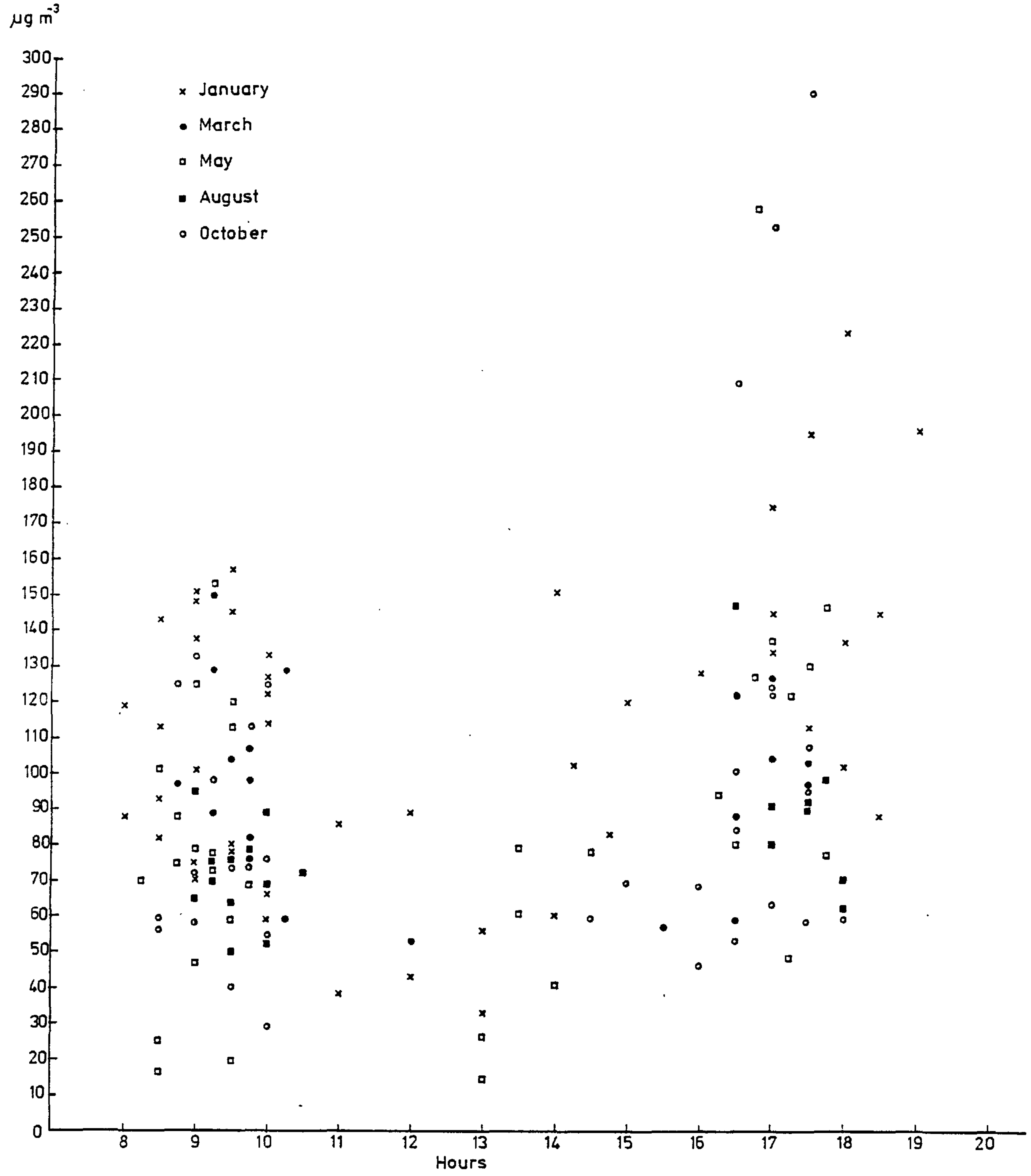


Fig 3·4(b) Hourly distribution of toluene measurements in Exhibition Road (January - October 1979)

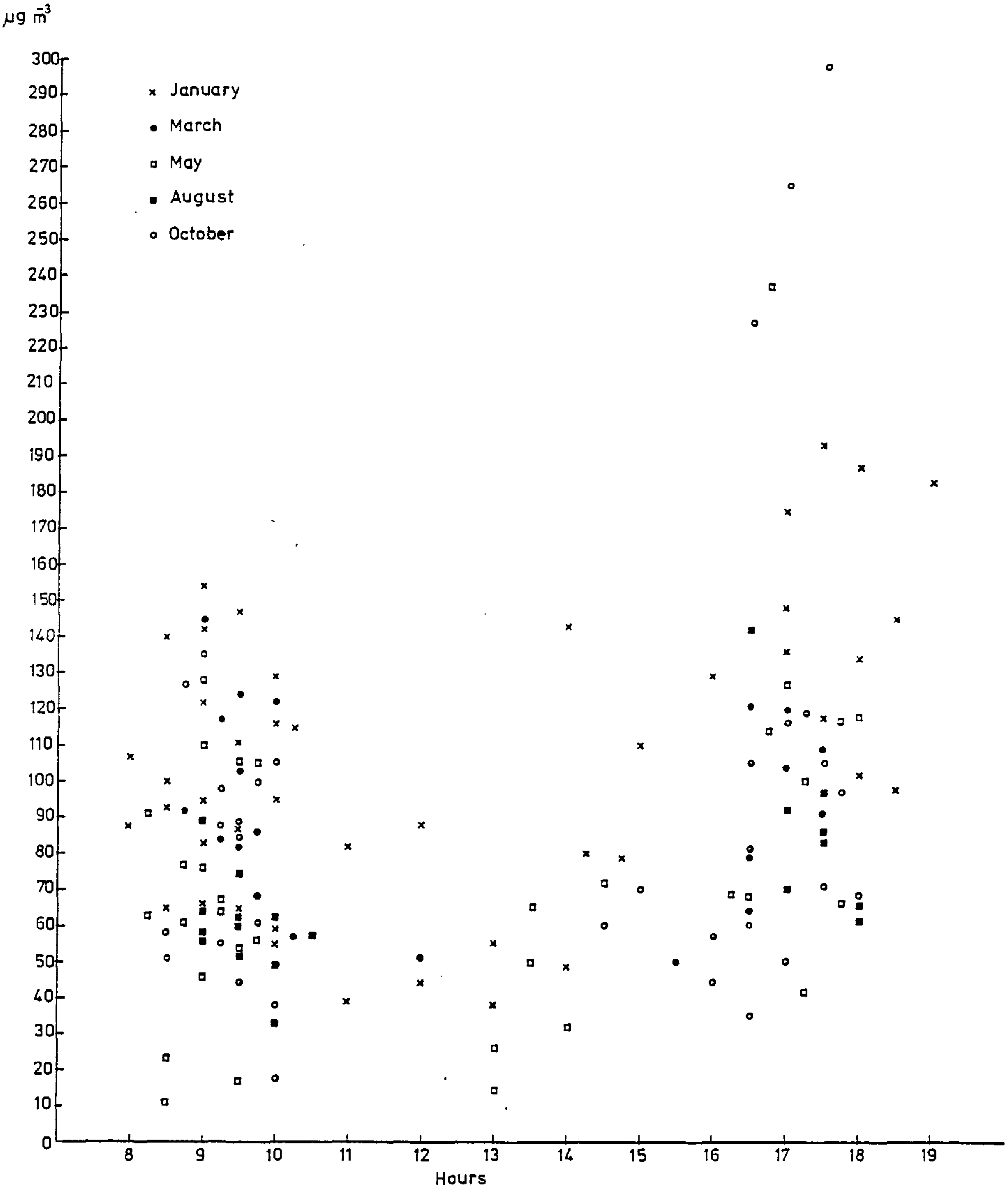


Fig 3·4(c) Hourly distribution of m+p-xylene measurements in Exhibition Road (January - October 1979)

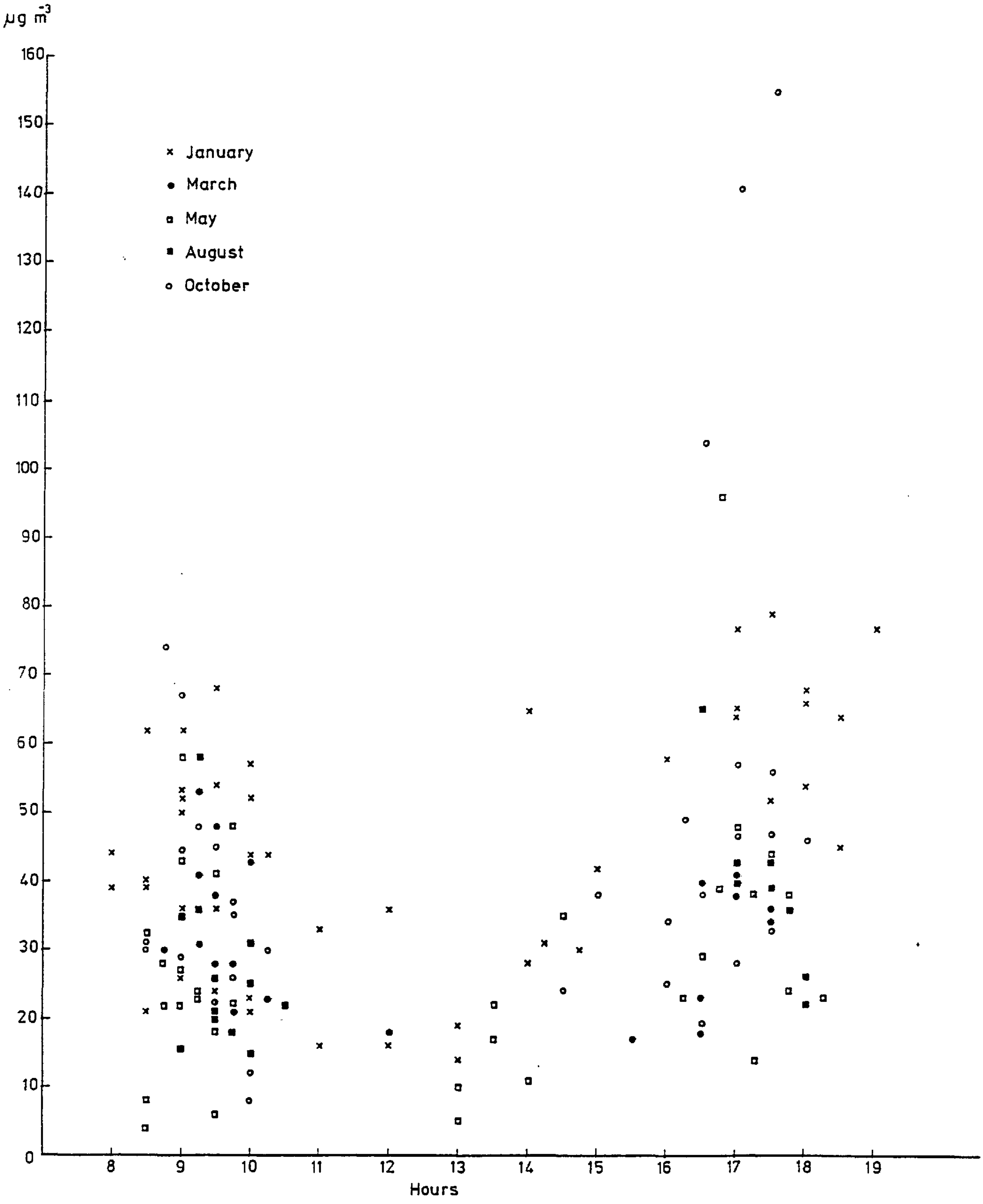


Fig 3·4 (d) Hourly distribution of O - xylene measurements in Exhibition Road (January - October 1979)

Comparison of fig. 3.4(a) and 3.4(b) shows a similarity in their distribution, although the difference of their concentrations is clearly indicated (axes y). This suggests the correlation between the two compounds in each air sample, which can be seen also in fig. 3.1 and fig. 3.3.

(c) Correlation between individual hydrocarbons

The ratio for toluene and benzene (C_7/C_6) is well known as 2.4:1 and is accepted as being indicative of pollution arising from vehicle exhaust emissions.

The mean ratio found between toluene and benzene in Exhibition Road air samples over the 10 month period was

$$\bar{x} = 2.45$$

with a standard deviation $\sigma_n = 0.38$, which indicates that with little variation, the correlation is very strong. This can be confirmed by reference to fig. 3.5, where benzene is plotted against toluene in a regression mode. The correlation between benzene and toluene in this normal distribution is as good as 0.966 and the linearity is expressed by the equation

$$y = 0.0623 + 0.416 \quad x_1$$

On the basis of this analysis, 93.4% of the found factors C_7/C_6, lie on the above regression line.

Referring back to fig. 3.4 it is apparent also that similarities exist between the distributions in (b) and (c), which indicates that m+p-xylene concentrations correlate well with toluene concentrations. Similarly, from fig. (c) and (d) it is clear that a correlation of o-xylene to m+p-xylene, representing approximately 30-40% of its concentrations, exists.

Taking as an example the four hydrocarbons and their behaviour, one can make similar assumptions for the other 12 compounds involved in this study, as is obvious from the variation of their concentrations presented in Appendix A. Particular examples are m+p-Ethyl-toluene and 1,2,4-Trimethyl-benzene which were the other two significant components in a chromatographic analysis, each one representing 5-7% of the total aromatic constituent.

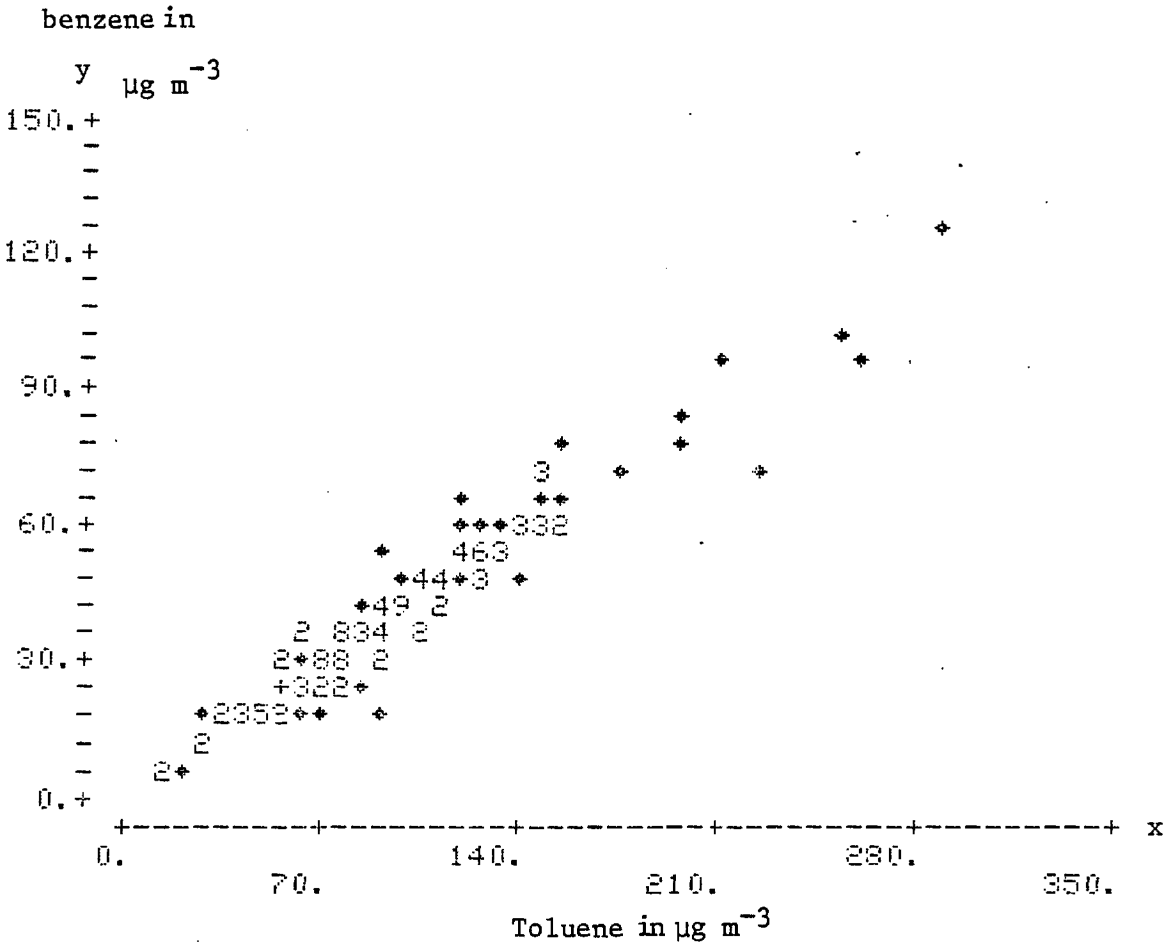


Fig. 3.5 Correlation of toluene and benzene concentrations

Correlation of y and x ; 0.966

Regression equation $y = 0.623 + 0.416\ x_1$

R-squared = 93.4%

An immediate observation from fig. 3.4 also, is that hydrocarbon concentrations during the morning rush hour period show less scatter than those in the afternoon. This indicates that the traffic during the afternoon is more disordered and diverted than in the morning, facts which contribute nevertheless to higher concentrations of these pollutants in the ambient air.

(d) Variation in hydrocarbon concentrations with season

This phenomenon was investigated on the basis of the 10 month period measurements in Exhibition Road. Referring again to fig. 3.4(a,b,c,d), the distribution of benzene, toluene, m+p-xylene and o-xylene is recorded separately for every month by different symbols. In this distribution is shown a slight elevation in January and October concentrations and a decrease in May concentrations of these pollutants. However any major variation is not shown as the concentrations found over the four seasons period varied within the same approximate levels. A particular observation relates to the afternoon of 24 May, when there was no perceptible wind and a high temperature (22°C) predominated. Then, the highest hydrocarbon concentrations over the May period were recorded, but they were still within the same levels related to the measurements over the 10 month period. During that afternoon, the highest concentration of EDB (1.26 µg m^{-3}) was also recorded, for all the Exhibition Road measurements. This is an indication that high temperatures and still conditions give rise to elevated concentrations of less volatile pollutants in a given area.

Given the differences in vapour pressures of benzene and toluene (80.1 and 110.6 at STP respectively) such indications could be obtained from the seasonal variation of the C_7/C_6 ratios shown in table 3.2.

Table 3.2 : Seasonal variation of C_7/C_6 ratios

Month	C_7/C_6	
	$\bar{x}$	σ_n
January	2.40	0.36
March	2.30	0.19
May	2.43	0.26
August	2.80	0.67
October	2.42	0.19

The trends observed in August in comparison with the other months give indeed such an indication resulting in higher toluene concentrations than those for benzene. However, more assumptions can not be extracted from the available data and there is a need for further investigation before definitive conclusions can be drawn.

(e) Statistical analysis

Regression analysis of the January to October hydrocarbon measurements at the Exhibition Road site, derived the frequency distributions for benzene, toluene, m+p-xylene and o-xy lene, shown in fig. 3.6(a,b,c,d).

In this figure the concentrations for these four compounds are presented in terms of percentiles. In other words, the probability for any concentration of the above compounds to occur at Exhibition Road during the 10 month period, is given by a regression line represented by the predictive equations recorded. The points lie roughly on a straight line which means that the concentrations obtained for the four compounds, were approximately normally distributed.

An immediate assumption from the regression analysis is that the probability of concentrations exceeding 130 μg m^{-3} for benzene, 290 μg m^{-3} for toluene, 298 μg m^{-3} for m+p-xylene and 150 μg m^{-3} for o-xylene at the Exhibition Road site over the 10 month period of measurements, was less than 1%.

3.1.2.2 Halocarbons

Appendix A includes all the data in μg m^{-3} for 1,2-dibromoethane (EDB) and 1,2-dichloroethane (EDC) obtained from the six month period (March to August 1979) measurements at the Exhibition Road site, under the numbers 17 and 18 respectively.

No vinyl chloride was found over this period in Exhibition Road air samples. Concentrations of EDB and EDC recorded at this site varied bewteen 0.07 and 1.26 μg m^{-3} and 0.48 and 2.14 μg m^{-3} respectively.

Frequency distributions of EDB and EDC concentrations in Exhibition Road are shown in fig. 3.7(a,b) where EDB and EDC are plotted against z_1 and z_2 values interpreted in percentiles.

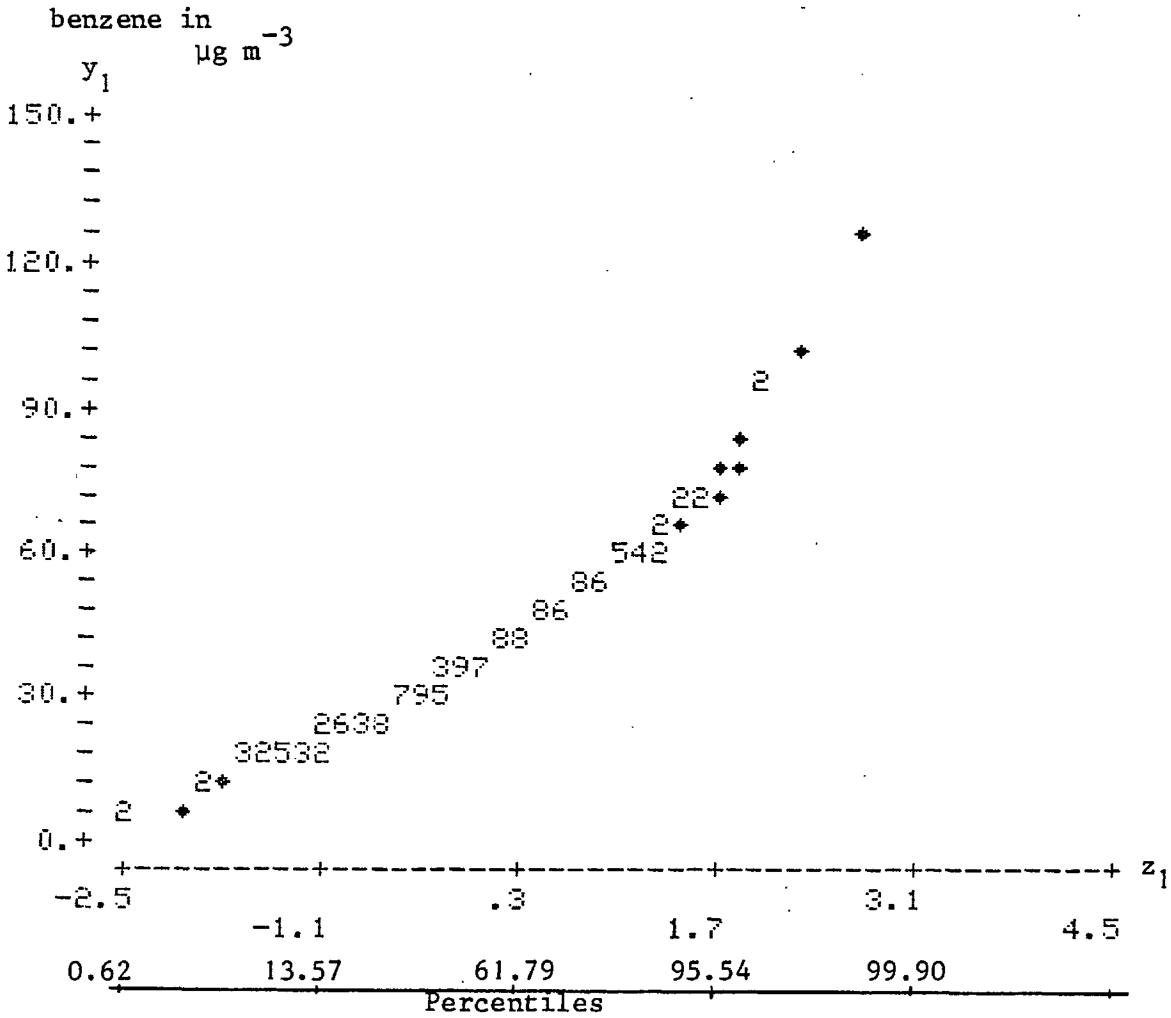


Fig. 3.6(a) Frequency distribution of benzene in Exhibition Road

Correlation of y_1 and z_1 = 0.969

Regression equation $y_1 = 40.1 + 19.2\ z_1$

R-squares = 93.9%

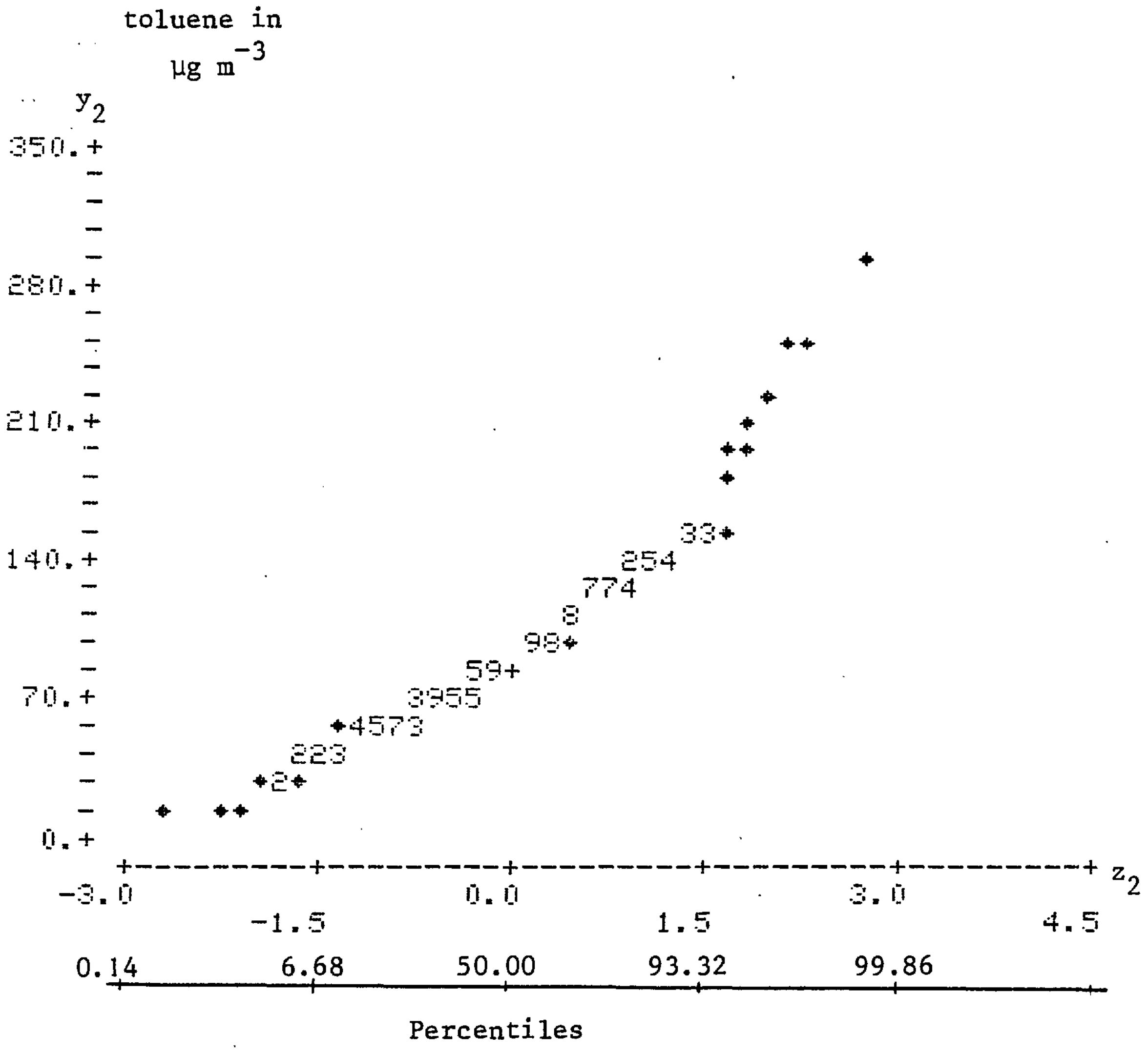


Fig. 3.6(b) Frequency distribution of toluene in Exhibition Road

Correlation of y_2 and z_2 = 0.957

Regression equation $y_2 = 96.3 + 44.0\ z_2$

R-squares = 91.5%

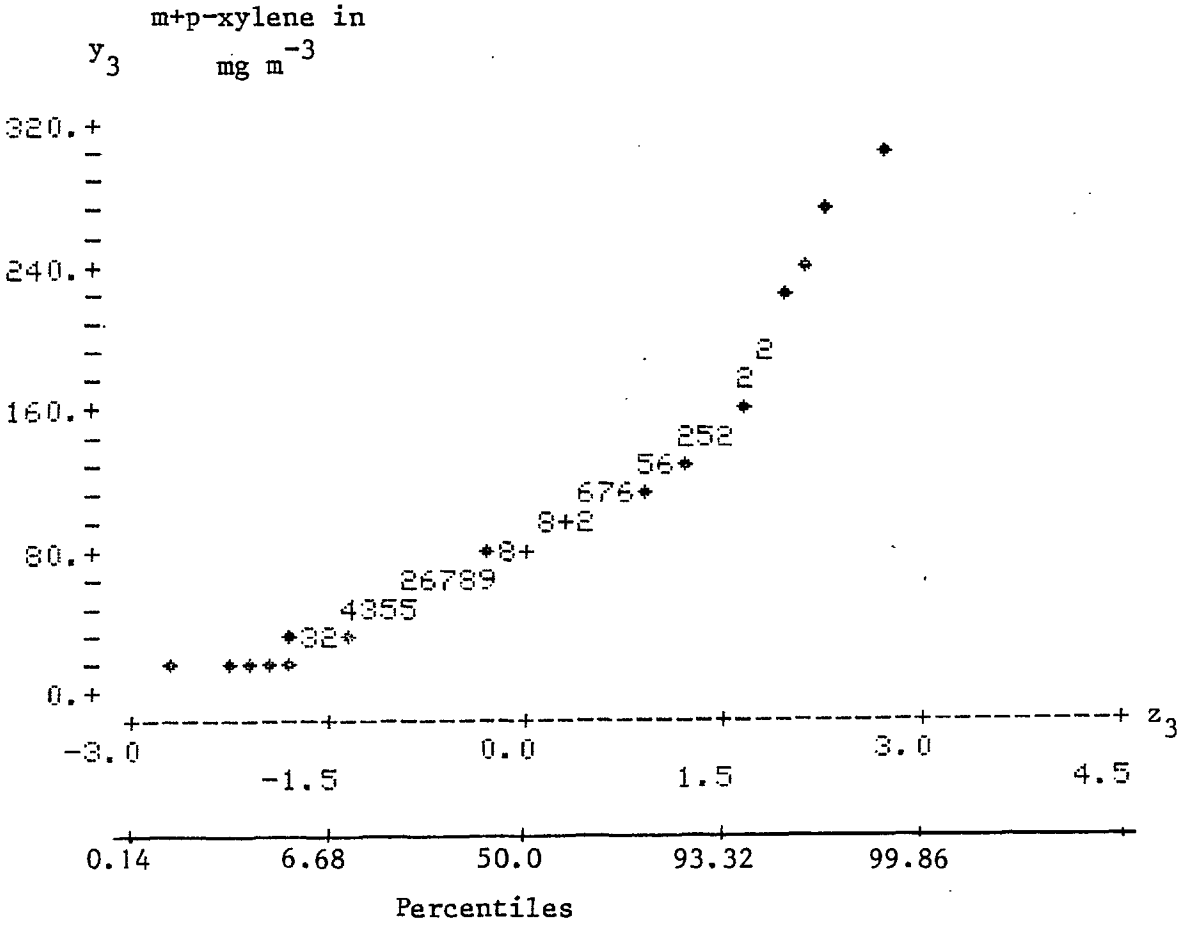


Fig. 3.6(c) Frequency distribution of m+p-xylene in Exhibition Road

Correlation of y_3 and z_3 = 0.950

Regression equation $y_3 = 90.4 + 43.7\ z_3$

R-squared = 90.2%

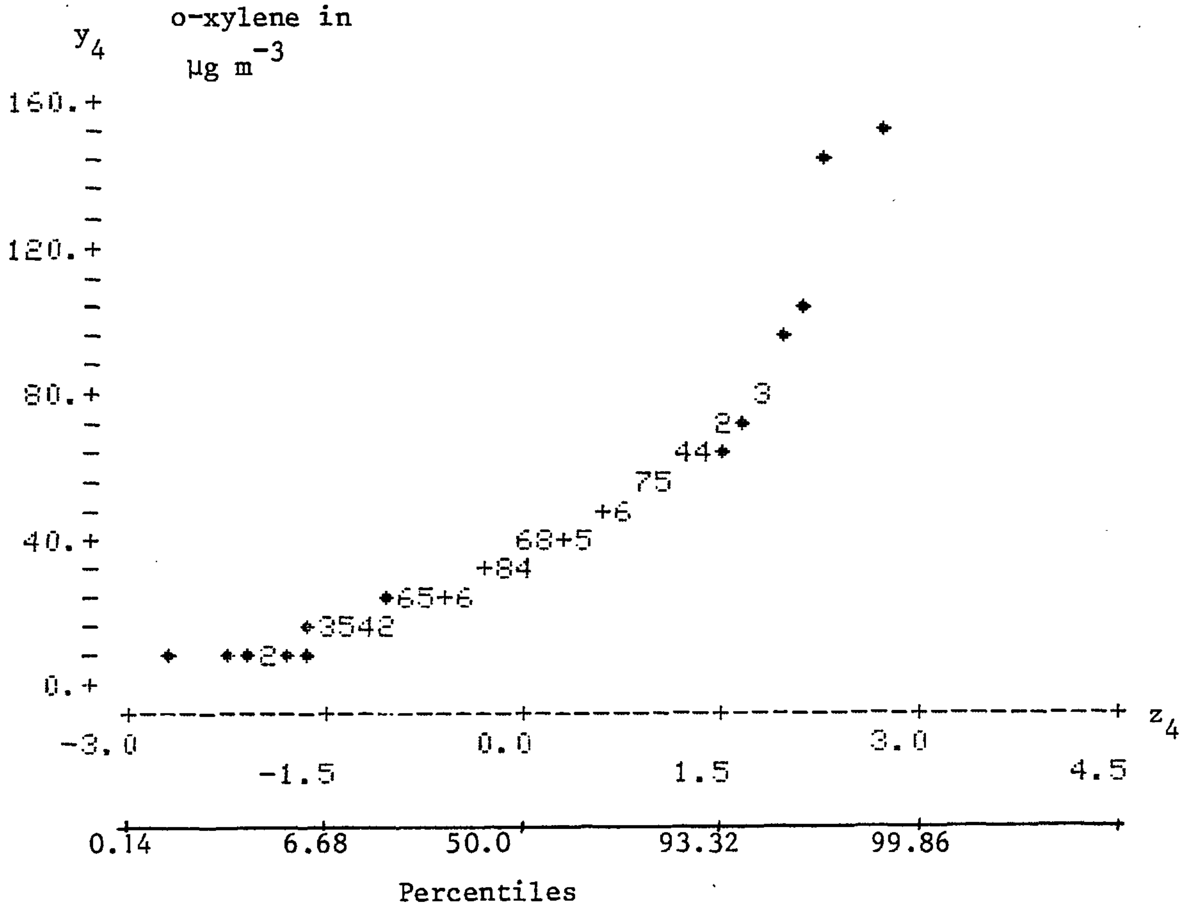


Fig. 3.6(d) Frequency distribution of o-xylene in Exhibition Road

Correlation of y_4 and z_4 = 0.931

Regression equation $y_4 = 5.57 + 81.1\ z_4$

R-squared = 86.8%

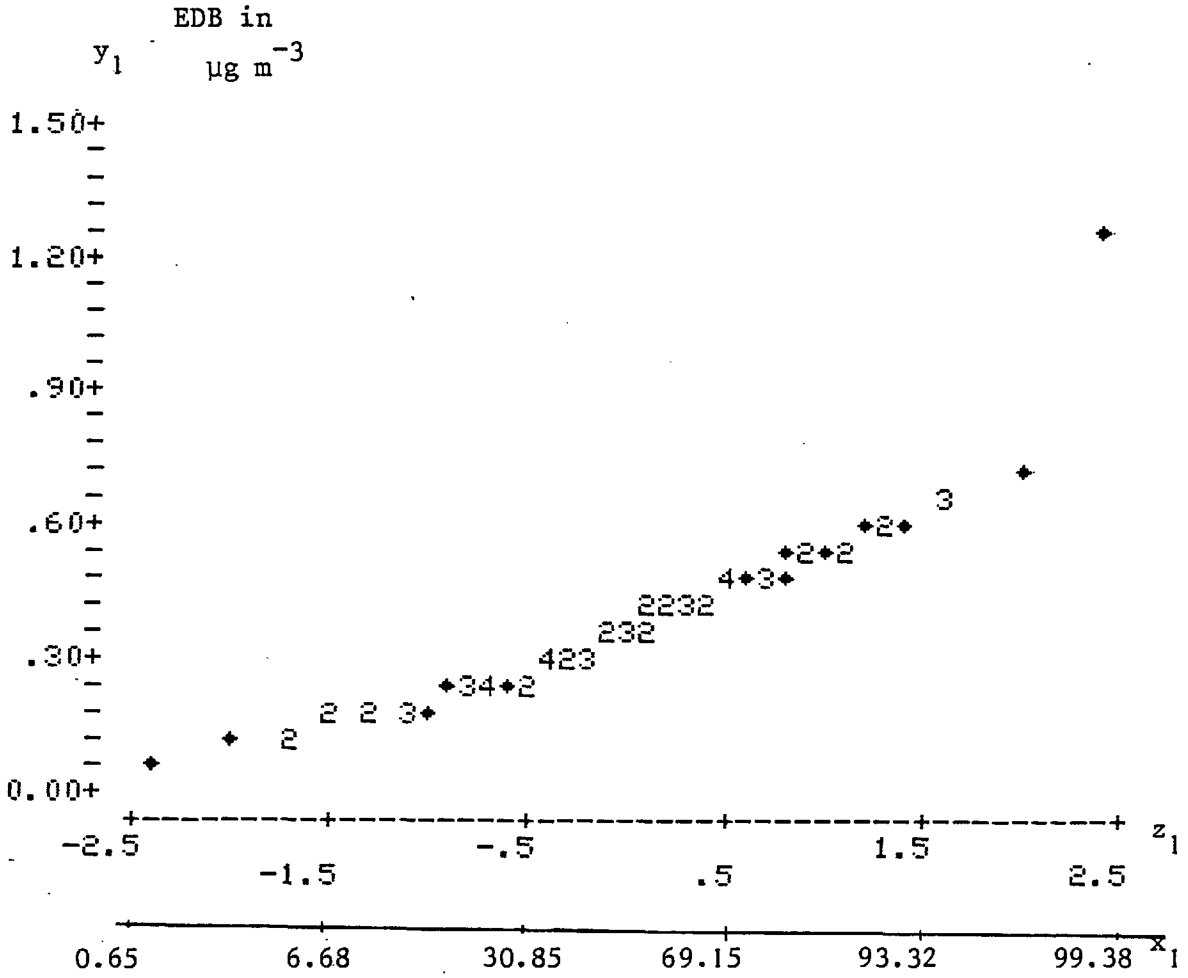


Fig. 3.7(a) Frequency distribution of EDB measurements in Exhibition Road

Correlation of y_1 and x_1 = 0.943

Regression equation = $y_1 = 0.375 + 0.177\ z_1$

R-squared ; 89.0%

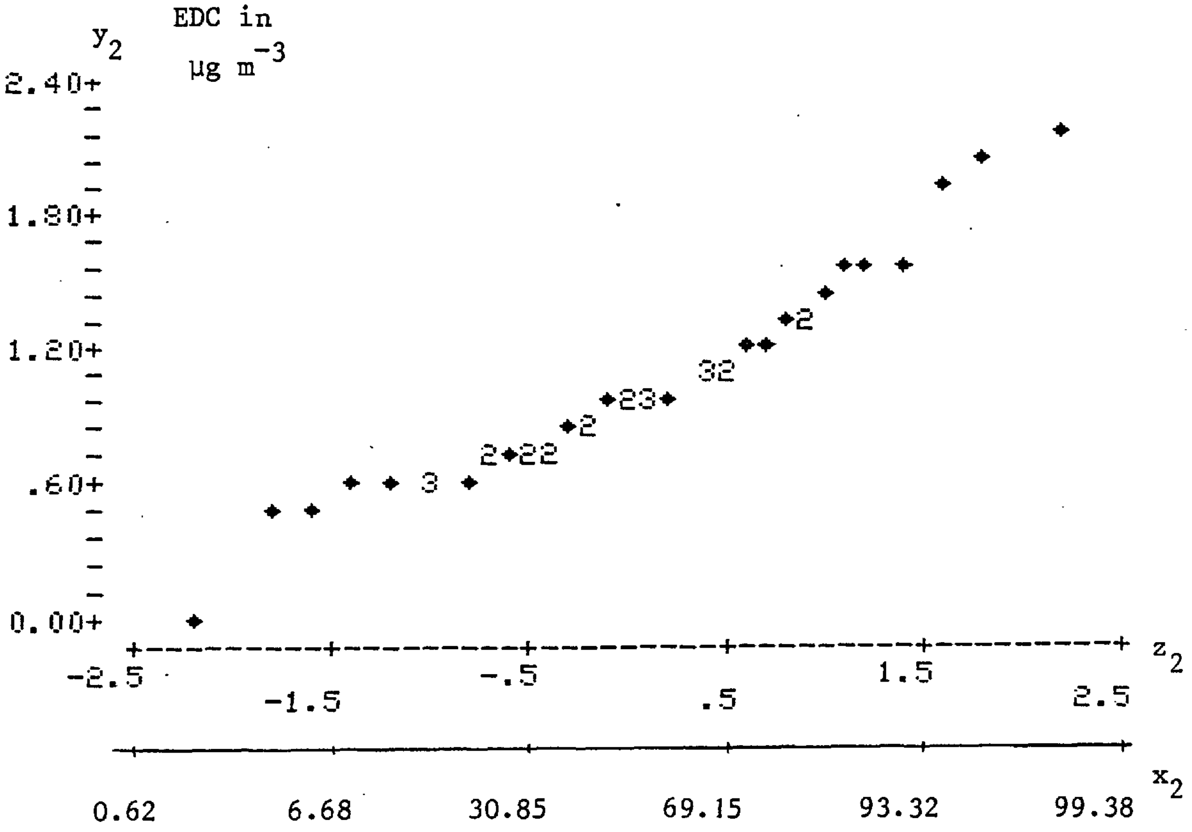


Fig. 3.7(b) Frequency distribution of EDC measurements in Exhibition Road

Correlation of y_2 and x_2 = 0.969

Regression equation $y_2 = 0.995 + 0.434\ z_2$

R-squared = 93.8%

Both the compounds exhibit an almost linear regression line with a strong correlation of 0.943 and 0.969 respectively, which indicates a normal distribution of the concentrations found in Exhibition Road.

An investigation of the variation of EDB and EDC concentrations in Exhibition Road, with respect to the variation of individual hydrocarbon concentrations, has led to a correlation of EDB levels to benzene levels not previously reported.

Benzene usually occurs at concentrations of two orders of magnitude higher than those of EDB and EDC. Even so, EDB concentrations showed good agreement with benzene concentrations in street air, and an overall mean ratio of $\bar{x} = 97.71$ was calculated over 72 analyses, with a standard deviation of $\sigma_n = 17.37$.

It is clear from fig. 3.8 to 3.11, that the variation of EDB is very closely correlated with the variation of benzene.

Table 3.3 is a summary of the mean ratios and standard deviations calculated in months and includes toluene to benzene (C_7/C_6) ratios, benzene to EDB (C_6/EDB) and EDC to EDB (EDC/EDB) ratios for the Exhibition Road measurements.

Table 3.3 : Mean ratios for toluene to benzene (C_7/C_6), benzene to EDB (C_6/ECB) and EDC to EDB (EDC/EDB)

	C_7/C_6		C_6/EDB		EDC/EDB	
Month	$\bar{x}$	σn	$\bar{x}$	σn	$\bar{x}$	σn
March	2.30	0.19	102.3	18.5	2.83	1.04
May	2.43	0.26	93.0	17.1	1.95	0.56
August	2.80	0.67	100.9	14.0	2.47	0.85

From the March and August measurements an $\bar{x} = 102.3$ and $\bar{x} = 100.9$ respectively results, whereas May measurements show a slight increase in EDB concentrations resulting in a ratio of $\bar{x} = 93.0$.

Given the generally low concentrations of EDB in comparison to those of aromatic hydrocarbons and the analytical error involved in both determinations, this correlation is particularly strong and is

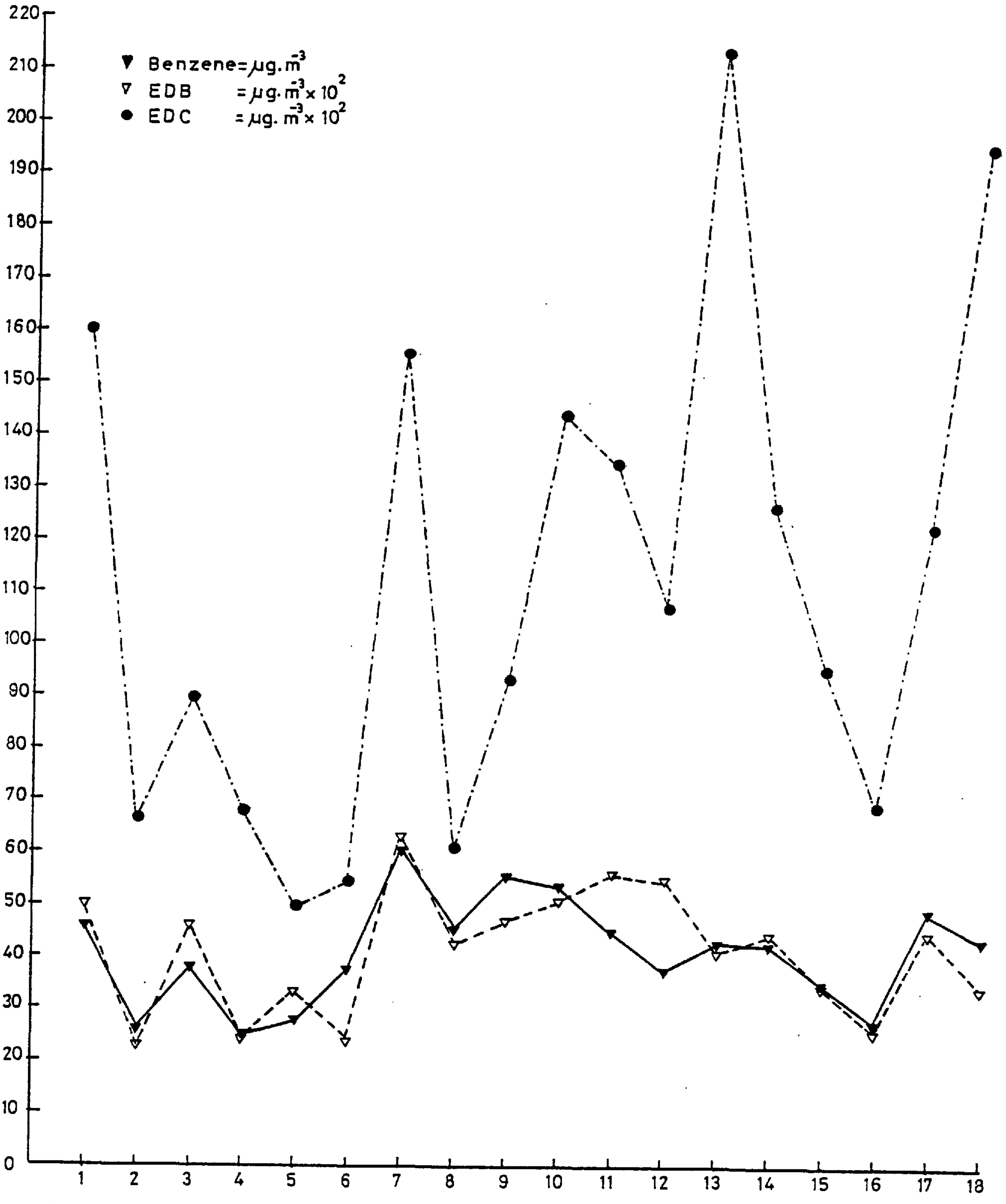


Fig 3·8 Variations of EDB, EDC and benzene over March 1979 measurements in Exhibition Rd.

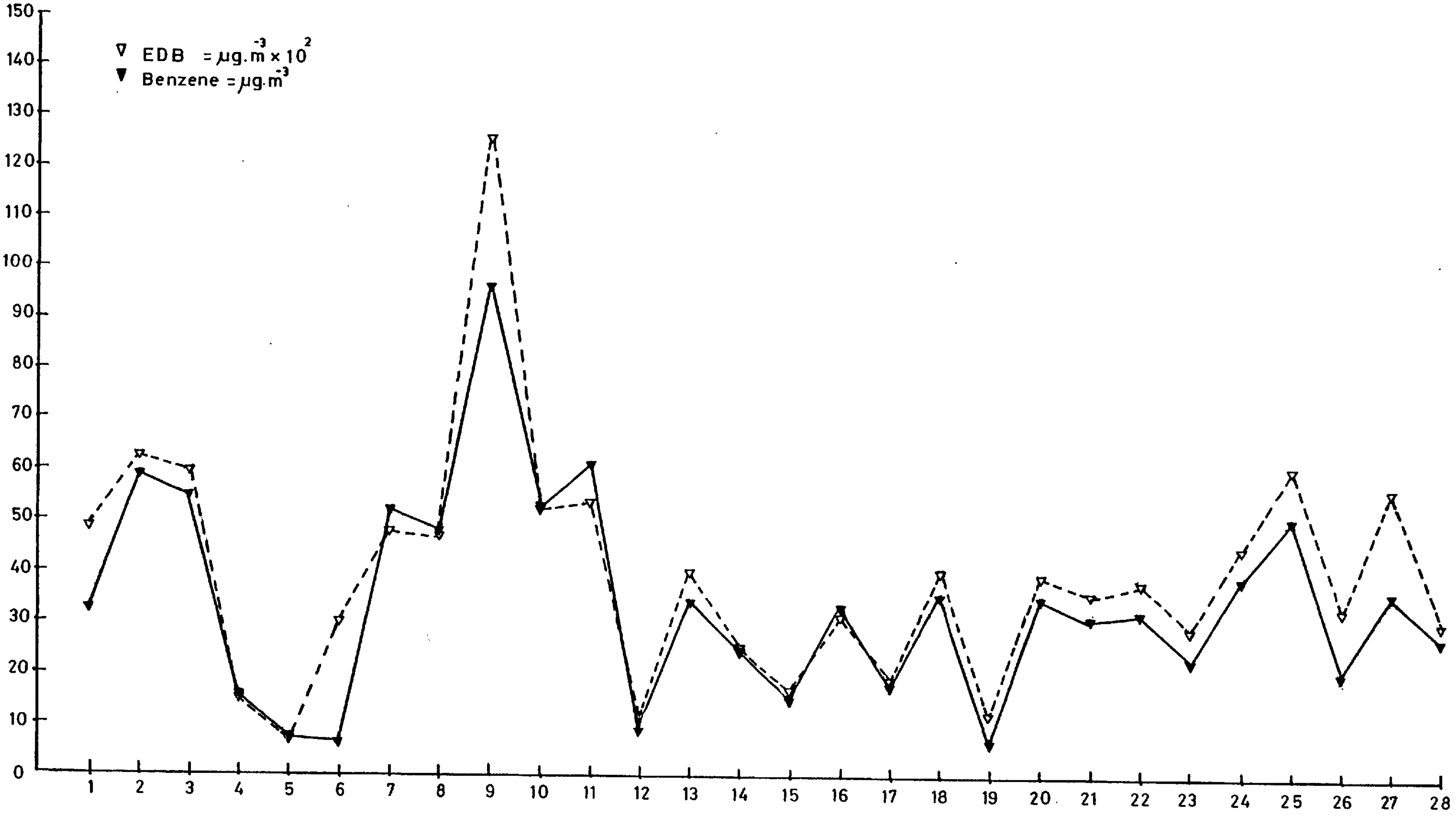


Fig 3·9 Variation of EDB and benzene over May 1979 measurements in Exhibition Road

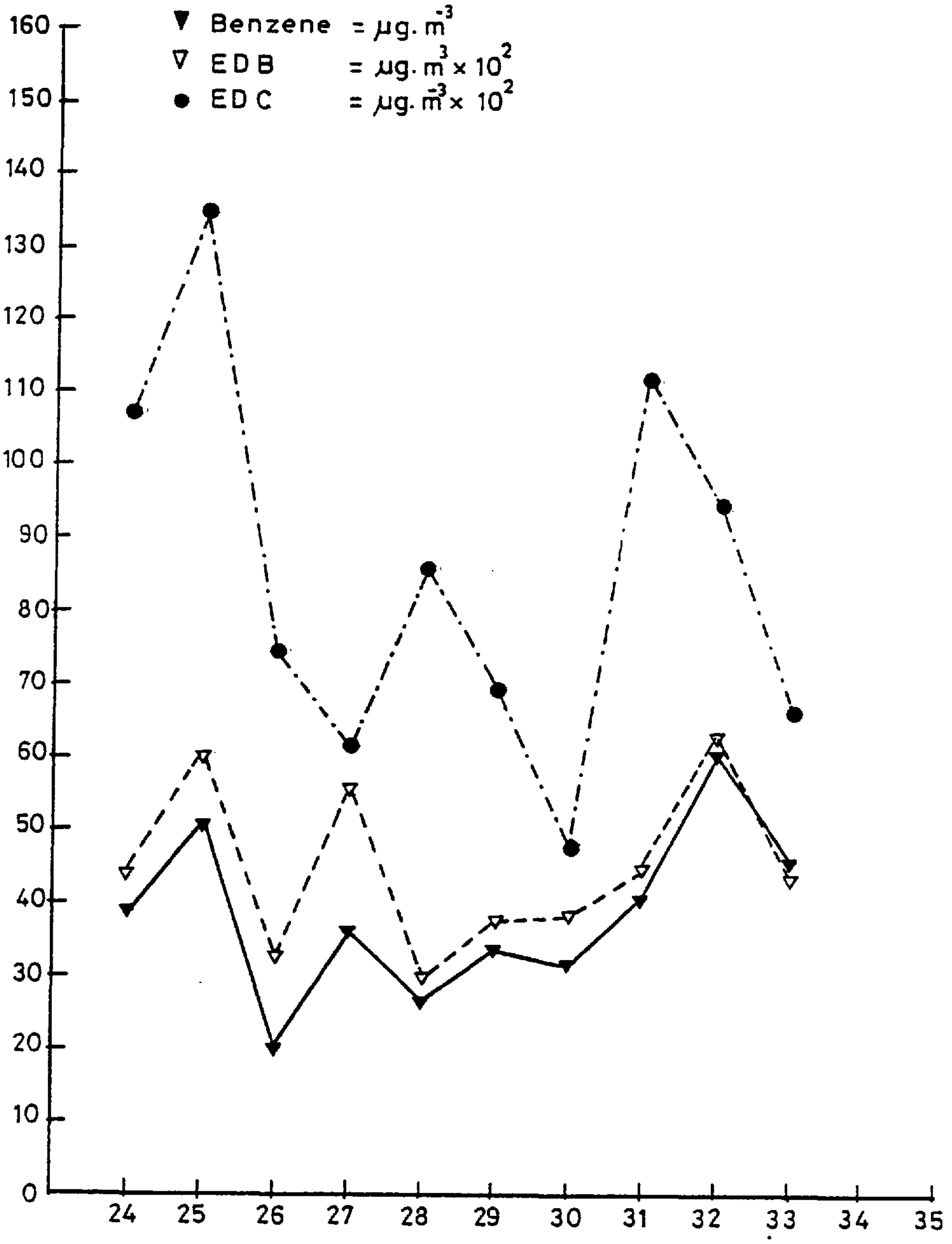


Fig 3·10 Variation of EDB, EDC and benzene over May 1979 measurements in Exhibition Rd

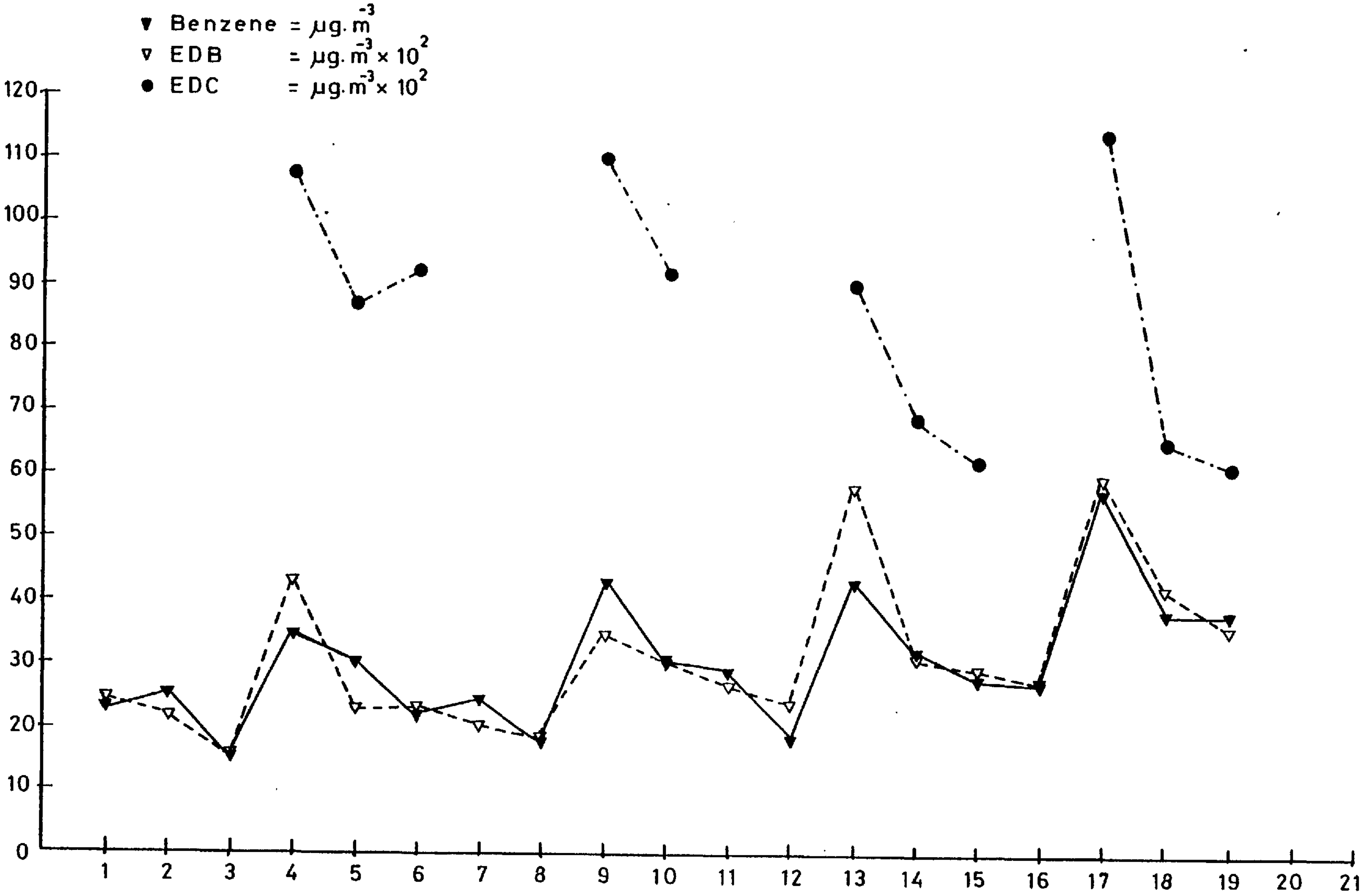


Fig 3·11 Variation of EDB, EDC and benzene over August 1979 measurements in Exhibition Rd well justified by the use of these materials as fuel components.

Statistical analysis of the data resulted in a very strong correlation between EDB and benzene concentrations. Figure 3.12 is a scatter diagram in which concentrations of EDB in $\mu g\ m^{-3}$ are plotted against benzene concentrations in $\mu g\ m^{-3}$, for the 72 measurements in Exhibition Road.

The line y represents the least squares linear regression line of "best fit" for the 72 points. The regression equation is:

$$y = -0.0100 + 0.0107\,x$$

with a correlation of y and x equal to 0.931.

The statistical analysis indicates that EDB concentrations in a given location can be predicted from benzene concentrations within an accuracy of 100%±13, a fact which becomes particularly useful where detailed analysis of ambient air is not feasible.

Considering the EDC concentrations in street air, it is apparent that there is a greater variation in EDC measurements, which do not correlate very well with EDB, although both the compounds are present in petrol on approximately a 50:50 weight to weight basis.

It seems that EDC occurs in street air in higher concentrations than EDB and for the limited quantity of data available (41) from Exhibition Road measurements, a mean ratio of $\bar{x} = 2.52$ $(\sigma_n = 0.96)$ is exhibited for EDC/EDB.

Figure 3.13 shows EDB plotted against EDC concentrations in a regression mode. All the points are scattered and the poor correlation is given by a factor of 0.430.

The higher concentrations of EDC in street air are in agreement with the lower efficiency of EDC as a lead scavenger compared to EDB, since proportionately more EDC will be released to the air. As for the greater variation in EDC concentrations, it is possible that this may be related to the photoreactivity of this compound in the air.

3.2 Dispersion of Individual Pollutants in Street Air

A great number of studies have been undertaken to define large scale dispersion models suitable for stationary or mobile sources. The intention here was to investigate how individual pollutants disperse vertically from the kerbside.

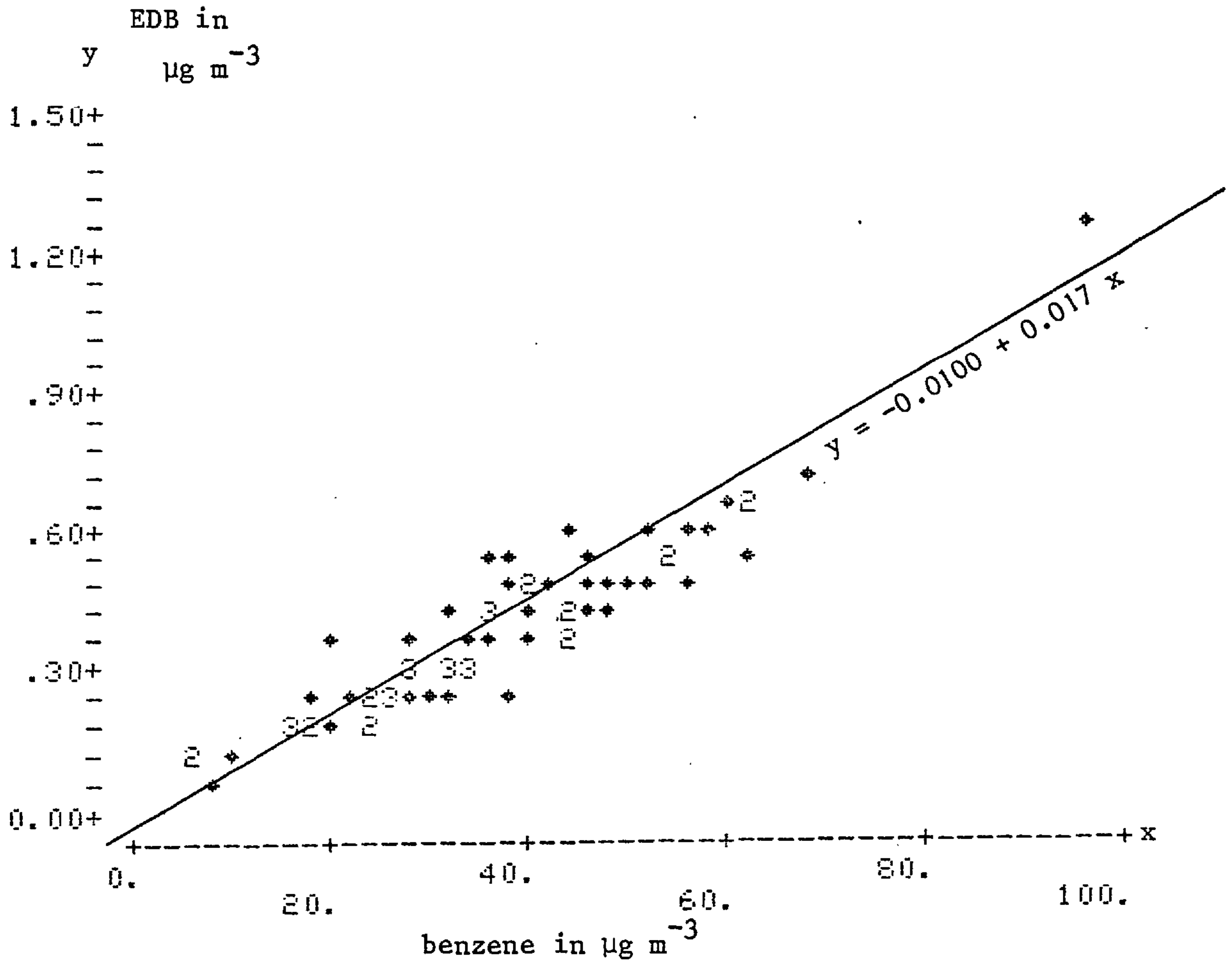


Fig. 3.12 Correlation of EDB and benzene

Correlation of y and x = 0.931

Regression equation y = -0.0100 + 0.017 x

R-squared = 86.8

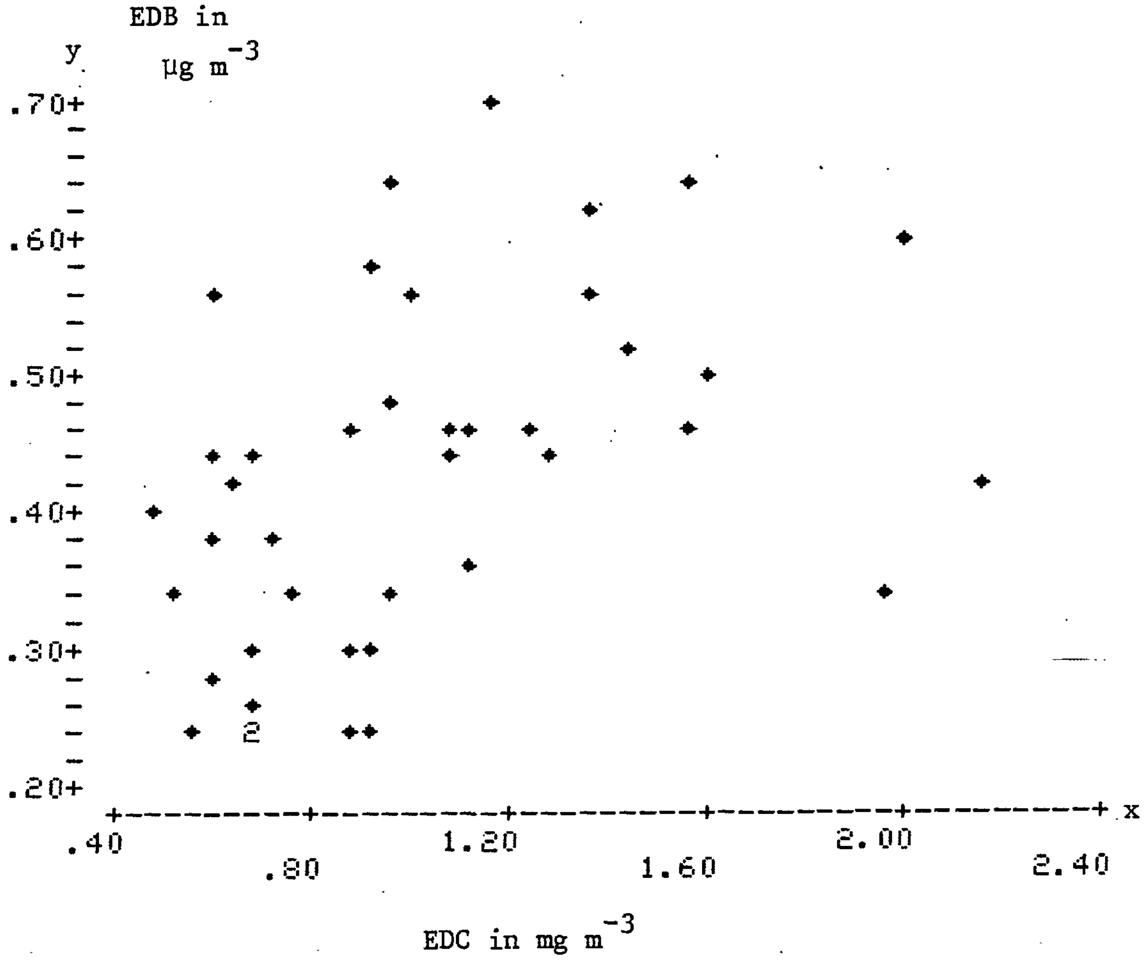


Fig. 3.13 Correlation of EDB and EDC

Correlation of y and x = 0.430

R-squared = 18.5%

In order to achieve this, three Du Pont constant flow pumps were employed and the sampling points were established first by the kerb, second 10 m away from the kerb and third 20 m from the kerb. Results including sixteen hydrocarbons are recorded in detail in Appendix A.

In fig. 3.14(a,b,c,d) some of the results of the triplicate analyses are presented graphically. They present the profiles of the analyzed hydrocarbons where each (1-16) is plotted against concentration in $\mu g\ m^{-3}$. It is clear that concentrations of these pollutants by the kerbside are higher than those at 10 or 20 m distances from the kerb. The degree of decrease varies between 10-50% for the first 10 metres and between 30-70% for the next 10 metres as calculated from table 3.4.

Table 3.4 : Variation of the cumulative concentrations ($\mu g\ m^{-3}$) of the 16 hydrocarbons with distance from the kerb

Date	Time	Kerb	10 m from the kerb	20 m from the kerb
19/ 3/79	09.00-09.30	648	438	348
	09.30-10.00	450	372	324
28/ 8/79	16.30-17.00	682	326	321
	17.00-17.30	411.5	372	266.4
	17.30-18.00	1510	859	406.5
29/10/79	09.00-09.30	907	482	344
	09.30-10.00	567	363	315

This can be said with certainty for the more volatile compounds (1-8, benzene to m+p ethyl-toluene), where a gradual decrease in concentration with distance is observed. Occasional deviations from this trend are observed for the number 9-16 hydrocarbons, which cannot be readily explained.

Table 3.5 shows the variation in the C_7/C_6 ratio for each set of measurements separately, where A refers to results by the kerb, B ; 10 m away and C ; 20 m away from the kerb.

The variation in columns 5 and 7 indicate that benzene is more readily dispersed than toluene, which, extrapolated for all the compounds

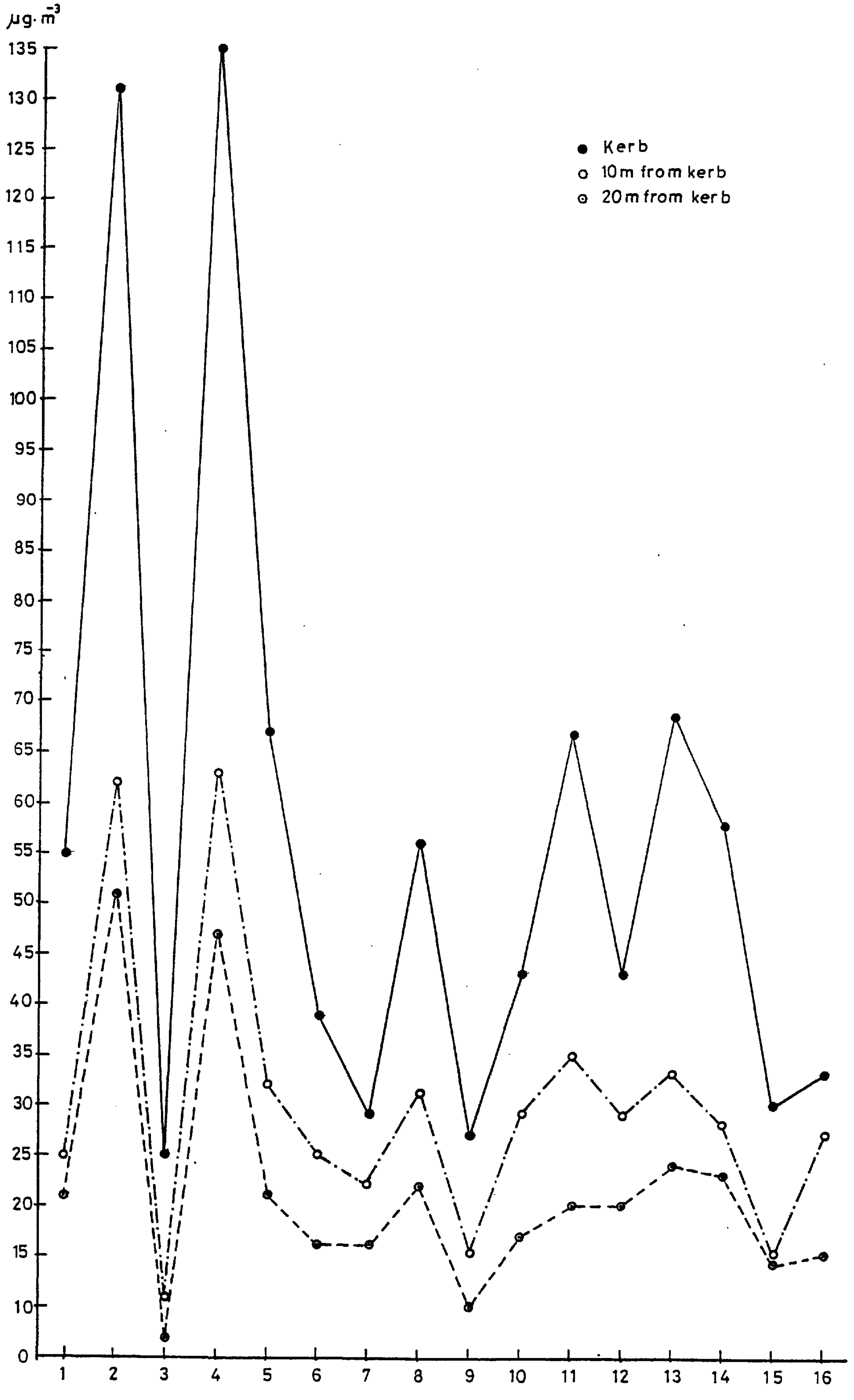


Fig3·14(a)Dispersion of hydrocarbons with distance from the kerb

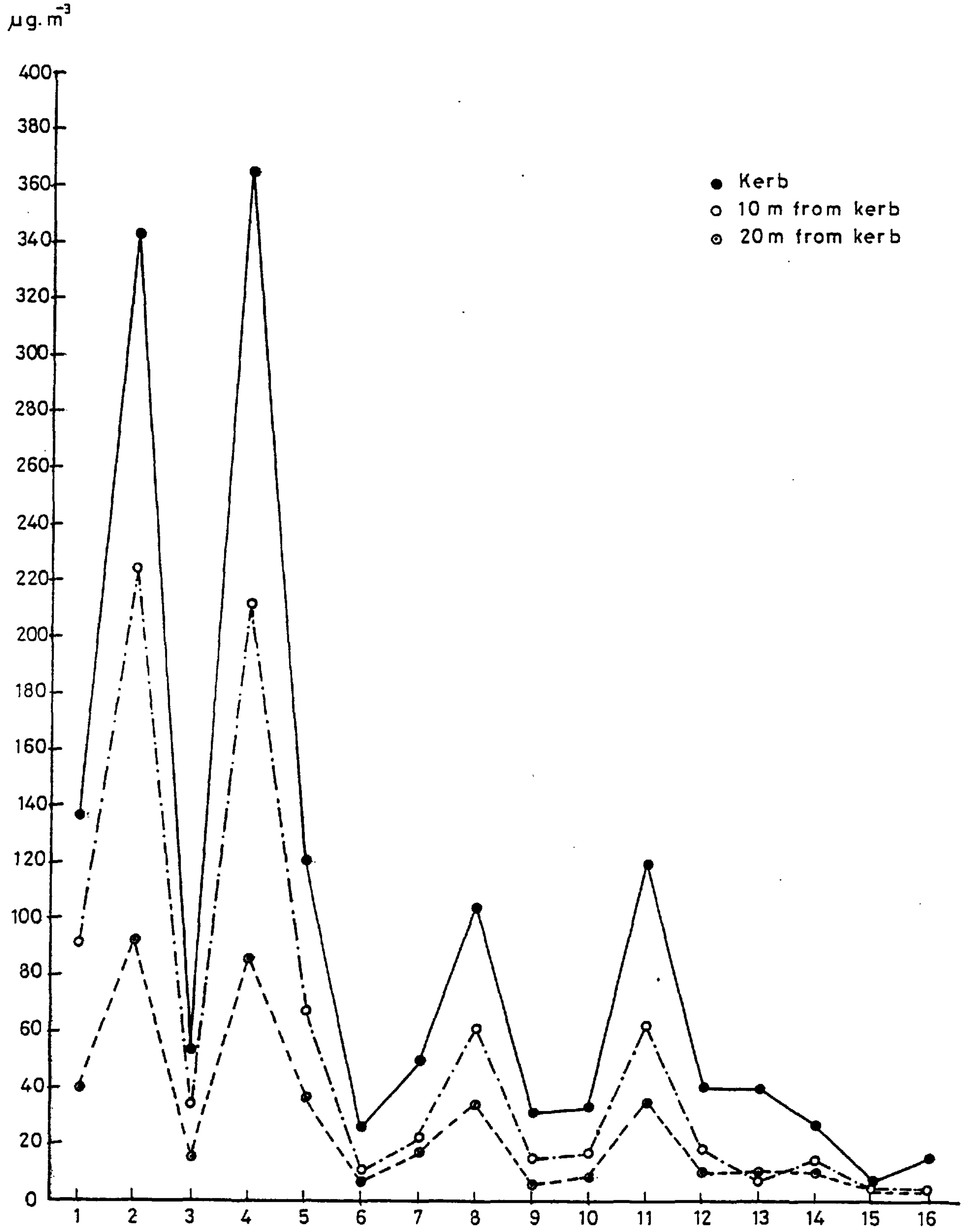


Fig 3·14(b) Dispersion of hydrocarbons with distance from the kerb

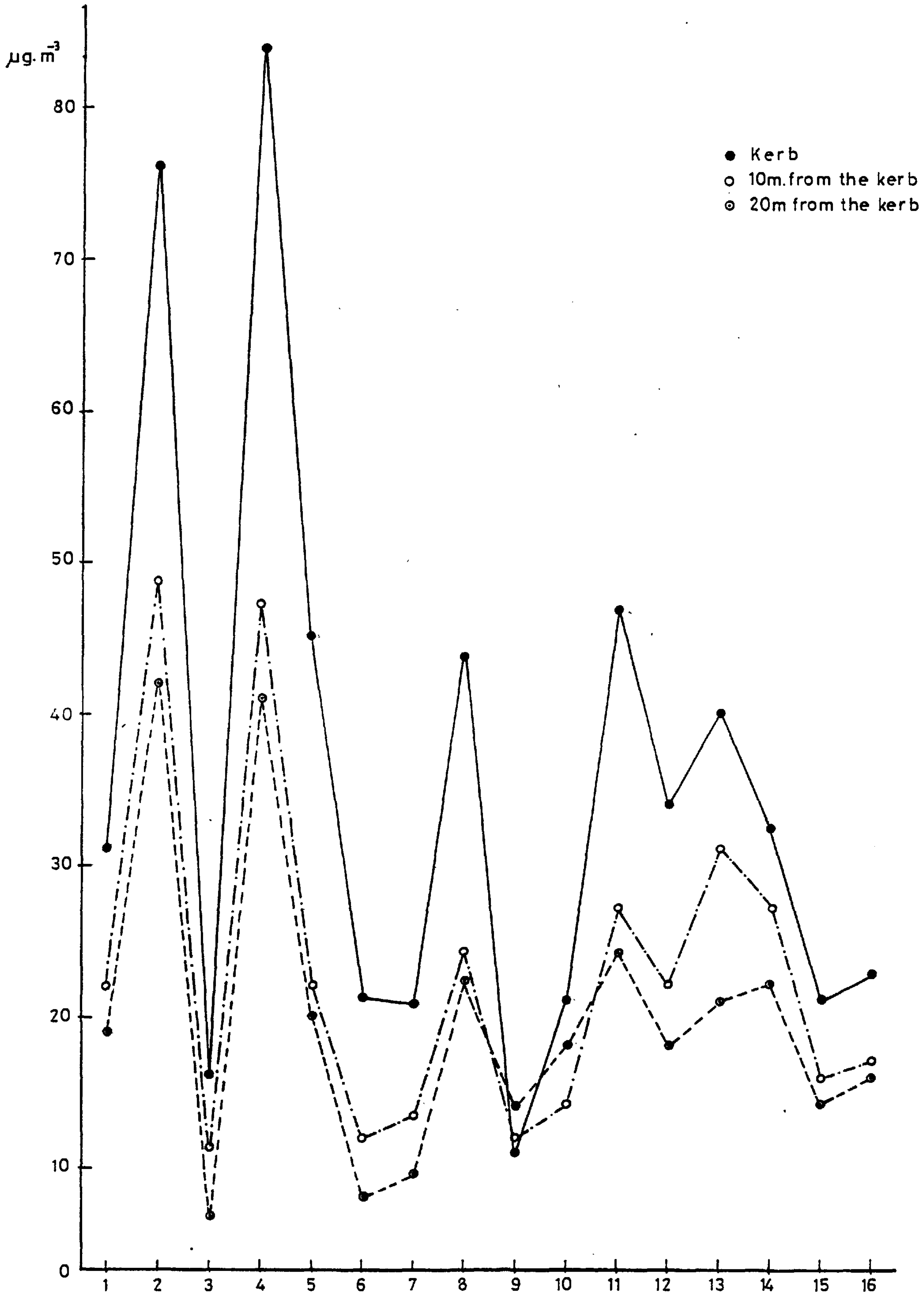


Fig 3·14 (c) Dispersion of hydrocarbons with distance from the kerb

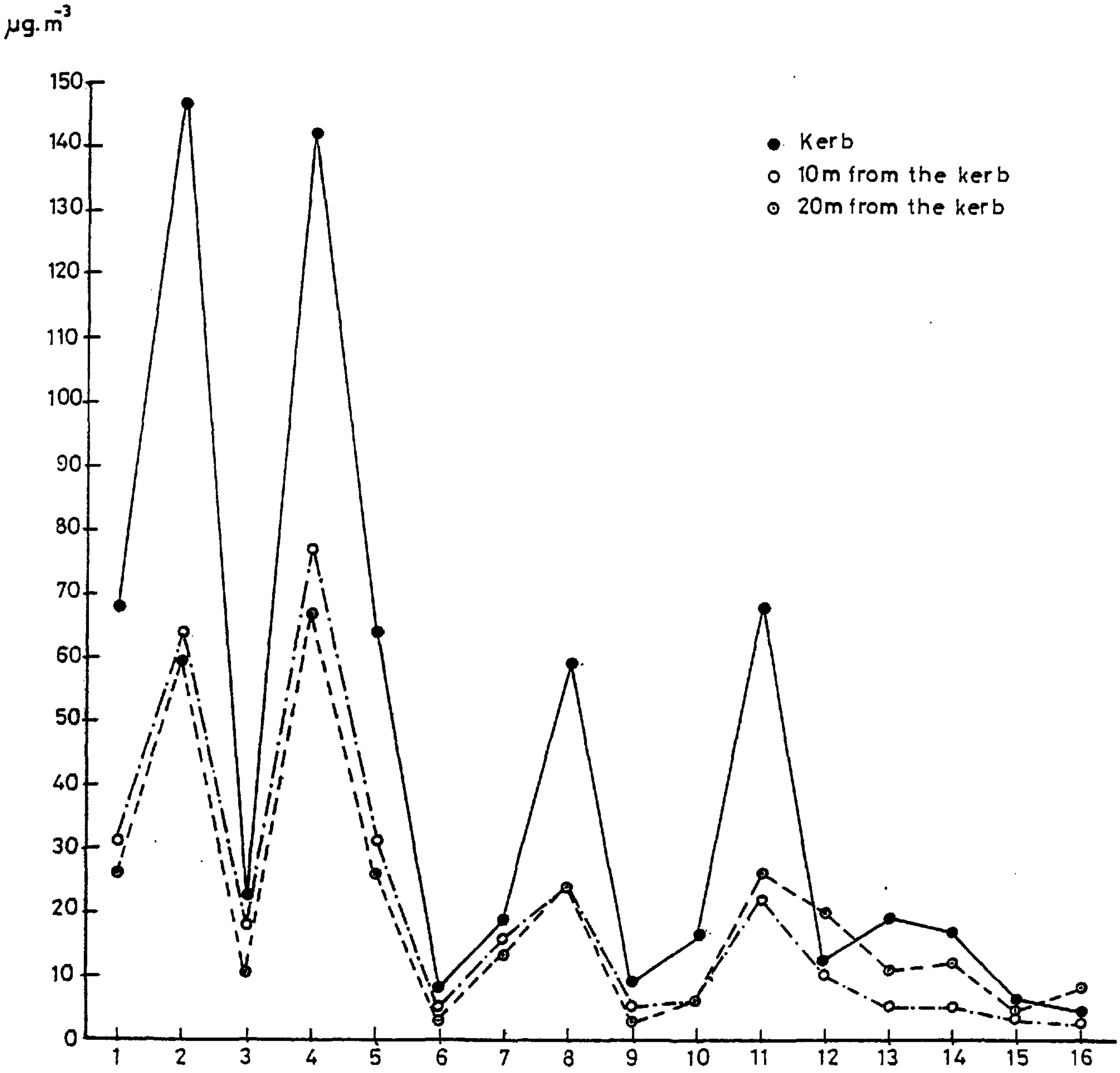


Fig 3·14(d) Dispersion of hydrocarbons with distance from the kerb

Table 3.5 : Variation of C_7/C_6 ratio with distance from the kerb

	1	2	3	4	5	6	7
A	2.46	2.09	2.16	2.33	2.50	2.38	2.45
B	2.71	2.52	2.06	2.24	2.43	2.48	2.23
C	2.16	2.48	2.31	2.30	2.36	2.43	2.21

means that those of higher volatility are more easily dispersed than the low volatility compounds. The variation of C_7/C_6 ratios in the other columns appears to indicate random dispersion in this particular case.

3.3 Hydrocarbons and Halocarbons in a Traffic Tunnel

A study was undertaken for measurements of carbon monoxide and other species in the Rotherhithe tunnel during February 1979.

This is a traffic tunnel in North East London; its length is about 1800 metres with a mean traffic flow of up to 1600 vehicles per hour (from the traffic data over that period). Two ventilation points exist along the tunnel, each one employing four big fans for removal of the polluted air from the tunnel.

For carbon monoxide measurements, four ecolyzers were employed, suitable for high levels of this pollutant.

The sampling positions were 10 m to the south and north of each ventilation shaft and approximately 3 m above the road level.

Additional sampling was concerned with levels and variation of individual hydrocarbons and halocarbons in such a place of high traffic and poor dispersion conditions.

Detailed data for sixteen hydrocarbons and EDB are included in Appendix A. The first two samples were taken on 2 February in the morning (02.00-03.00 h) when the tunnel was closed to traffic and with only service vehicles present. The other samples were taken during the weekdays in normal working hours.

All the results relating to the pollutants of concern were one order of magnitude higher than those resulting from Exhibition Road measurements.

Investigating the C_7/C_6 and C_6/EDB ratios, the following mean values were calculated:

C_7/C_6 $\bar{x} = 2.60$ $\sigma_n = 0.38$

C_6/EDB $\bar{x} = 108$ $\sigma_n = 18.13$

These values agree very well with those calculated for Exhibition Road, indicating that the magnitude of concentrations has little influence over the correlation of the individual compounds.

Figure 3.15 shows the variation of benzene and EDB over the measurements of these compounds in the tunnel during a period of one month. The close similarity of both variations indicates that such a correlation tends to prevail independently of location and concentrations.

Given that pollution in the tunnel results exclusively from the traffic, this work could be used to derive the specific characteristics of traffic pollution.

In fig. 3.16 are shown the profiles of two random samples taken from the tunnel, where the sixteen aromatic hydrocarbons of concern (1-16), are plotted against their concentrations in $\mu g\ m^{-3}$. Although a large difference exists between the concentrations of hydrocarbons in the two samples, the similarity in the overall profiles they exhibit is particularly good.

A comparison of these profiles with the profiles of two random samples in Exhibition Road (fig. 3.17) indicates that the latter profiles are very similar to those from the tunnel, despite the difference in concentration levels which is approximately one order of magnitude. This results in an immediate assumption that pollution in Exhibition Road is predominantly caused by traffic. The same similarities can be seen in the profiles of fig. 3.14(a,b,c,d).

Carbon monoxide levels, measured in the traffic tunnel, varied from a few ppm to 450 ppm, a value which was exceeded at times, particularly when traffic jams occurred in the tunnel. A distribution of hourly mean carbon monoxide levels at the four sampling points is given in table 3.6.

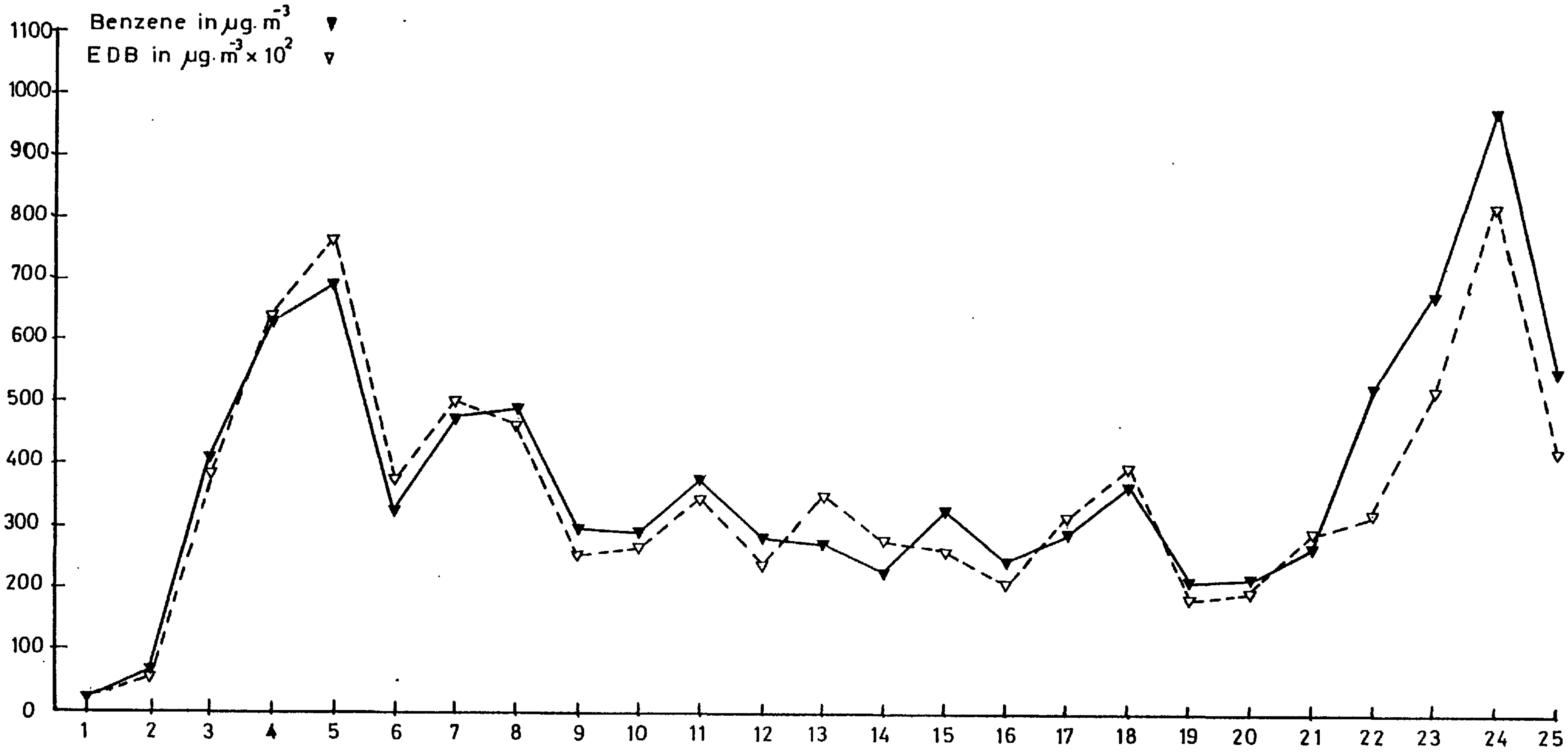


Fig 3·15 Variation of benzene and EDB concentrations in the traffic tunnel measurements

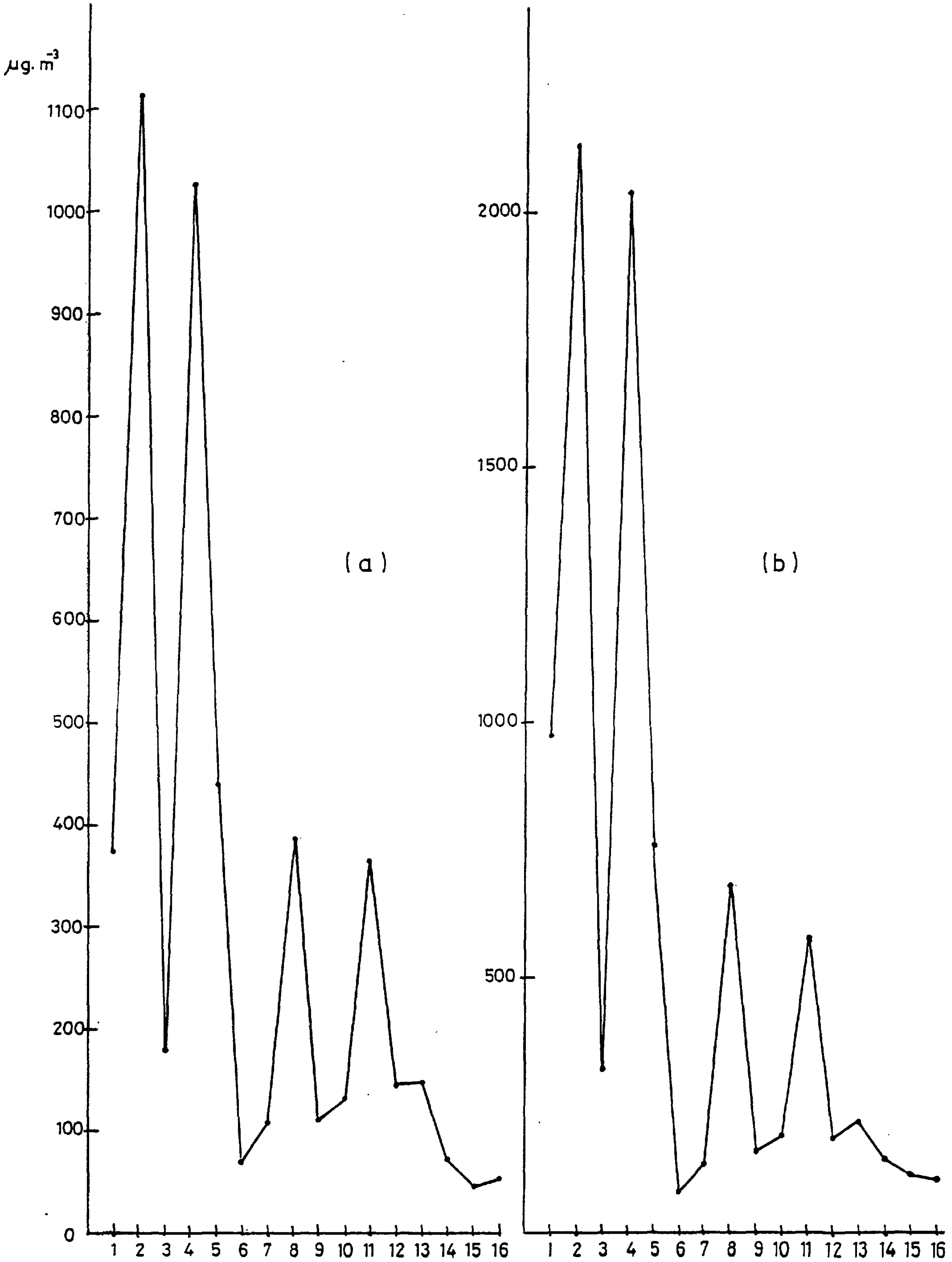


Fig 3·16 Profiles of aromatic hydrocarbons (1-16) obtained from the traffic tunnel

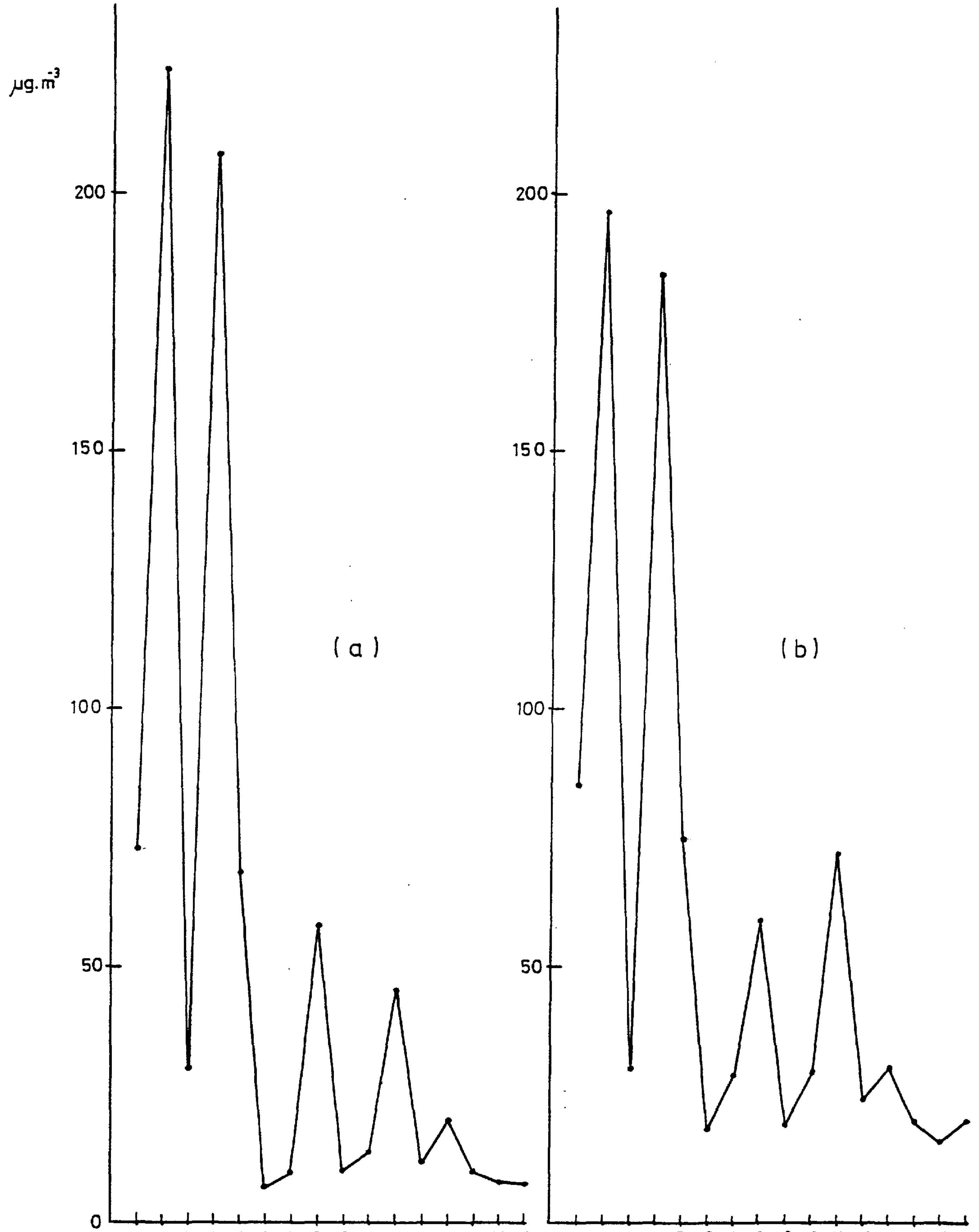


Fig 3·17 Profiles of aromatic hydrocarbons (1-16) obtained from Exhibition Rd

Table 3.6 : Distribution of hourly mean CO levels in ppm at the 4 sampling sites

	Shaft 2				Shaft 3			
	A		B		A		B	
Period	9.00	17.00	9.00	17.00	9.00	17.00	9.00	17.00
6/2	62	44	100	75	85	85	60	40
8/2	60	105	122	110	145	55	65	35
15/2	35	50	75	75	85	35	50	35
16/2	37	50	135	70	105	46	48	40

Carbon monoxide is a predominantly vehicle generated pollutant and its correlation with exhaust emissions is shown clearly in fig. 3.18, where variations in the traffic flow result immediately in variation of carbon monoxide concentrations.

In the same context, carbon monoxide concentrations should be correlated well with individual hydrocarbons determined in the tunnel over the same sampling periods. Indeed, such a correlation is shown in fig. 3.19 where carbon monoxide concentrations observed at the given sampling times are plotted together with benzene and toluene concentrations. The overall measured concentrations during this study in the tunnel were 45-2136 $\mu g\ m^{-3}$ for individual hydrocarbons and 1.88-8.21 $\mu g\ m^{-3}$ for EDB.

3.4 Hydrocarbons and Halocarbons in the Airedale Valley

Air pollution levels were investigated during a study undertaken in the Airedale Valley, alongside the A650 trunk road. The area is well known for its abundance of both small and large factories, thus giving rise to the high traffic flows on the A650 which carries up to 2000 vehicles per hour.

Three sampling sites were selected for the survey: one south of Keighley at a point where the traffic was relatively free flowing; a second, in the centre of Bingley at a position subject to frequent traffic congestion; and a third in Shipley, where traffic tended to "tail back" during rush hours.

Total hydrocarbons, non-methane hydrocarbons, carbon monoxide,

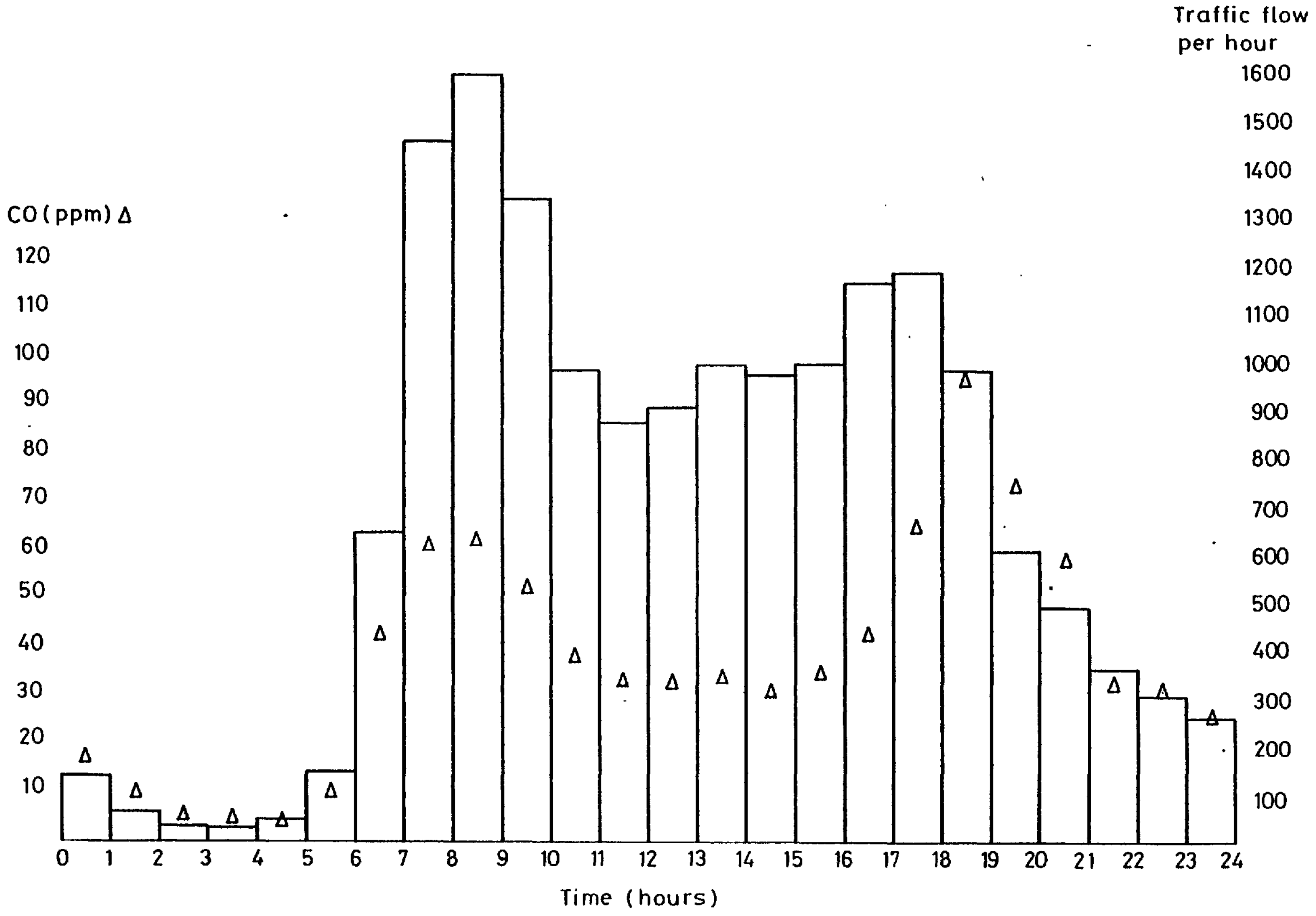


Fig 3·18 Mean traffic flow and CO data for shaft 2 (3rd - 19 th February 1979)

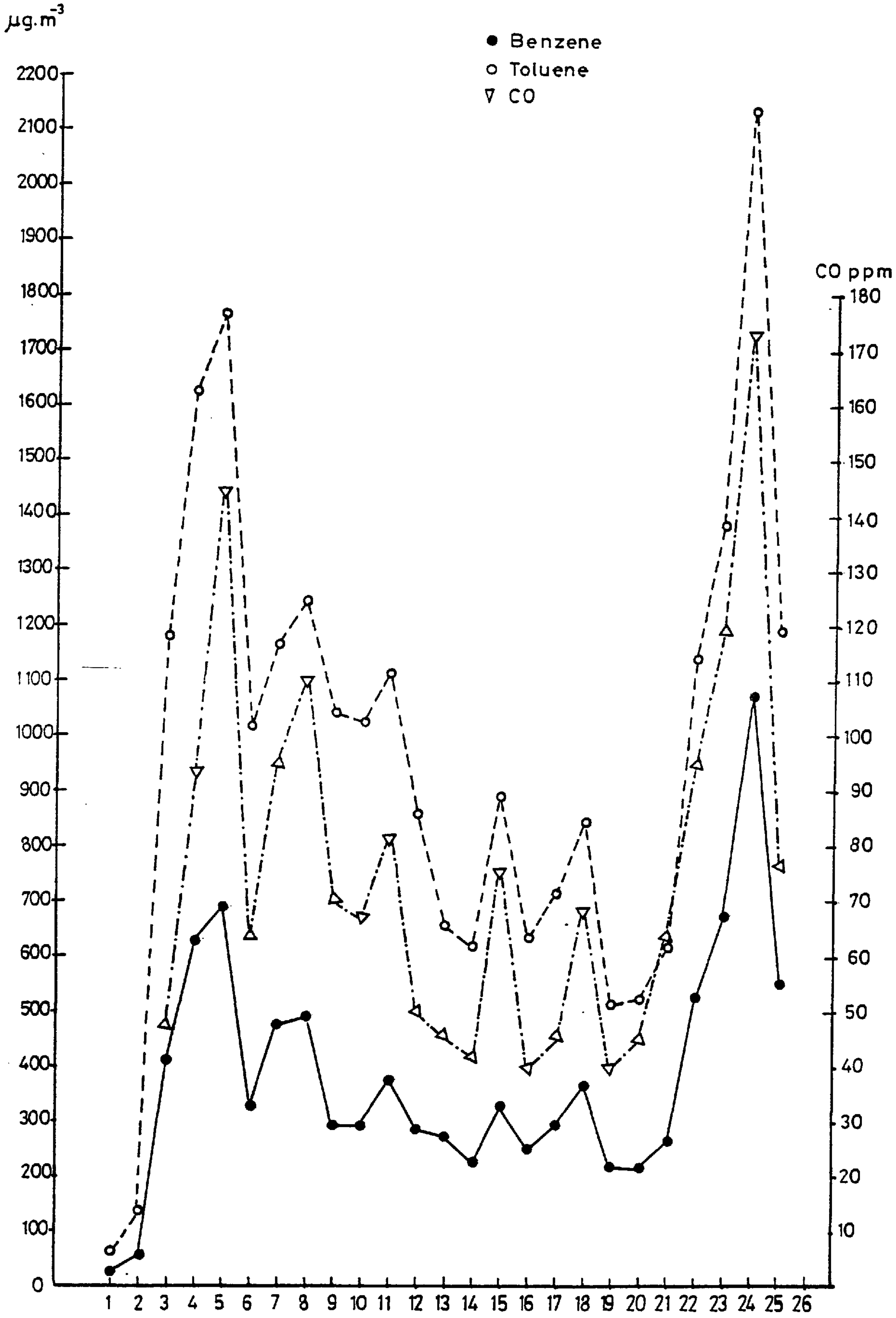


Fig 3·19 Variation of toluene, benzene and CO in the tunnel measurements oxides of nitrogen and lead were determined for a week at each of the three sites.

Additional work concerned the levels of individual hydrocarbons and halocarbons in these locations.

Measurements of the general air pollutants were carried out on a continuous basis using the techniques described in Chapter 2. Summaries of pollutant data for the three sites are included in Appendix A, together with figures showing the variation of the pollutants at these sites.

Detailed results from the analyses of individual hydrocarbons and halocarbons are also included in Appendix A for the three sites.

A statistical analysis of the C_7/C_6 and C_6/EDB ratios gave the results included in table 3.7.

Table 3.7 : Mean ratios C_7/C_6 and C_6/EDB at 3 sites in Airedale

Site	C_7/C_6		C_6/EDB	
	$\bar{x}$	σ_n	$\bar{x}$	σ_n
Keighley	2.68	0.06	103.5	3.50
Bingley	2.46	0.12	82.5	2.50
Shipley	2.86	0.25	100.0	18.90

These ratios again agree very well with those found in Exhibition Road and the traffic tunnel with the exception of the Bingley site, where higher concentrations of EDB resulted in a lower C_6/EDB ratio.

This is also shown clearly in fig. 3.20 where benzene, toluene and EDB are plotted together.

Figure 3.21 shows the profiles of individual hydrocarbons at the three sites, which compared favourably with those obtained from Exhibition Road and the traffic tunnel, show the same traffic pollution pattern, indicating the similarity in correlation between the sixteen measured hydrocarbons.

It was observed during this survey that unusually high concentrations of toluene were recorded in certain samples taken for individual hydrocarbons. This apparent peculiarity was further compounded

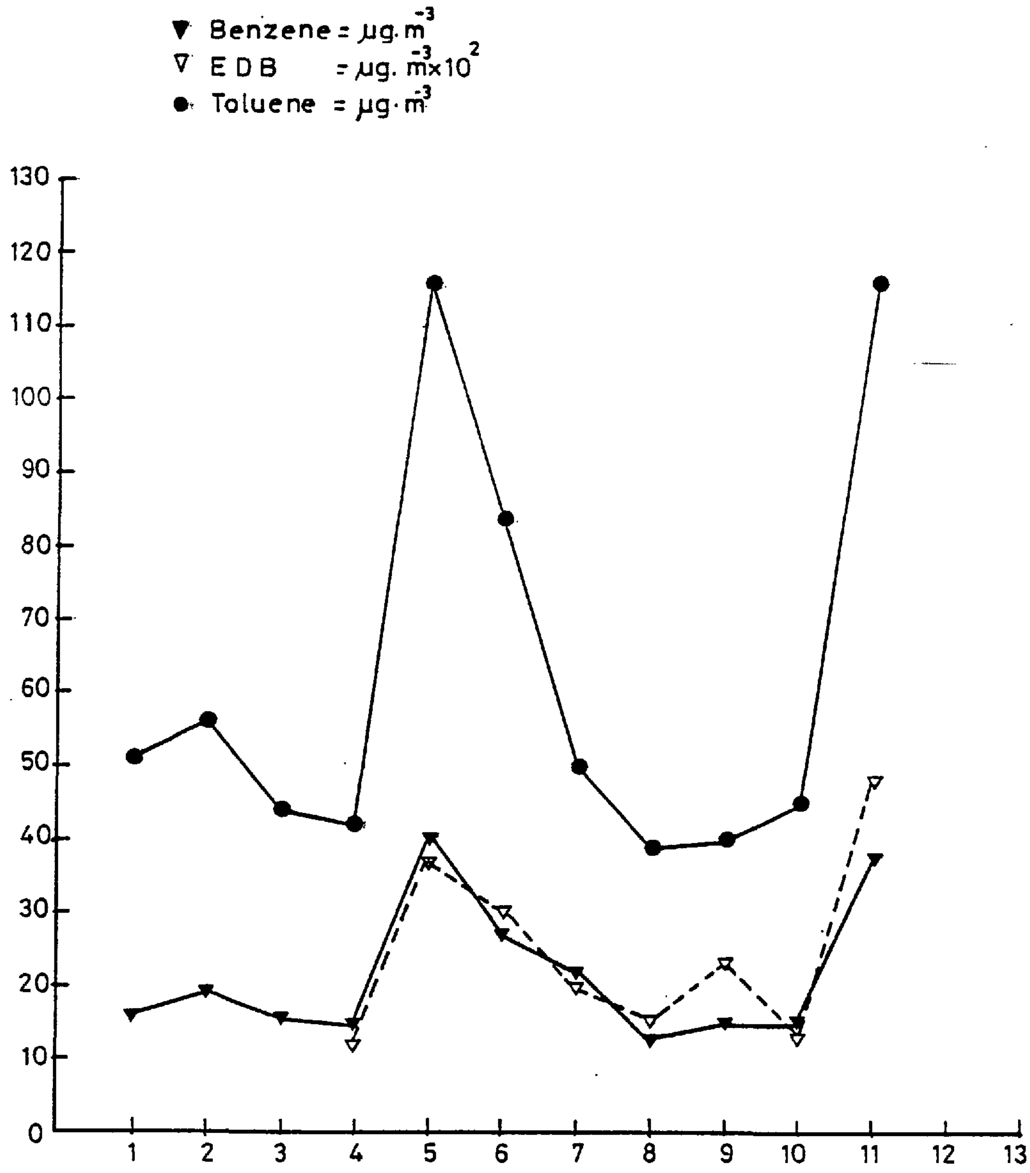
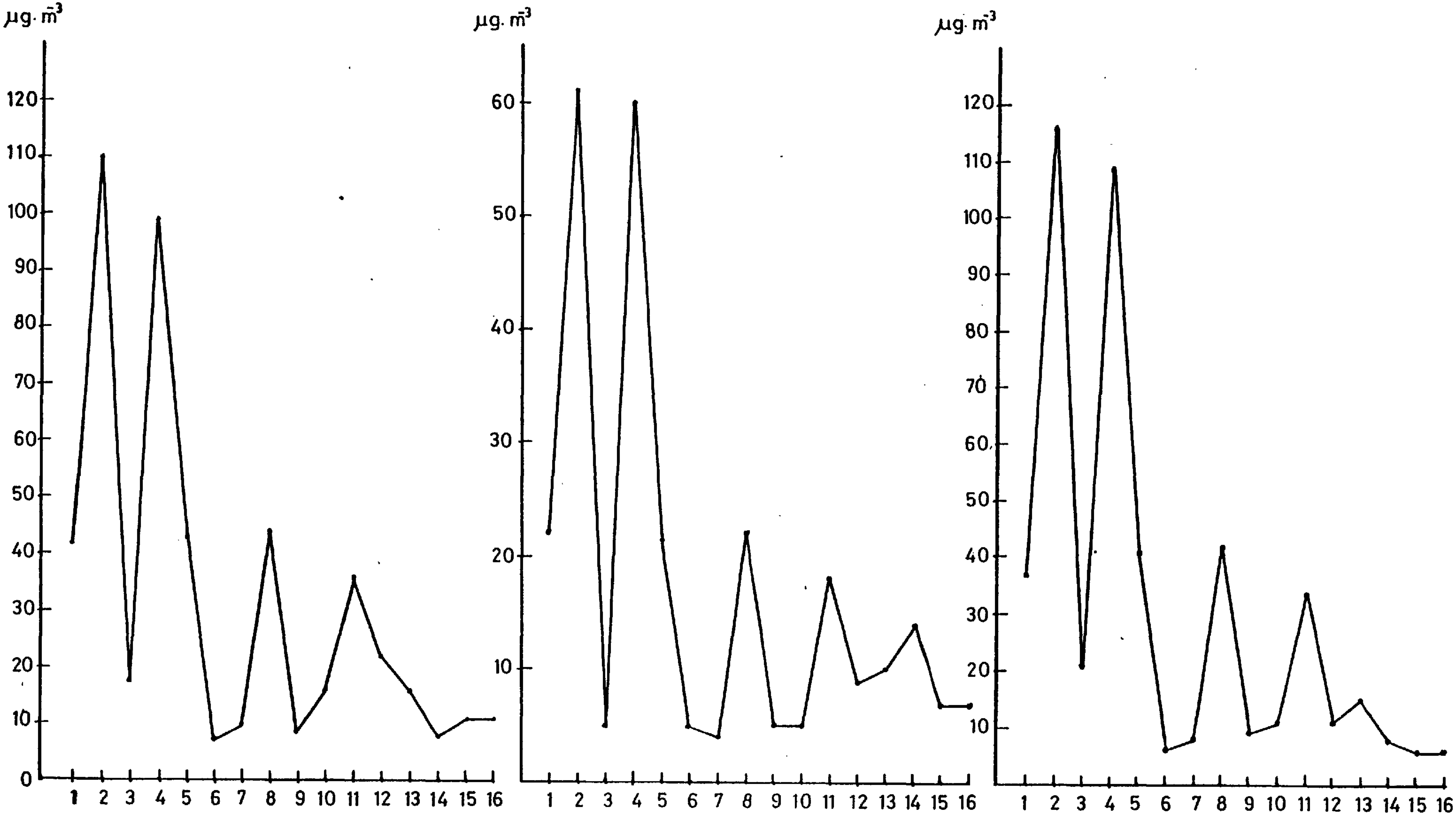


Fig 3·20 Variation of benzene, toluene and EDB in Airedale Valley measurements



KEIGHLEY 10/4/78 BINGLEY 9/4/78 SHIPLEY 10/4/79

Fig 3·21 Profiles of individual hydrocarbons in the Airedale Valley by the occurrence of occasional short duration high levels of total hydrocarbons recorded during the early hours of the morning (05.00-06.00 h), with no concommitant increase in vehicle numbers. This was observed predominantly at the Keighley site. In table 3.8 some measurements for benzene, toluene and m+p-xylene are recorded, with higher than expected toluene concentrations.

Table 3.8 : Concentrations of benzene, toluene and m+p-xylene in the Airedale valley area ($\mu g\ m^{-3}$)

Place	Date		benzene	toluene	m+p-xylene	C_7/C_6
Keighley	25/3/79	15.00-15.30	24	90	4	3.75
"	"	15.30-16.00	28	84	2.7	3.00
Keighley	26/3/79	8.30- 9.00	33	102	2	3.09
Keighley	28/3/79	8.30- 9.00	37	115	5	3.11
"	"	16.30-17.00	16	48	3	3.00
Keighley- SW hill	"	18.00-18.30	10	39	0.6	3.90
Bingley	30/3/79	9.00- 9.30	9.9	43.6	2.7	4.40
"	4/4/79	9.00- 9.30	10	52.5	4.7	5.25
"	"	9.30-10.00	12.6	52.8	6.1	4.19
"	"	16.30-17.00	3.8	30	2.3	7.89
"	"	17.00-17.30	7.6	38	8.9	5.00
" - NE hill	"	18.00-18.30	5.5	28	1.5	5.09
Shipley - S hill	6/4/79	12.00-12.30	7.6	43.8	4.6	5.76
" - SW hill	7/4/79	14.00-14.30	74	390	15	5.27

These concentrations derive a mean C_7/C_6 ratio of $\bar{x} = 4.54$ with $\sigma_n = 1.27$. The very high toluene concentrations observed, compared to those of benzene and m+p-xylene, could not by any means be associated with traffic pollution. The occurrence of these high toluene levels was deemed to be related to gaseous emissions from one or more of the large number of factories in the area.

Interferences occurred when the wind was prevailing from the source to the sampling point. An investigation of the wind direction with respect to the sampling point at the time, resulted in the conclusion that the alternative sources were located at Keighley.

Their contribution was perceptible, predominantly at the Keighley and at the Bingley sampling sites when the wind was from the north. It was never observed at the Shipley site which was not directly down-wind of the Keighley site, but it was perceptible in the area of the SW hill opposite to the sampling point. The profile of such an unusual analysis of individual hydrocarbons is shown in fig. 3.22, which represents partially traffic pollution (hydrocarbons number 3-16) and a major contribution to the toluene peak by other sources.

The overall measurements of pollutants recorded at the Airedale Valley sites as shown in table 3.9 were of the same orders of magnitude as those reported elsewhere, with the exception of total hydrocarbon levels, which were higher than have been determined at urban sites with similar carbon monoxide levels. Lead levels (0.5-5.1 μg m^{-3}) were similar to those reported for the more heavily polluted Coventry site (1), but were only approximately 25-35% of levels which have been determined in London.

Table 3.9 : Hourly mean concentrations during working week (Monday-Friday, 07.00-19.00 h)

Site Pollutants		Keighley	Bingley	Shipley
Carbon monoxide	(ppm)	1.6	1.0	1.2
Total hydrocarbons	(ppm)	4.8	5.6	3.6
Total oxides of nitrogen	(ppm)	0.15	0.10	0.12
Lead	(μg m^{-3})	2.6	3.2	3.2

3.5 Remote Areas

In order to gain an appreciation of the background concentrations of the studied air pollutants, samples were taken and analyzed from locations remote from traffic activity.

Table 3.10 includes levels for three hydrocarbons measured in such areas together with details of the date and location. The rest

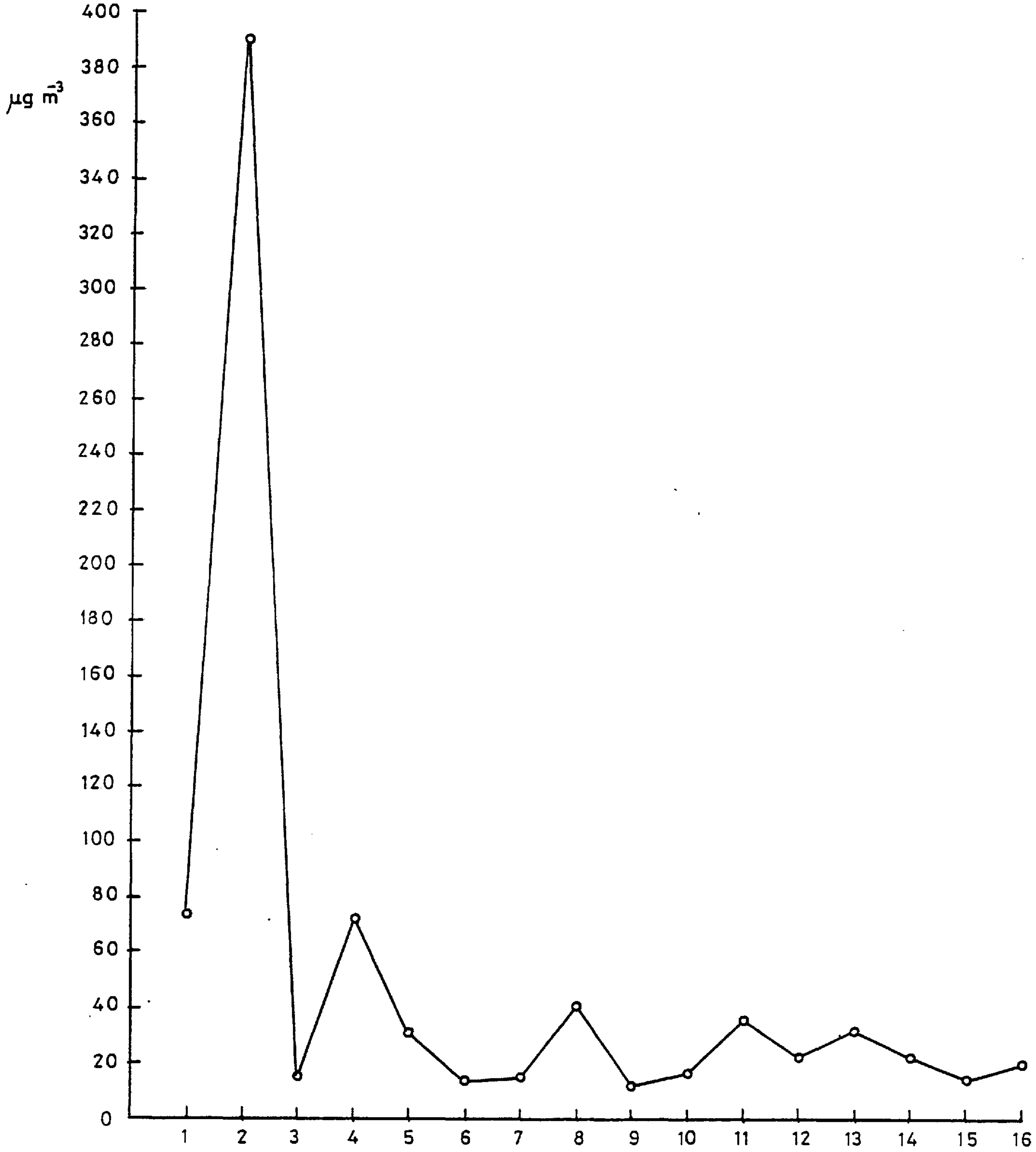


Fig 3·22 Profile of individual hydrocarbons showing traffic pollution mixed with industrial contribution in Airedale Valley

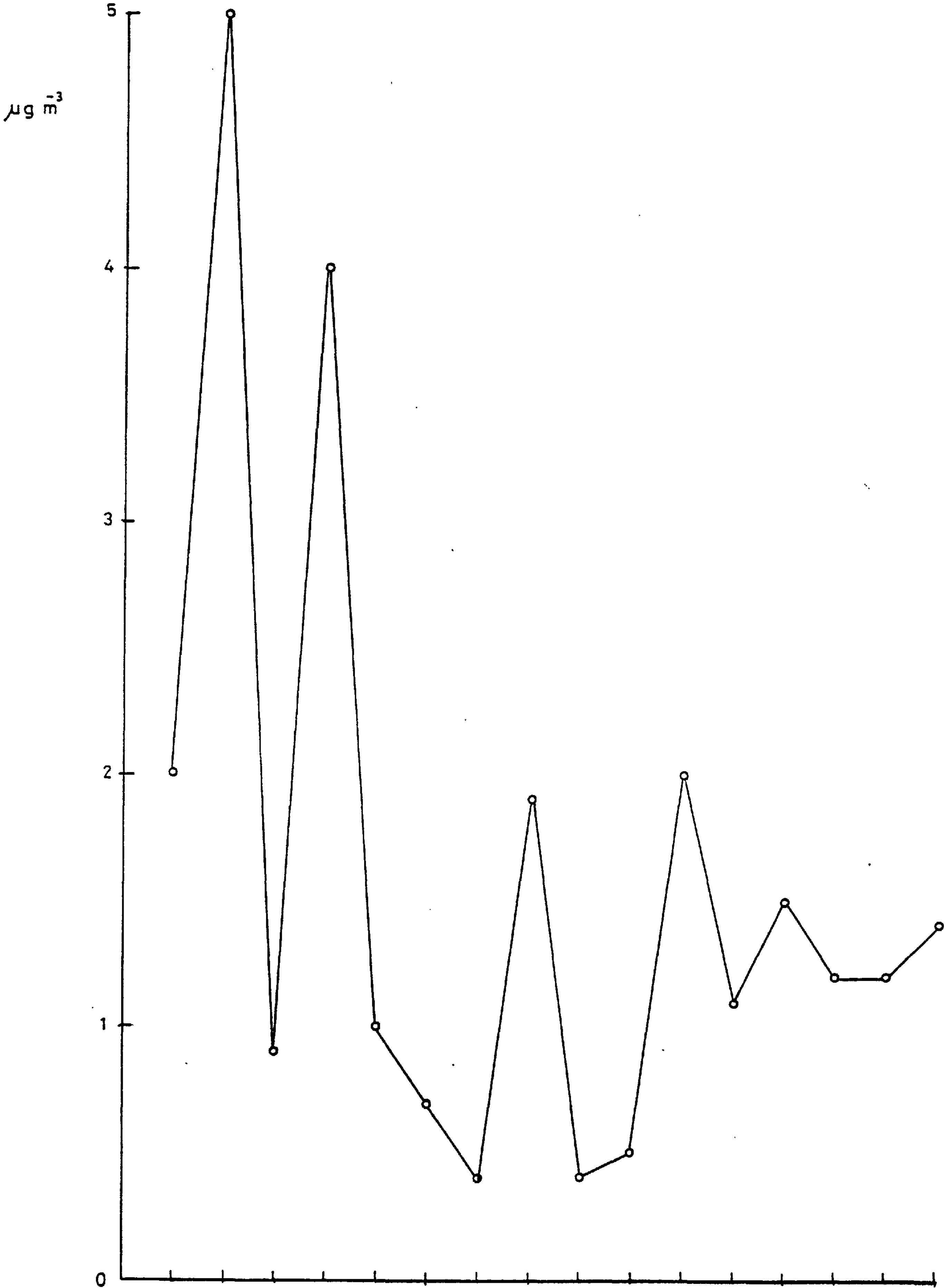


Fig 3·23 Profile of individual hydrocarbons in a remote area of the 13 hydrocarbons under consideration gave very low values and some are recorded in Appendix A.

Table 3.10 : Concentrations of hydrocarbons in remote areas (µg m^{-3})

Location	Date	benzene	toluene	m+p-xylene
1. Keighley NE hill	28/3/79	0.35	1.00	0.20
2. " "	29/3/79	0.50	1.80	1.80
3. " "	29/3/79	0.50	1.60	1.60
4. " remote N area	29/3/79	0.30	1.05	0.70
5. " NW hill	29/3/79	0.26	0.73	0.42
6. Bingley surroundings	30/3/79	1.07	3.30	2.97
7. Shipley "	6/4/79	0.70	3.02	3.27
8. Windermere Lake	9/4/79	5.0	13.0	12.0
9. Remote field	9/4/79	2.0	5.0	4.0

The lowest results were obtained from the hills lying to the north of Keighley. Presumably, it is much more likely that clean air should be found on top of a hill, where the air movement is greater than over a low level field, even if it is remote.

The development of the last analysis in a profile of hydrocarbons gave the pattern shown in fig. 3.23, which resembles a typical traffic pollution pattern.

3.6 General Discussion

The results of the 18 determined individual hydrocarbons and halocarbons in the different locations, showed an overall consistent correlation of these pollutants on a repetitive basis.

The diurnal variations demonstrated by the individual hydrocarbons and the general pollutants in all locations, indicate the close dependence of these air pollutants on the traffic flows, to such an extent that no significant variation owing to meteorological conditions could be observed.

However during this study, in the UK, climatic conditions did not show a great variation and therefore it is not possible to demonstrate such relationships. This may only be feasible after extended observation over a period of years.

The correlation factors C_7/C_6 and C_6/EDB showed very good consistency through overall measurements with little variation.

Only one previous study of benzene, EDB and EDC concentrations in air has been reported, undertaken in Sweden (2),which involved the analysis of these species in street air and other locations. Results reported for busy street air analyses, were: 71-240 $\mu g\ m^{-3}$ for benzene, 0.34-1.70 $\mu g\ m^{-3}$ for EDB and 0.62-1.70 $\mu g\ m^{-3}$ for EDC. Manipulation of these data for street air, produced a C_6/EDB ratio $\bar{x} = 161$ with standard deviation $\sigma_n = 47$ and EDC/EDB ratio $\bar{x} = 1.22$ with standard deviation $\sigma_n = 0.36$.

The C_6/EDB ratio is in excellent agreement with that produced from the Exhibition Road measurements if one considers the differences in the composition of petrol consumed in Sweden and UK during the respective periods of measurements as indicated in table 3.11 (3).

Table 3.11 : Composition of fuels in UK and Sweden (w/v)

Country	benzene	EDB	EDC
UK	4.0%	0.025%	0.025%
Sweden	6.1%	0.020%	0.020%

This means there is less benzene (34.5%) and more EDB and EDC (20%) in the UK petrol compared with petrol in Sweden, a fact which explains the higher C_6/EDB ratio found in Sweden street air samples.

No vinyl chloride was found in street air samples despite vigorous efforts, which may be due to the inherent instability of this compound. A further possibility is that VCl does not survive during the combustion process because it breaks down at a temperature of 500°C, whereas higher temperatures (at least up to 800°C) prevail in the combustion chamber.

Finally, if VCl is indeed formed and is emitted with the exhaust gases, then its concentration may be below the detection limits of the analytical methods used (less than 10^{-9} g l^{-1}).

From the health hazard perspective, concentrations found in urban locations do not represent any immediate threat to human health although the effects of long-term exposure to low levels of such compounds are not yet well elucidated.

In the traffic tunnel however, the threshold limits, valid in the USA for such pollutants, were frequently exceeded, particularly the carbon monoxide limit (10 ppm for 8-hour exposure or 40 ppm for 1-hour exposure) and the non methane hydrocarbons (0.24 ppm for a 3 hour exposure) (4).

On the other hand, the street air concentrations found may be regarded as potential photochemical precursors although climatic conditions in the UK do not particularly favour such processes.

The overall aromatic content from analyses of some types of petrol was found to be 66-67%, being recently confirmed by direct information from refineries (3). Referring to the profile of the sixteen studied hydrocarbons from a petrol analysis, as shown in fig. 3.24, the traffic pollution pattern is readily recognized as similar to that obtained from any site where work has been carried out.

This clearly indicates that it is the internal combustion engine which predominantly causes pollution with aromatic hydrocarbons in a trafficked location.

Diesel engine traffic is unlikely to contribute significantly for the following reasons:-

(a) The very low aromatic content in diesel fuel.

(b) The mode of operation and efficiencies of diesel engines as demonstrated in Chapter 1.

(c) The much lower number of diesel engine vehicles in circulation compared to the internal combustion engines in an urban or a suburban situation.

A comparison of a large number of profiles obtained from air samples indicated that composition with respect to the individual components did not vary at all. Variations were observed frequently regarding the correlations studied (C_7/C_6, C_6/EDB and EDC/EDB).

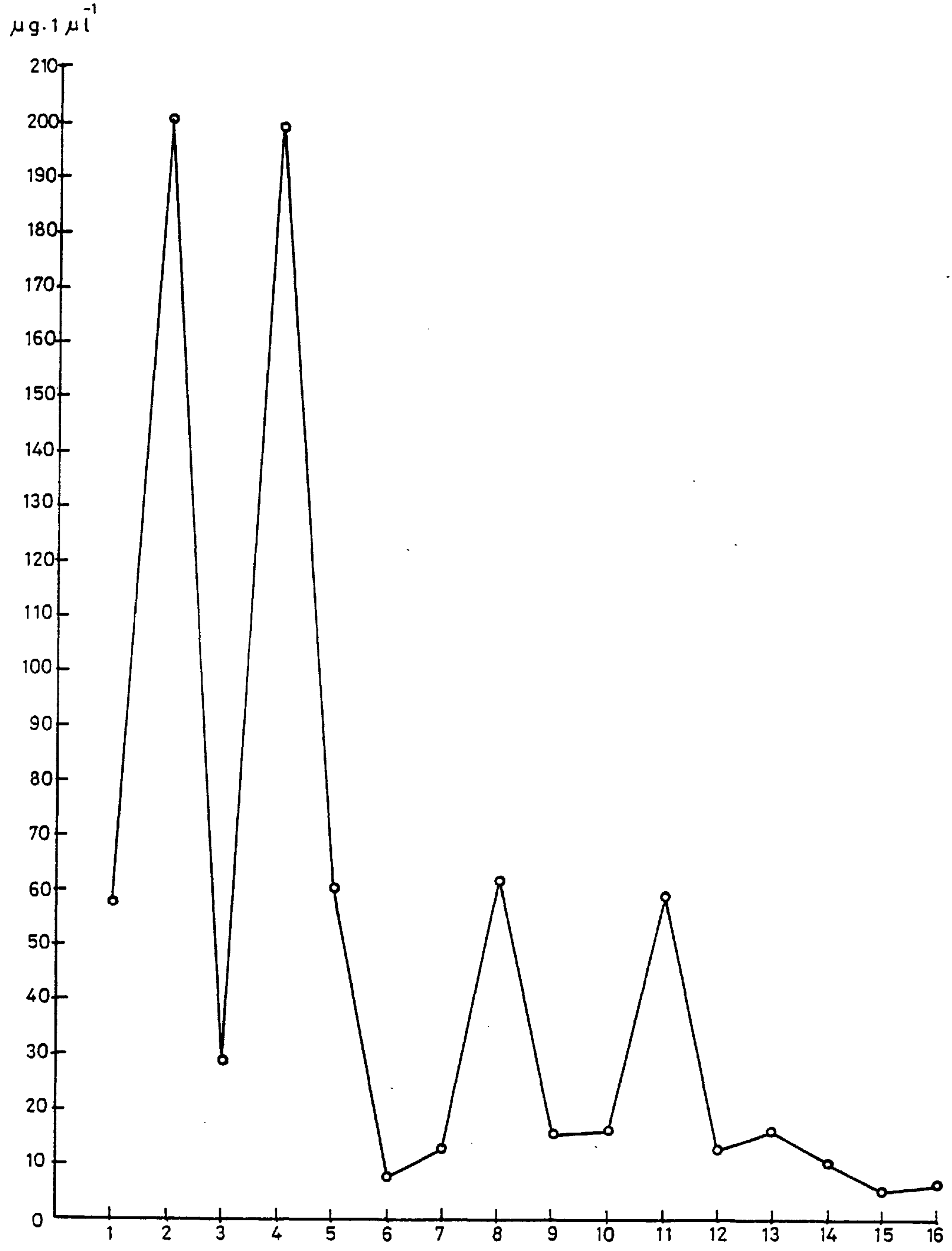


Fig 3·24 Profile of aromatic hydrocarbons (1 - 16) from a petrol analysis

Factors influencing these variations may be related to the individual physical and chemical characteristics of each constituent, such as vapour pressure, combustibility, thermal stability and photoreactivity in the atmosphere.

The variety of vehicles with their own individual characteristics and combustion efficiencies give rise to additional unknown parameters influencing the observed variations.

Finally, incomplete combustion and evaporative losses both contribute in their own respective ways to vehicle generated air pollution, but evaluation of each factor separately has not yet been feasible.

A further investigation of raw exhaust emissions could possibly elucidate the sequence of petrol-internal combustion-generation of pollutants and their distribution into the atmosphere.

3.7 Conclusions

(a) The variations in the concentrations of general and individual air pollutants studied were found at every trafficked location to be very closely related to the traffic flows, a fact which establishes vehicle exhaust emissions as the main source of these pollutants.

(b) Trends in the concentrations of individual air pollutants were very similar to those exhibited by the general air pollutants during the same sampling periods at the same locations.

(c) High temperatures and still conditions gave rise to elevated concentrations of the studied air pollutants, especially those of relatively low volatility.

(d) Concentrations of individual hydrocarbons in a trafficked location were highest alongside the kerb and decreased with distance from the kerbside (10-50% for the first 10 m and 30-70% for the next 10 m).

(e) An overall consistent correlation was observed between the sixteen aromatic hydrocarbons under study, independent from the determined concentrations at every site of work.

(f) A consistent correlation has been found between benzene and EDB in air samples at every sampling site (∿100:1), irrespective of the determined concentrations. Accordingly at a site where vehicle generated air pollution occurs it is possible to assume that EDB concentrations may be predicted from benzene measurements (within an accuracy of 100% ± 13).

(g) The development of the profiles of the sixteen aromatic hydrocarbons under study from air sample analyses (relating to conclusion e), and the establishment of the traffic pollution pattern provided a useful criterion for the identification of the pollutant source.

On that basis it has been found that pollution by aromatic hydrocarbons in a trafficked location is caused predominantly by internal combustion engines.

Similarly, an alternative to traffic pollution source in a trafficked and industrialized area, has been identified, which emitted significant quantities of toluene into the atmosphere.

(h) The overall concentrations of general and individual pollutants found at any location - except the traffic tunnel - do not represent any immediate threat to human health (as they did not exceed the threshold limits valid in the U.S.A.), but the effects of long-term exposure to low levels of these pollutants are not yet well known.

3.8 References

1. Hickman, A.J. et al., TRRL Report 695, Department of the Environment, 1976.
2. Jonsson, A. and Berg, S., Report from Statens Naturvärdsverk, 1978.
3. Larbey,R.J., Associated Octel Company Limited, Personal communication.
4. U.S. Code of Federal Regulations: Title 40, S.50, Office of the Federal Register, 1974.

CHAPTER 4 : ENGINE DYNAMOMETER STUDIES

4.1 Introduction

Concentrations of individual hydrocarbons, halocarbons and general vehicle associated air pollutants, were studied in raw vehicle exhaust under varying conditions of engine load and operation, by the use of a dynamometer.

The use of different driving cycles (described in Chapter 1) under the control of a dynamometer, is a commonly used technique to certify that manufactured vehicles meet the mandatory exhaust emission regulations prevailing in a particular country. The driving cycles are designed upon an assessment of the driving conditions existing on the roads of a particular country and thus introduce certain variations in test conditions.

However, the test driving cycles only partially represent the real situation prevailing on the road and a considerable controversy has developed worldwide upon the criteria used by each country in designing their particular driving cycle (1).

Different types of dynamometers are in use and this also introduces variations in the data produced. The types of dynamometers in use may be divided into two categories according to their mode of operation.

(i) Hydraulic

(ii) Electric

The principle of operation for both the types is the same, but the electric dynamometer allows for a greater variety of its loadings corresponding to the variation of speed through a driving cycle. There is a need for an evaluation of the different driving cycles and types of dynamometers in use, to determine how realistically they reproduce real road conditions, which is a very difficult process.

Problems arise from the difficulties associated in the collection of real exhaust samples under actual driving conditions on the road. However, some indications based only on lead measurements, which unlike the other emissions can be readily collected, are given in table 4.1 (2).

Table 4.1 : Typical lead emissions under different driving tests (2)

Driving test	Type of exhaust	Lead emitted	
		% Input	mg km^{-1}
ECE cycles	Standard	30	15
	lead filter	12	6
Federal cycles	Standard	60	25
	lead filter	25	10
"Over the road" (all forms of driving)	Standard	70	30
	lead filter	20	9

This experiment indicates that the U.S. Federal driving cycle approximates more closely to the real situation on the road, at least for lead emissions, than the ECE driving cycle.

The use of a dynamometer in order to study vehicle generated emissions of pollutants is however the only method ensuring the collection of raw exhaust samples on a standard and repeatable manner.

4.2 Experimental Work

4.2.1 Dynamometric Facilities

For this study a Clayton C_{150}, twin-roll, hydraulic chassis dynamometer was used, equipped with all the sampling and analytical facilities required by the prevailing regulations.

The vehicle under study was mounted on the dynamometer as shown in plate 3. A 150 mm o.d. pipe was connected to the end of the exhaust manifold, in order to permit the collection of the exhaust emissions into large plastic bags. Prior to entering the sampling bags the raw exhaust was passed through a heat exchanger in order to remove most of the moisture.

Two types of sampling system were used:

(a) A pair of large bags for the collection of all the raw gas emitted under the ECE driving test, where the exhaust of the first part of the driving cycle was collected in bag 1 and the second part in bag 2.

(b) A pair of smaller bags for the collection of diluted exhaust, achieved by a constant volume sampling (CVS) unit during the U.S. Federal driving cycle. The CVS unit was a G. Cussons Ltd model incorporating a Rootes blower design acting as a positive displacement pump (PDP). Total flow of diluted exhaust gas was calculated from the number of revolutions of the PDP, multiplied by its volumetric displacement per revolution.

Analytical evaluation of exhaust emissions for the regulated pollutants in each sample was carried out in association with operatives of Associated Octel, using methods reviewed in Chapter 1 (flame ionisation (FID) or non-dispersive infra red (NDIR) techniques for total hydrocarbons, NDIR for carbon monoxide and a chemiluminescence technique for the oxides of nitrogen).

All the required analytical instruments were available mounted on a rig, and standard calibration gases covering a wide range of concentrations, supplied by BOC, were used for calibration purposes.

4.2.2 Sampling Procedure

Samples for the determination of individual hydrocarbons and halocarbons were collected as described in Chapter 2 and after the completion of each driving cycle. Sampling periods were limited to 1 min (100 ml) for the raw exhaust and 10 min (1 1) for the diluted one, in order to ensure a "safe" sampling volume and to avoid overloading of the analyzers.

The sampling point was directly from the plastic bags via a teflon tube. In the case of constant speed tests, where the exhaust was not collected in bags, the samples were taken directly from the exhaust pipe extension as shown in Plate 3.

Analysis of individual hydrocarbons and halocarbons was carried out as described in Chapter 2.

4.2.3 Total Hydrocarbons, Carbon Monoxide and Oxides of Nitrogen

The concentrations of these pollutants in raw exhaust emissions under different driving cycles were determined utilizing the analytical techniques described in Chapter 2.

The samples were pumped from the sampling bags into the instruments through a teflon tube (6.4 mm o.d.) connector.

Plate 3 : Engine dynamometer laboratory

4.2.4 Programme of Work

The emissions from different types of engines were studied, using the following vehicles:

(i) Ford Granada automatic (3 1 engine) with standard exhaust (recorded mileage 20.000);

(ii) Chrysler Alpine (1.6 1 engine) with standard exhaust (recorded mileage 45.000);

(iii) British Leyland Mini (0.85 1 engine) with standard exhaust (recorded mileage 35.000);

(iv) The same Mini as in (iii) but with the standard exhaust replaced by a lead filter.

The lead filter used was of the Axial type (allowing a direct flow through it), consisting of a stainless steel wired matrix, covered by gama alumina (volume 5.2 1 and surface area 104.000 m^2 for the stainless steel matrix and 208.000 m^2 for the gama alumina. Mileage recorded 12.000).

The following types of fuel were used:

(i) Motor mix (0.4 g 1^{-1} TEL + 0.2 g 1^{-1} EDC + 0.2 g 1^{-1} EDB) for the 3 1 engine;

(ii) Motor mix (0.5 g 1^{-1} TEL + 0.25 g 1^{-1} EDC + 0.25 g 1^{-1} EDB) for the 1.6 1 engine;

(iii) Aviation mix (0.5 g 1^{-1} TEL + 0.5 g 1^{-1} EDB) for the 1.6 1 engine;

(iv) Motor mix (0.45 g 1^{-1} TEL + 0.225 g 1^{-1} EDC + 0.225 g 1^{-1} EDB) for the 0.85 1 engine, equipped either with standard exhaust or with the lead filter.

The following tests were carried out on each case:

(a) ECE driving cycle, with a cold start first and next a hot start of the engine;

(b) ECE/CVS test, consisting of an ECE driving cycle as in (a) and collection of samples in the CVS mode;

(c) U.S. Federal 1973 driving cycle, with a hot start and in some cases also a cold start of the engine and sample collection in the CVS mode;

(d) Constant speed tests with the engine running: "idle", at "20 mph" (32.2 Kmph), "30 mph" (48.3 Kmph), "40 mph" (64.4 Kmph), and 50 mph (80.5 Kmph), and samples taken immediately from the exhaust pipe extension.

For a cold start test of the engine, the vehicle was "soaked" in the laboratory, this was achieved by leaving the vehicle mounted on the dynamometer, usually overnight, at a temperature between $20^{o}-30^{o}C$. For a hot start test the car was kept running at 50 Kmph (third gear) until the engine was fully warmed, before the start of the test.

Dynamometer load was preset to a value representing the wind friction rolling resistance, which the vehicle would experience on a level road at 50 Kmph for the ECE driving cycle test and 50 mph (80.5 Kmph) for the U.S. Federal test.

Inertia weights were also attached to the dynamometer rollers to simulate the weight of the vehicle on the road.

4.3 Results and Discussion

Detailed results of the study for general vehicle associated pollutants, sixteen individual hydrocarbons and two halocarbons are included in Appendix B.

4.3.1 Assessment of Emissions from Three Different Vehicles

Data relating to four individual compounds under study, obtained from the exhaust of the 3 l Granada engine under the different tests are included in table 4.2.

The similarity in the behaviour of the individual hydrocarbons and halocarbons during the different driving cycles of the engine, are shown in fig. 4.1 where the four compounds (benzene, toluene, EDC and EDB) are plotted together.

Statistical analysis of these data gave the mean ratios ($\overline{x}$) and standard deviations (σ_n) included in table 4.3, and these indicate the situation in the exhaust gases of this particular vehicle.

The ratio of toluene and benzene shows a very consistent trend over the different modes of engine operation (1.89-2.83) and the mean

Table 4.2 : Concentrations of individual pollutants in the exhaust emissions of a 3 l engine under different driving tests (μg m^{-3})

Test		benzene	toluene	EDB	EDC	C_7/C_6	C_6/EDB	EDC/EDB
ECE								
Cold start	bag 1	147402	320446	562	3250	2.17	262	5.75
	bag 2	81279	201312	292	1616	2.48	278	5.53
Hot start	bag 1	98107	210789	234	1465	2.15	419	6.26
	bag 2	90332	195624	200	1180	2.17	452	5.90
ECE/CVS								
	bag 1	5592	15827	25	132	2.83	224	5.28
	bag 2	5442	13925	14	66	2.56	389	4.71
U.S. Federal		6063	15754	48	97	2.60	126	2.02
Constant speed								
	idle	236575	665582	878	3987	2.81	269	4.54
	20 mph	151678	411642	618	2000	2.71	245	3.24
	30 mph	179650	508440	669	2253	2.83	269	3.37
	40 mph	60000	123400	180	800	2.06	333	4.44
	50 mph	48454	91338	98	339	1.89	494	3.46

Table 4.3 : Statistical analysis of data obtained from the exhaust emissions of the 3 l engine under different driving tests

Ratios	$\bar{x}$	σ_n
C_7/C_6	2.44	0.32
C_6/EDB	313	102
EDC/EDB	4.54	1.23

value found (2.44) is very close to that calculated from the Exhibition Road measurements (2.45).

The good correlation of benzene and toluene for this particular situation can be readily seen in fig. 4.2, where benzene has been plotted against toluene in a regression mode. The correlation of the two

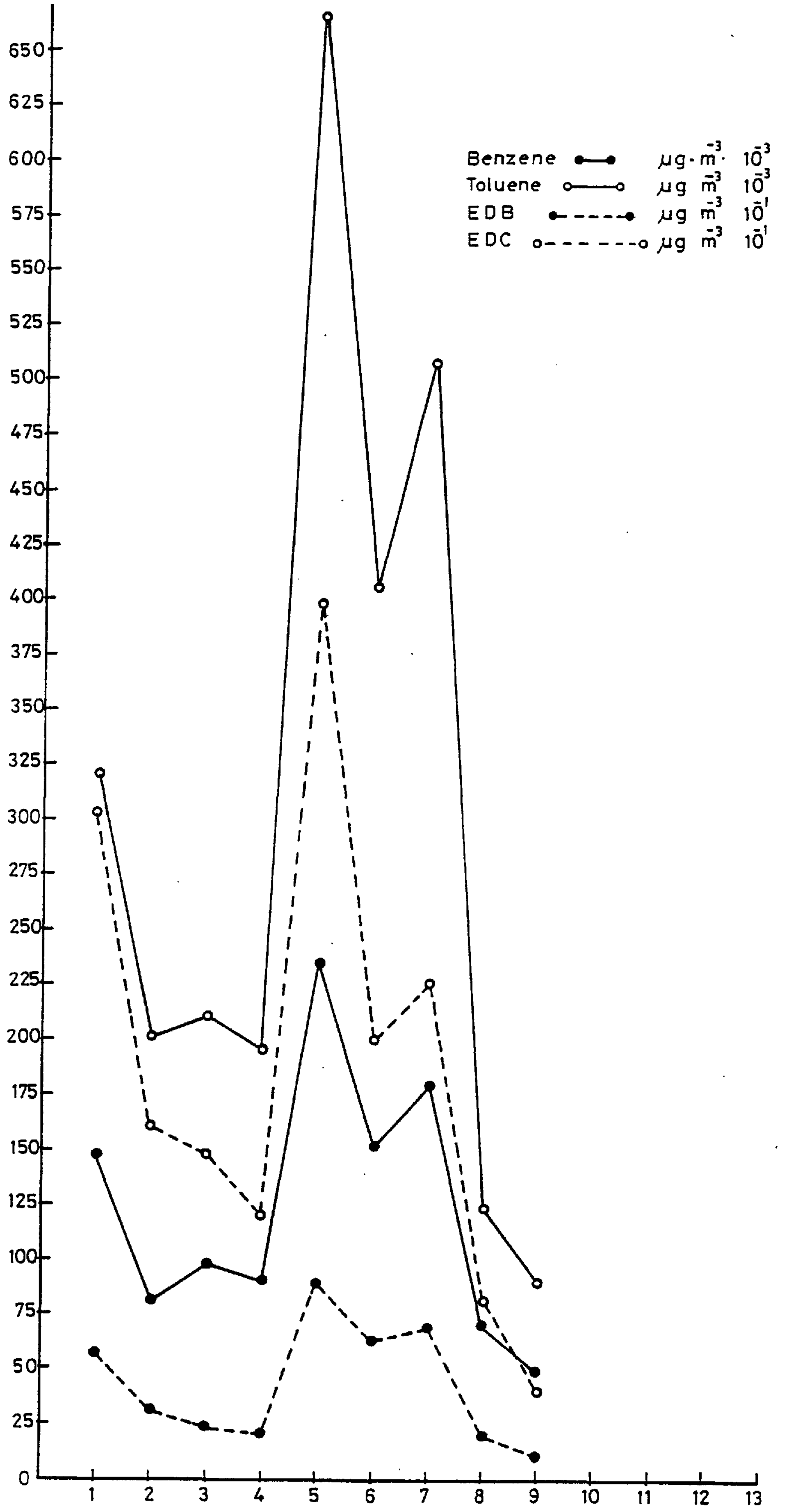


Fig 4·1 Variation of benzene, toluene, EDB and EDC in exhaust emissions of a 3l engine under different driving tests

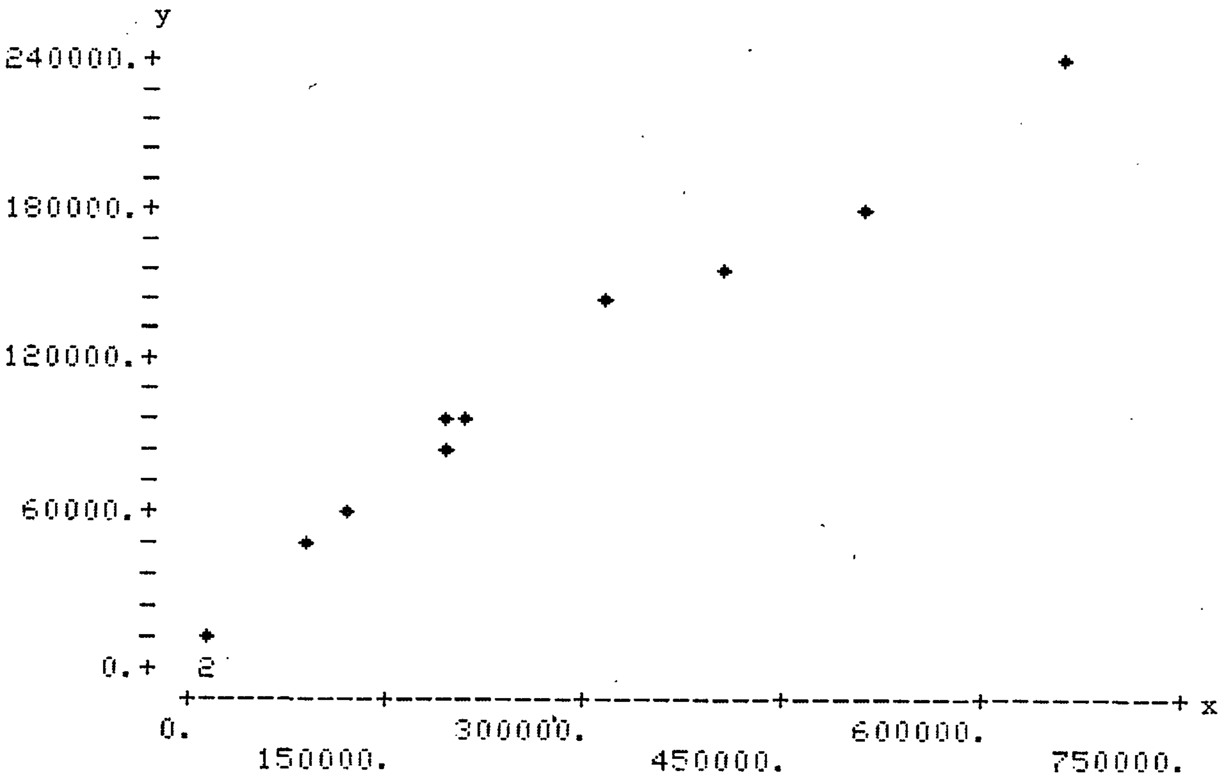


Fig. 4.2 Correlation of benzene and toluene in the exhaust emissions of a 3 l engine

Correlation factor = 0.988

Regression equation $y = 11350 + 0.351\ x_1$

R-squared = 97.6%

compounds is very good given by the factor 0.988 and dictated by the linear equation:

$$y = 11.350 + 0.351\ x_1$$

From table 4.2 it can be seen that a greater variation in C_6/EDB ratio (126-494) and EDC/EDB (2.02-6.26) occurred during the different driving cycles, which indicates a greater dependence for the generation of EDB and EDC upon the driving conditions.

Nevertheless, despite the variation observed, a good correlation between EDB and benzene existed as shown in fig. 4.3, where EDB is plotted against benzene. The correlation factor is very good (0.979) with a linearity dictated by the equation:

$$y = -35.9 + 0.0038\ x_1$$

This correlation factor for EDB and benzene compared to the one obtained from a similar regression analysis from the Exhibition Road measurements (0.931) shows an even higher correlation of the two compounds for the particular case of the 3 l engine.

In fig. 4.4 the correlation of EDB to EDC is shown, where EDB is plotted against EDC. The correlation factor for these two compounds resulting from the regression analysis is 0.944 with good linearity given by the equation:

$$y = 10.3 + 0.215\ x_1$$

This correlation factor for EDB and EDC when compared to the one resulting from a similar regression analysis upon the Exhibition Road measurements (0.430) is far better. This suggests that the explanation for the very low correlation of EDB and EDC in street air is not in the combustion process.

It is evident from table 4.2 that emissions of individual pollutants are greatest during a cold start of the engine, the concentrations of benzene, toluene, EDB and EDC being 1.50, 1.52, 2.40, 2.20 times higher respectively than the concentrations resulting from a hot start. This is indicative of the reduced efficiency of the combustion process at low temperatures.

Of these four compounds, benzene exhibits the highest combustibility at the lower temperatures and the other compounds fall in the sequence

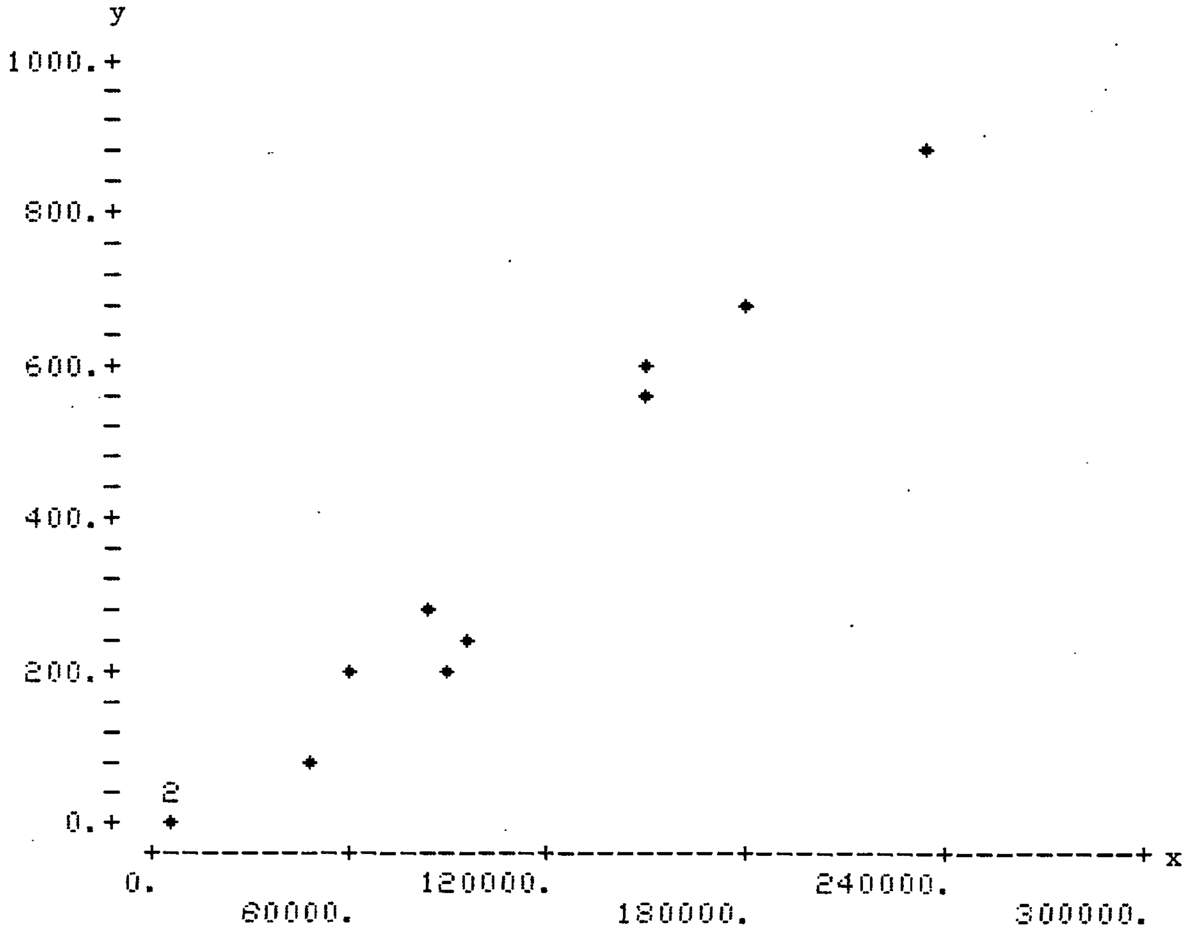


Fig. 4.3 Correlation of EDB and benzene in the exhaust emissions of a 3 l engine

Correlation factor = 0.979

Regression equation $y = -35.9 + 0.0038\ x_1$

R-squared = 95.8%

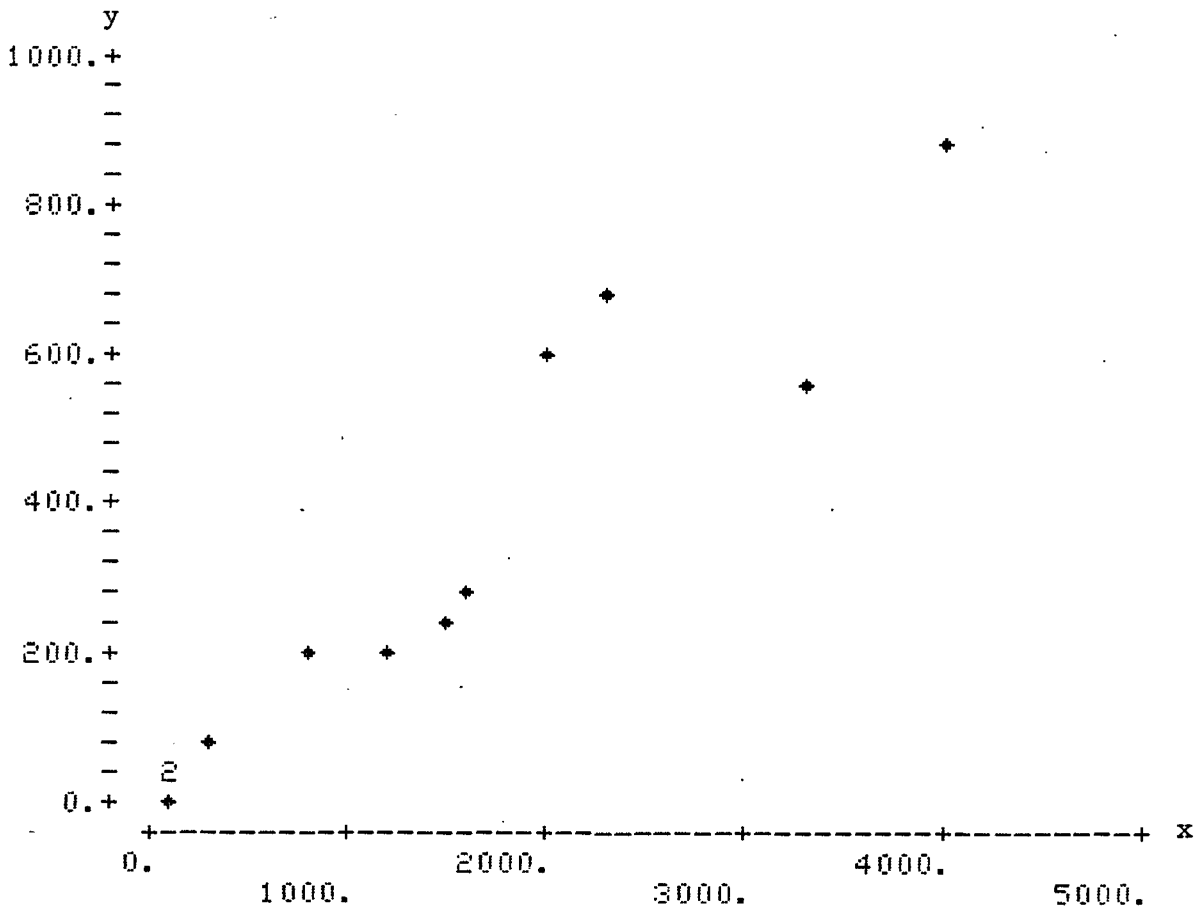


Fig. 4.4 Correlation of EDB and EDC in the exhaust emissions of a 3 l engine

Correlation factor = 0.944

Regression equation $y = 10.3 + 0.215\ x_1$

R-squared = 89.1%

benzene > toluene > EDC > EDB

From the constant speed tests it is evident that the higher the speed the lower the concentrations of these pollutants in the exhaust emitted, with the highest concentrations recorded when the engine is running idle.

Such an assumption may be made for total hydrocarbons and carbon monoxide as indicated in table 4.4, which includes data obtained during the same series of experiments.

Table 4.4 : Total hydrocarbons (THC), carbon monoxide (CO) and oxides of nitrogen (NOx) in the exhaust emissions of the 3 l engine under different tests

Test	THC ppm	CO %	NOx ppm
ECE			
Cold start bag 1	460	5.35	800
bag 2	260	1.35	1470
Hot start bag 1	440	1.44	1400
bag 2	410	1.65	1530
EEC/CVS			
bag 1	23	620 (ppm)	78
bag 2	22	680 (ppm)	81
U.S. Federal	30	870 (ppm)	155
Constant speed			
idle	1350	1.00	-
20 mph	970	1.42	-
30 mph	950	0.45	-
40 mph	130	0.58	-
50 mph	70	0.42	-

An exception to this general trend is evident in the variation of the concentrations of the oxides of nitrogen (for reasons discussed in Chapter 1). This may be seen in fig. 4.5.

The behaviour of the individual hydrocarbons is similar to

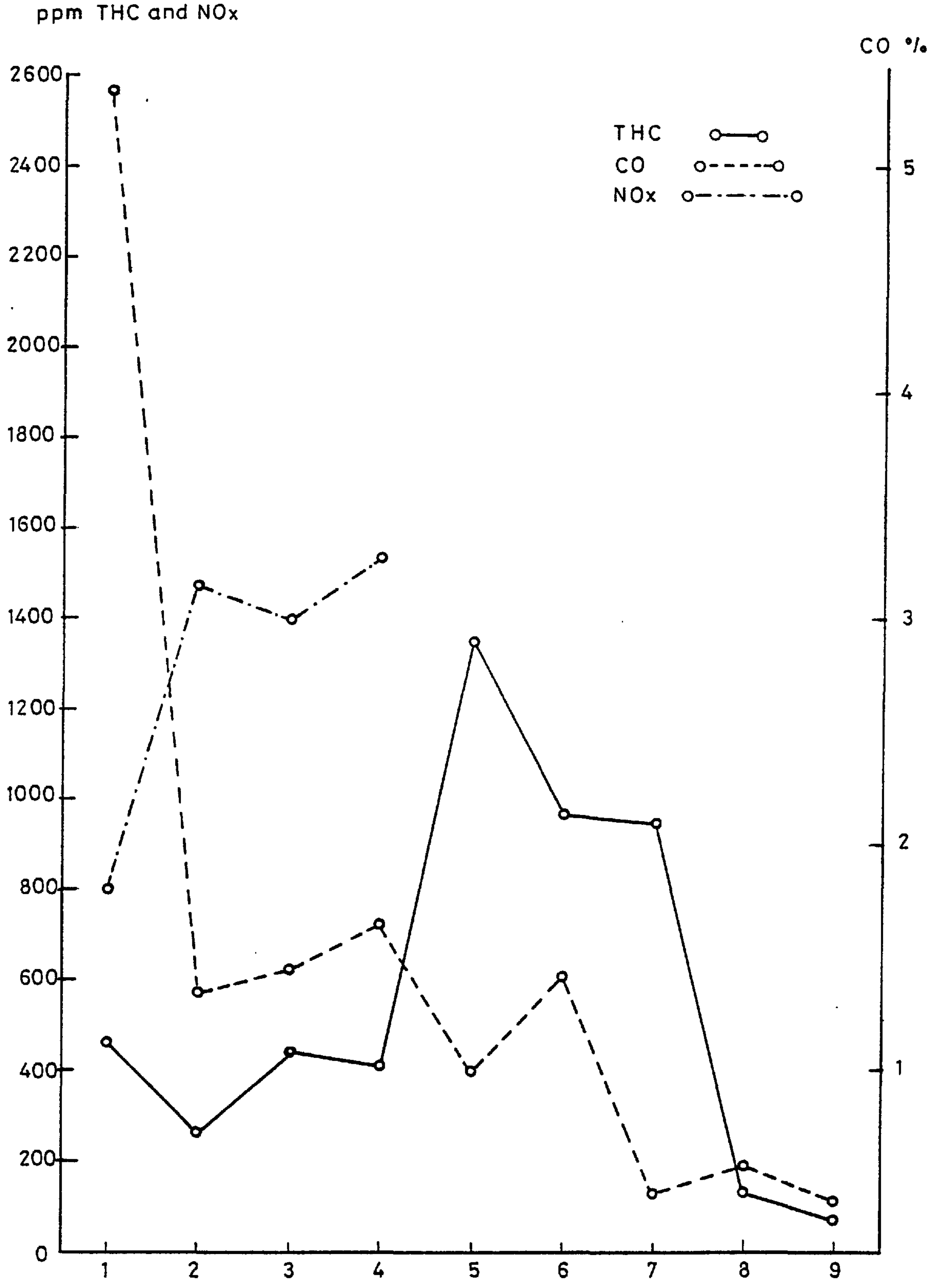


Fig. 4·5

Trends in the concentrations of THC, CO and NOx in the exhaust emissions of a 3l engine under different driving tests

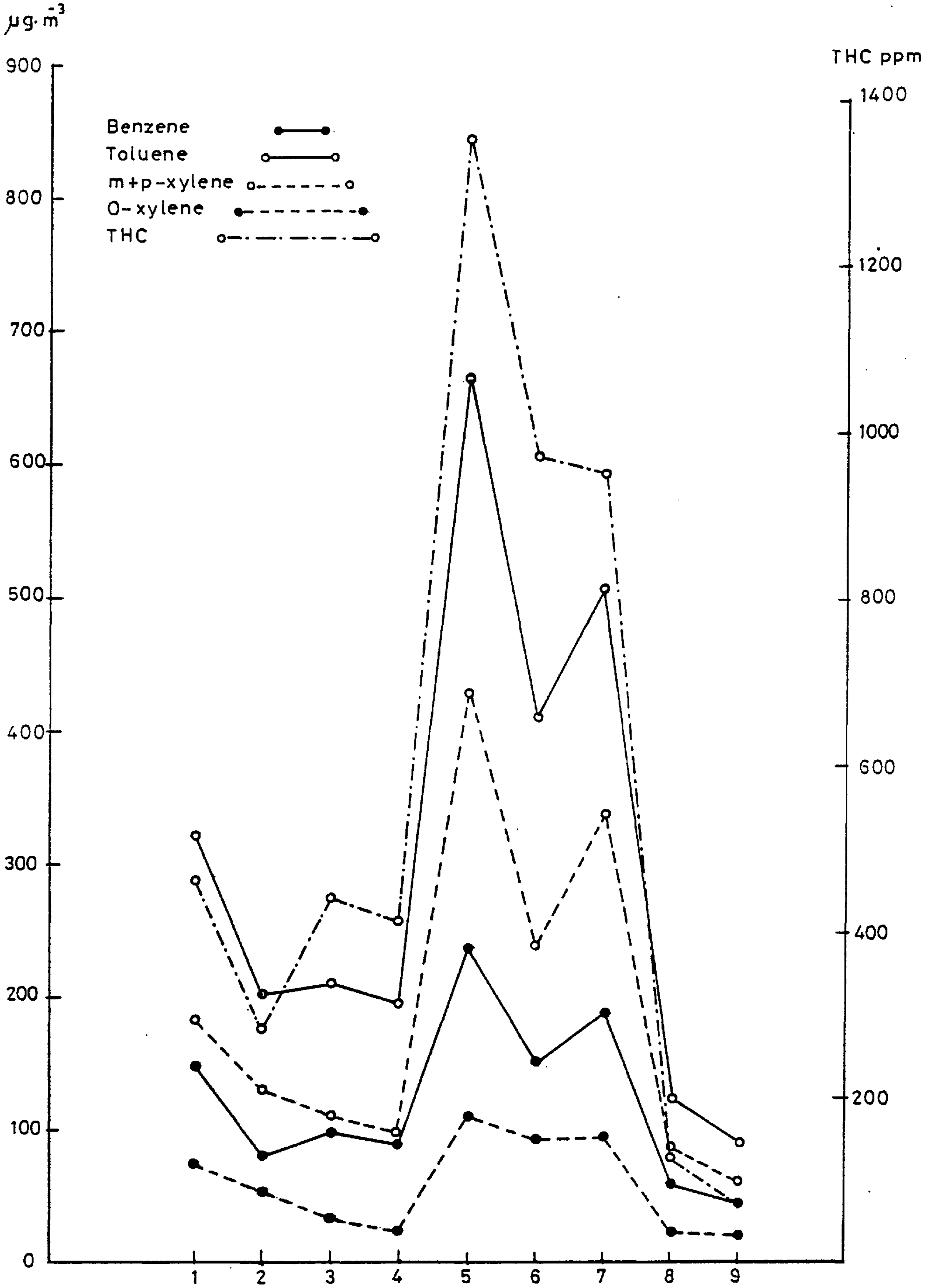


Fig 4·6

Variation in the concentrations of four individual hydrocarbons and THC in the exhaust emissions of a 3l engine under different driving tests that of the total hydrocarbons in the different exhaust emission samples, and this is shown in fig. 4.6 where the four hydrocarbons (benzene, toluene, m+p-xylene, o-xylene) and total hydrocarbons are plotted together.

The situation in street air samples for the same individual compounds (table 4.2) suggests that the U.S. Federal driving test would readily display a street air situation (after a dilution 1:100), which is in very good agreement with reference (2) (table 4.1).

Similar assumptions can be drawn from the results for the same pollutants in the exhaust emissions from the Mini 0.85 l engine, when operating under the same driving tests. These data are included in tables 4.5, 4.6 and 4.7.

Table 4.5 : Concentrations of individual pollutants in the exhaust emissions of a 0.85 l engine under the different driving tests (μg m^{-3})

Test	benzene	toluene	EDB	EDC	C_7/C_6	C_6/EDB	EDC/EDB
ECE							
Cold start bag 1	185800	718100	1360	1215	3.86	137	0.89
bag 2	81340	310200	733	675	3.81	111	0.92
Hot start bag 1	109735	340045	538	760	3.10	204	1.41
bag 2	108100	333300	533	735	3.11	200	1.38
ECE/CVS							
bag 1	5850	17837	26	38	3.05	225	1.46
bag 2	4580	12250	34	38	2.67	135	1.12
U.S. Federal							
Cold Start	7512	244475	29	71	3.26	259	2.45
Hot start	7563	24519	22	65	3.24	344	2.95
Constant speed							
idle	173200	396000	332	372	2.29	522	1.12
20 mph	56271	129380	165	365	2.30	341	2.21
30 mph	58628	143028	155	315	2.44	378	2.03
40 mph	60179	160929	139	217	2.67	433	1.56
50 mph	56938	139018	135	189	2.44	422	1.40

Table 4.6 : Statistical analysis of data obtained from the exhaust emissions of the 0.85 l engine under different driving tests

Ratios	$\bar{x}$	σ_n
C_7/C_6	2.94	0.51
C_6/EDB	285	125
EDC/EDB	1.61	0.60

Table 4.7 : Total hydrocarbons (THC), carbon monoxide (CO) and oxides of nitrogen (NOx) in the exhaust emissions of a 0.85 l engine under different driving tests

Test	THC ppm	CO %	NOx ppm
ECE			
Cold start bag 1	790	3.60	1300
bag 2	340	1.85	1550
Hot start bag 1	400	1.75	1450
bag 2	330	2.00	1520
ECE/CVS			
bag 1	19.2	900 (ppm)	66
bag 2	18.5	860 (ppm)	62
U.S. Federal			
Cold start	27.7	1665 (ppm)	96
Hot start	23.8	1560 (ppm)	110
Constant speed			
idle	230	6.90	-
20 mph	97	0.57	-
30 mph	83	0.35	-
40 mph	70	0.56	-
50 mph	62	1.23	-

For this particular vehicle a greater variation in C_7/C_6 was found (2.29-3.86) a fact which indicates how different engines can influence the variation of this ratio in street air samples. Nevertheless a close correlation between these two compounds was obtained as can be seen in fig. 4.7 where benzene and toluene are plotted together in a regression mode and a correlation factor of 0.951 was obtained.

Statistical analysis of the results obtained from the tests with this particular vehicle produced a mean C_6/EDB ratio $\bar{x} = 285$ and a mean EDC/EDB ratio $\bar{x} = 1.61$. A comparison of the C_6/EDB ratio with the one calculated for the 3 1 engine ($\bar{x} = 313$), indicated lower concentrations of EDB in the 3 1 engine emissions. This was however in part caused by the use of different fuel during the tests with the 3 1 engine, which contained less EDB (20%) than the fuel used during the 0.85 1 engine tests.

The EDC/EDB ratio for the 0.85 1 engine appeared much lower than that in the 3 1 engine ($\bar{x} = 4.54$) which can not be easily explained, but this indicates a higher relative contribution from the 3 1 engine for the EDC emissions than that for EDB, compared to the 0.85 1 engine.

The correlation of EDB and benzene in the exhaust gases from that test is shown in fig. 4.8, and the factor 0.801 shows a relatively poor correlation compared to that for the 3 1 engine (0.979).

The correlation of EDB and EDC in the emissions of the 0.85 1 engine is shown in fig. 4.9 where a factor of 0.962 for the two compounds is given. This in comparison to that found from measurements in Exhibition Road (0.430) is far better and is very close to that of the 3 1 engine (0.944).

Comparison of the 0.85 1 engine (table 4.5) with the street air analyses, indicates that the U.S. Federal driving cycle simulates a street air situation better than the ECE cycle. This can be seen by a comparison of the profiles of individual hydrocarbons, which resulted from the two cycles (fig. 4.10) with the profiles obtained from air samples in different locations, already presented in Chapter 3 (fig. 3.16, 3.17 and 3.21).

Results obtained from the Alpine 1.6 1 engine under the same

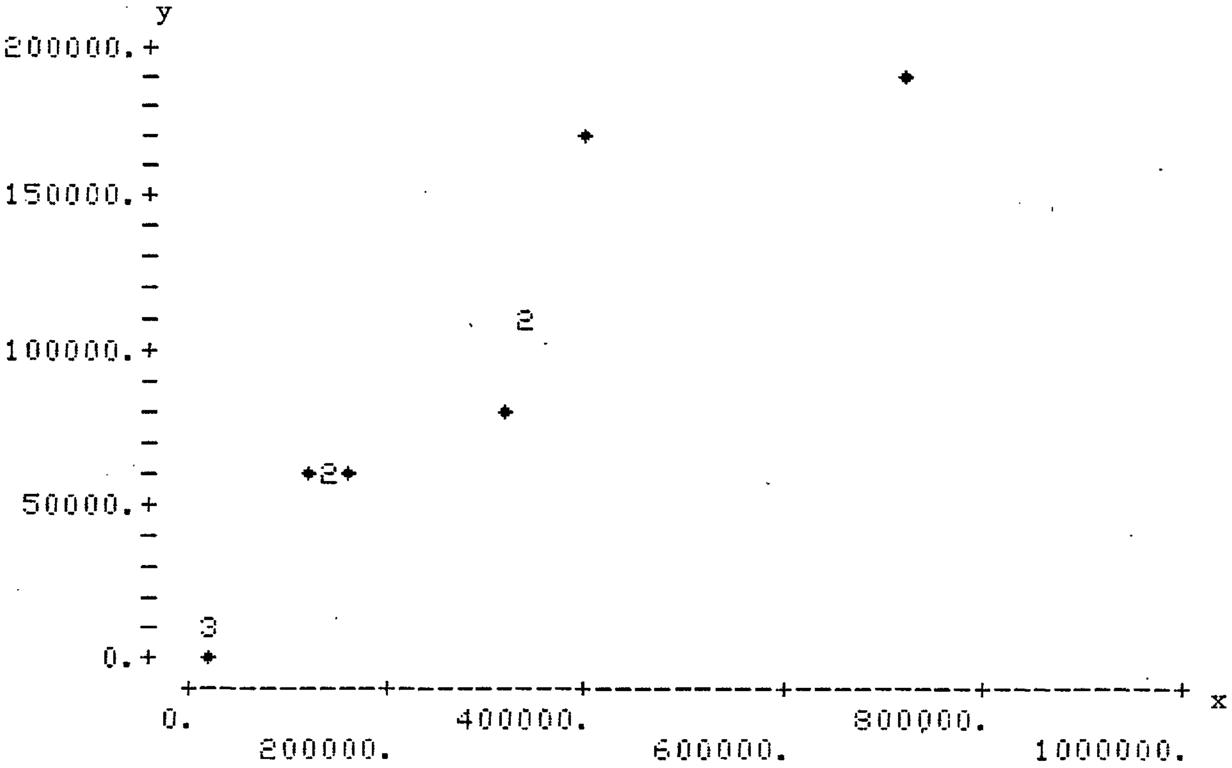


Fig. 4.7 Correlation of benzene and toluene in the exhaust emissions of an 850 cc engine

Correlation factor = 0.951

Regression equation = 10657 + 0.288 x_1

R-squared = 90.4%

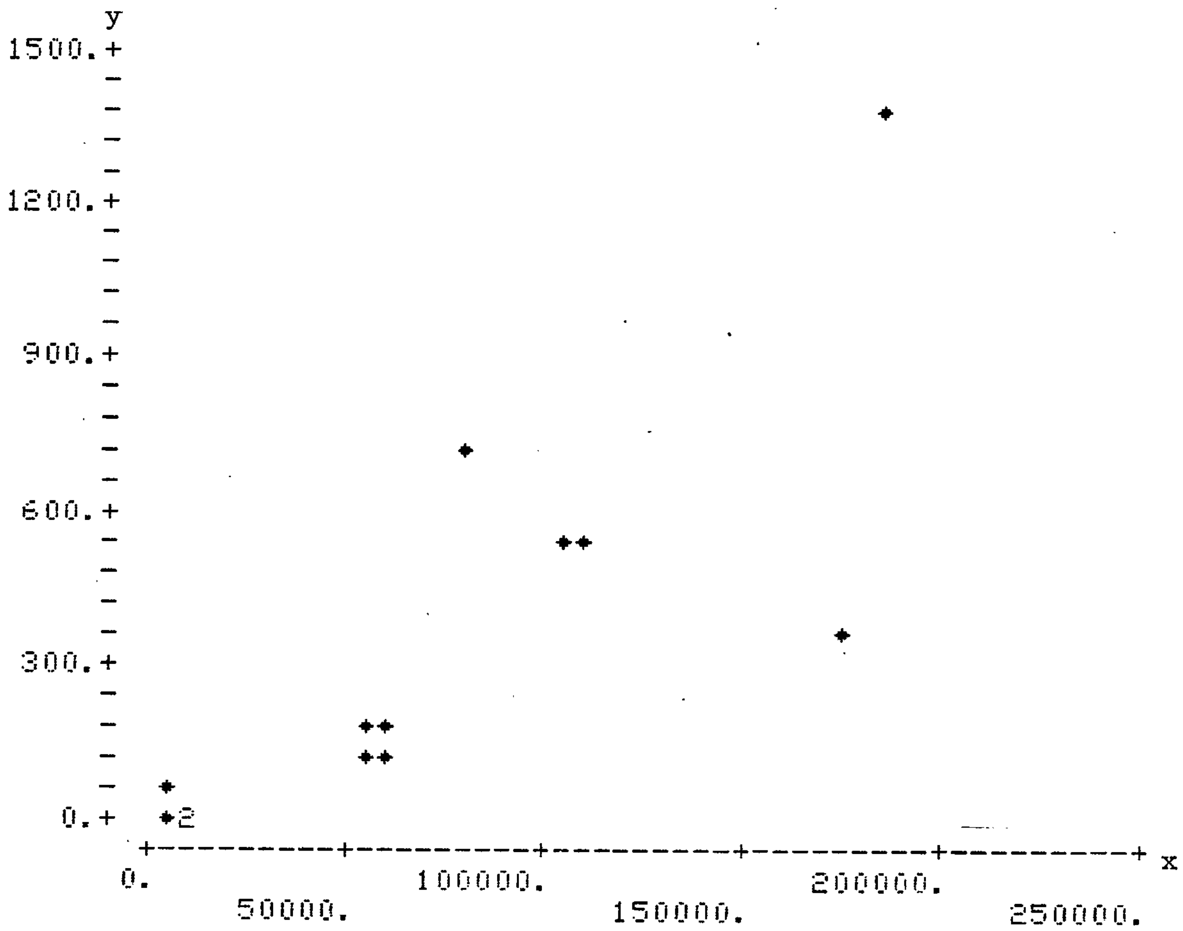


Fig. 4.8 Correlation of EDB and benzene in the exhaust emissions of an 850 cc engine

Correlation factor = 0.801

Regression equation $y = -38.0 + 0.0051\ x_1$

R-squared = 64.1%

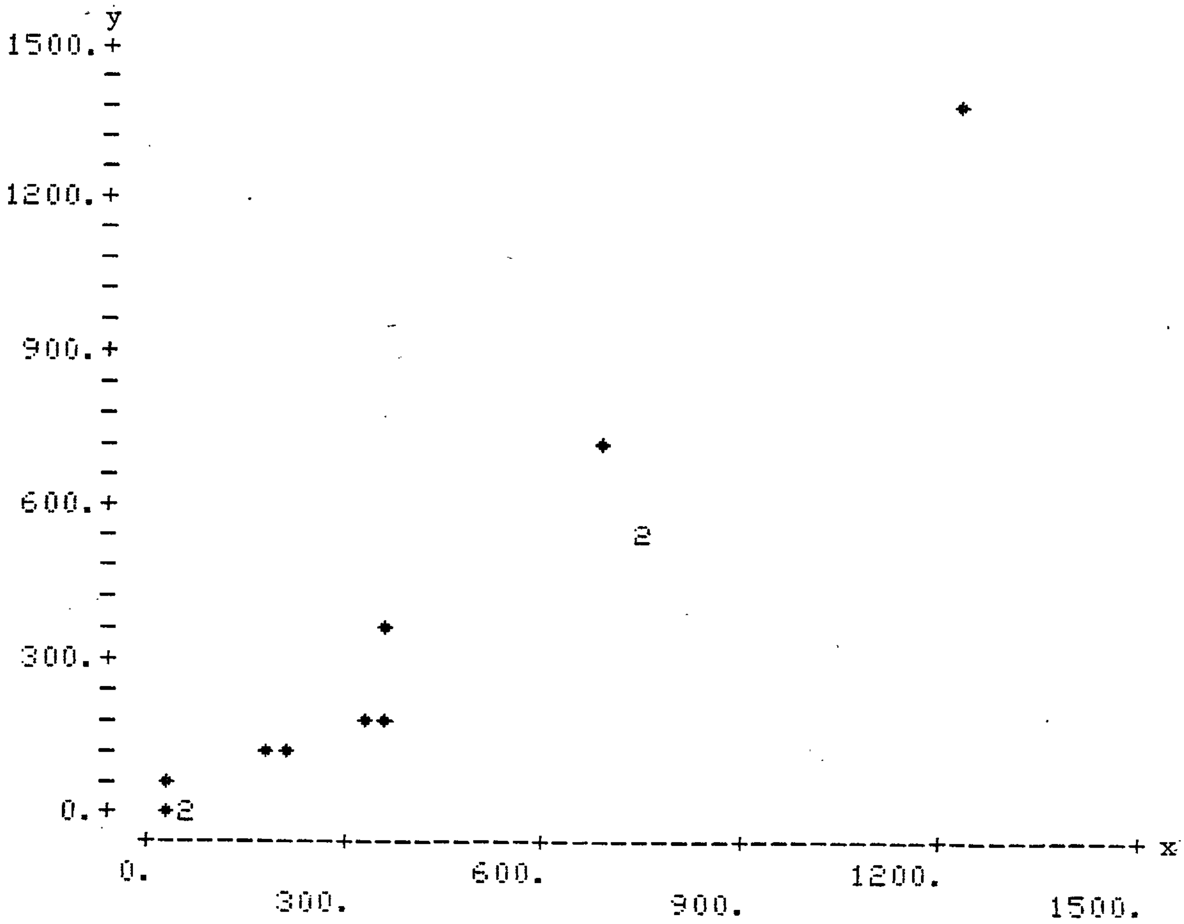


Fig. 4.9 Correlation of EDB and EDC in the exhaust emissions of an 850 cc engine

Correlation factor = 0.962

Regression equation $y = -80.3 + 1.04\ x_1$

R-squared = 92.5%

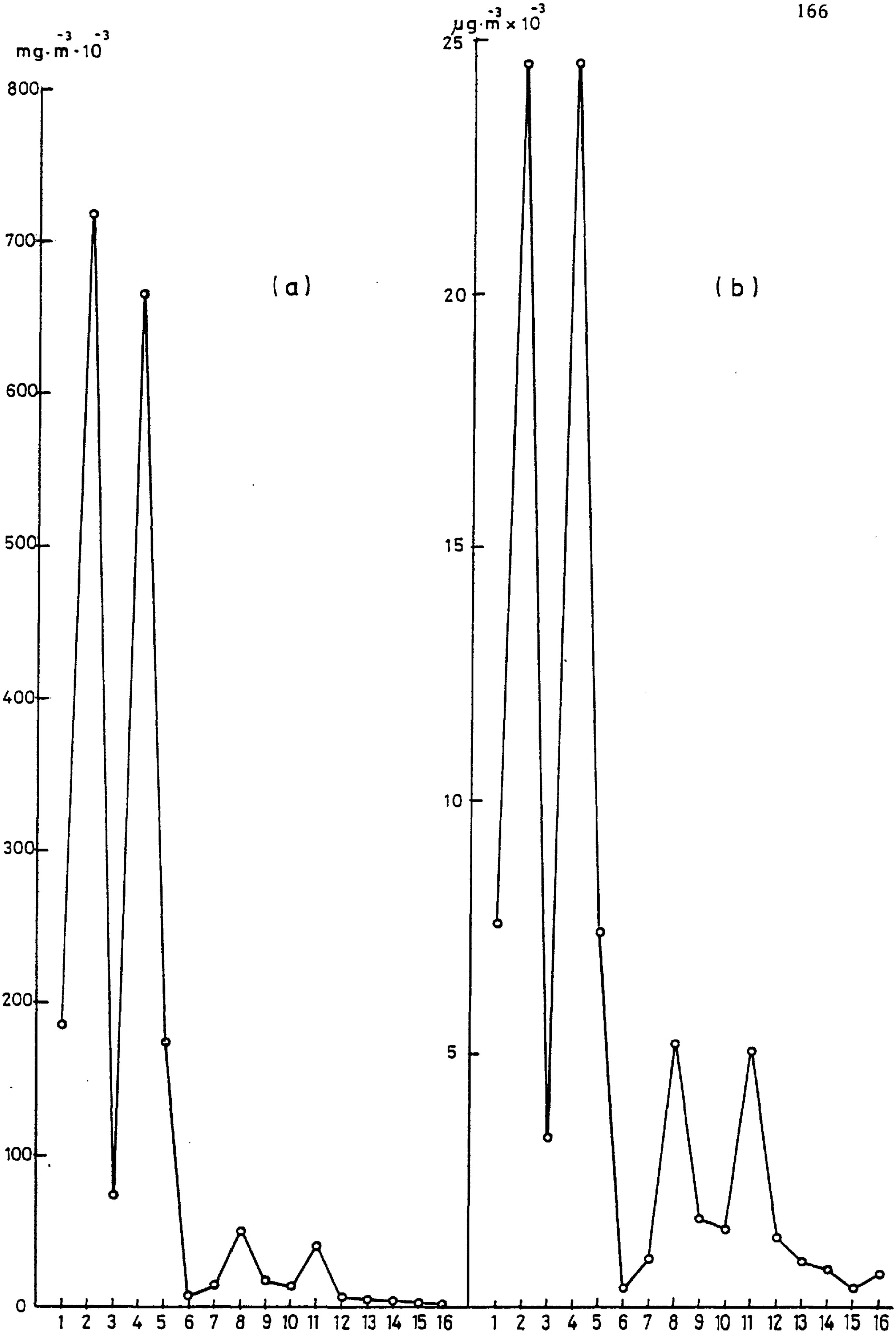


Fig 4·10 The profiles of individual hydrocarbons (1-16) in raw exhaust gases of an 850cc engine under (a) an ECE cycle and (b) a U S Federal driving cycle sequence of driving tests for the general pollutants and two individual compounds (EDB and EDC) are included in table 4.8.

Table 4.8 : Total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NOx) EDB and EDC in the exhaust gases of a 1.6 l engine under different driving tests

Test	THC ppm	CO %	NOx ppm	EDB $\mu g\ m^{-3}$	EDC $\mu g\ m^{-3}$
ECE					
Cold start bag 1	429	2.80	700	690	1690
bag 2	413	2.97	740	670	2350
Hot start bag 1	429	2.67	720	390	3340
bag 2	405	3.00	710	450	2226
ECE/CVS					
bag 1	25.4	1390 (ppm)	50	69	109
bag 2	23.8	1980 (ppm)	46	42	59
U.S. Federal	27.7	3080 (ppm)	70	46	209
Constant speed					
idle	455	5.24	-	480	640
20 mph	255	1.60	-	130	510
30 mph	285	2.70	-	210	720
40 mph	330	2.50	-	101	300
50 mph	280	3.30	-	127	260

EDC/EDB $\bar{x} = 3.30$

$\sigma_n = 1.94$

The trends appear to be similar to those previously described for the 3 l and the 0.85 l engines. A mean EDC/EDB ratio of $\bar{x} = 3.39$ was obtained and this value lies between the two obtained for the two engines studied previously.

From the concentrations determined for the general and individual pollutants for the three engines, no clear conclusion can be drawn as to the relative contribution of each particular vehicle (with respect to the engine size) unless all the produced volume of exhaust gases is taken into account.

4.3.2 Influence of Fuel Composition on the Concentrations of Halocarbon Emissions

Results for the determination of EDB and EDC in the exhaust gases of the Alpine 1.6 l engine under exactly the same driving tests

Table 4.9 : EDB and EDC (µg m^{-3}) in the exhaust gases of a 1.6 l engine when running on fuels of different compositions

Test	Motor Mix		Aviation Mix	
	EDB	EDC	EDB	EDC
ECE				
Cold start bag 1	690	1690	620	-
bag 2	670	2350	600	-
Hot start bag 1	390	3340	850	-
bag 2	450	2226	840	-
ECE/CVS				
bag 1	69	109	60	-
bag 2	42	59	66	-
U.S. Federal				
Hot start	46	209	87	-
Constant speed				
idle	480	640	260	-
20 mph	130	510	250	-
30 mph	210	720	400	-
40 mph	101	300	690	-
50 mph	127	260	490	-
mean concentrations	$\bar{x}_1=283.8$	$\bar{x}_2=1034.4$	$\bar{x}_3=434.4$	-
standard deviations	$\sigma_n=231$	$\sigma_n=1043$	$\sigma_n=278$	-

for two different fuel compositions are recorded in table 4.9. (motor mix 0.25 g l^{-1} of EDC and 0.25 g l^{-1} EDB, aviation mix only EDB 0.50 g l^{-1}).

These results suggest that EDB is a good lead scavenger by itself, independently of the presence of EDC. When the EDB concentration in the fuel was doubled, its concentration in the exhaust gases was increased by only 35% (calculated from the $\bar{x}_1$ and $\bar{x}_3$ mean concentrations). This indicates that more lead atoms reacted to form $PbBr_2$ than reacted in the presence of both the scavengers to form halides ($PbClBr$, $PbCl_2$, $PbBr_2$).

In other words a complete substitution of EDC by EDB will result in a more efficient lead removal from the engine and less halocarbon emission into the atmosphere.

4.3.3 The Effect of a Lead Filter on Exhaust Emissions

Concentrations of the individual and general pollutants in exhaust emissions of the 0.85 l engine equipped with a lead filter under different driving cycles, are presented in the tables 4.10, 4.11 and 4.12.

Table 4.10 : Concentrations of individual pollutants in the exhaust emissions of a 0.85 l engine equipped with a lead filter, under different driving tests (μg m^{-3})

Test	benzene	toluene	EDB	EDC	C_7/C_6	C_6/EDB	EDC/EDB
ECE							
Cold start bag 1	248180	1000194	1951	2022	4.03	127	1.04
bag 2	108434	391678	798	1207	3.61	136	1.51
Hot start bag 1	81985	280896	422	597	3.43	194	1.41
bag 2	91938	325842	388	578	3.54	237	1.49
ECE/CVS							
bag 1	5173	17047	25	54	3.30	207	2.16
bag 2	6129	21065	25	29	3.44	245	1.16
U.S. Federal							
Cold start	8761	30585	43	58	3.49	204	1.35
Hot start	8275	29059	31	51	3.51	267	1.65
Constant speed							
idle	164941	406286	251	297	2.46	657	1.18
20 mph	55080	160080	143	283	2.91	385	1.98
30 mph	57596	172516	126	292	3.00	457	2.32
40 mph	63002	178246	117	215	2.83	538	1.84
50 mph	74714	189179	113	190	2.53	661	1.68

Table 4.11 : Statistical analysis of data obtained from the exhaust emissions of the 0.85 l engine equipped with a lead filter, under different driving tests

Ratios	$\bar{x}$	σ_n
C_7/C_6	3.24	0.44
C_6/EDB	332	181
EDC/EDB	1.60	0.38

Table 4.12 : Total hydrocarbons (THC), carbon monoxide (CO) and oxides of nitrogen (NOx) in the exhaust emissions of a 0.85 l engine equipped with a lead filter, under different driving tests

Test	THC ppm	CO %	NOx ppm
ECE			
Cold start bag 1	900	3.40	1000
bag 2	360	1.80	1250
Hot start bag 1	288	1.62	1380
bag 2	320	1.85	1550
ECE/CVS			
bag 1	17.8	850 (ppm)	59
bag 2	17.6	750 (ppm)	60
U.S. Federal			
Cold start	-	-	-
Hot start	8.46	1450 (ppm)	110
Constant speed			
idle	430	7.30	-
20 mph	220	0.90	-
30 mph	220	0.40	-
40 mph	147	0.64	-
50 mph	128	1.35	-

Results produced under identical conditions (using the same driving tests and the same fuel composition) for the same engine equipped with a standard exhaust instead of the lead filter, are recorded in tables 4.5, 4.6 and 4.7 respectively.

From tables 4.6 and 4.11 it is evident that the lead filter preferentially traps more benzene than toluene, which results in an increase of the C_7/C_6 mean ratio (2.94 to 3.24). Moreover it also traps proportionally more EDB and EDC than benzene, since the C_6/EDB mean ratio was increased (285 to 332) whereas the EDC/EDB mean ratio appears to be almost the same (1.61 to 1.60).

The preferential retainment of these four compounds by this particular filter was in the order,

EDC > EDB > benzene > toluene

On the other hand the correlation of the individual components such as benzene to toluene appears to be more consistent and higher in the emissions, when using the lead filter. This can be seen in the standard deviations of C_7/C_6 mean ratios (0.51 and 0.44) and from the correlation diagram in a regression mode of the two compounds shown in fig. 4.11 (correlation factor 0.969 compared to the 0.951).

In the same mode of analysis, correlation of EDB to benzene and EDB to EDC (as shown in figs. 4.12 and 4.13) appeared to be higher in the emission gases when the filter was used (0.855 and 0.983 compared to 0.801 and 0.962 respectively).

An immediate assumption from tables 4.5 and 4.10 is that upon a cold start of the engine equipped with a lead filter, greater absolute amounts of pollutants were released in the emission gases than those released by the same engine without lead filter. The contrary occurs during a hot start of the engine.

Calculation indicates that in a cold start more benzene (25%), toluene (28%), EDB (30%) and EDC (40%) were emitted by the engine when equipped with the lead filter. Correspondingly, in a hot start less benzene (25%), toluene (18%), EDB (22%) and EDC (22%) were emitted by the engine when equipped with the lead filter than from the same engine equipped with standard exhaust.

Similar behaviour for total hydrocarbons is evident from examination of tables 4.7 and 4.12 where more hydrocarbons (13%) are emitted from the engine equipped with the lead filter during a cold start, compared to those emitted by the same engine with standard exhaust, whilst during a hot start less hydrocarbons (28%) are emitted

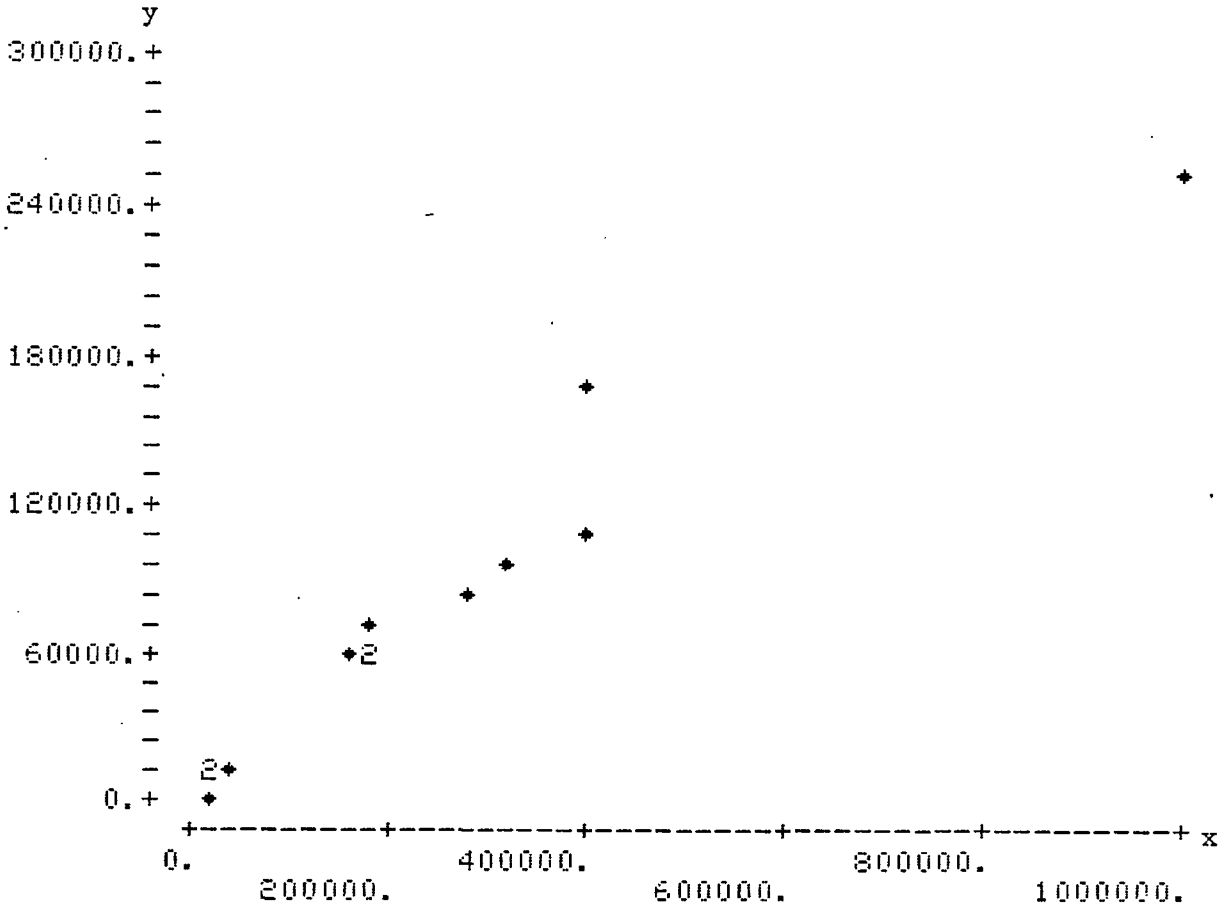


Fig. 4.11 Correlation of benzene and toluene in the exhaust emissions of an 850 cc engine equipped with a lead filter

Correlation factor = 0.969

Regression equation $y = 11.755 + 0.256\ x_1$

R-squared = 94.0%

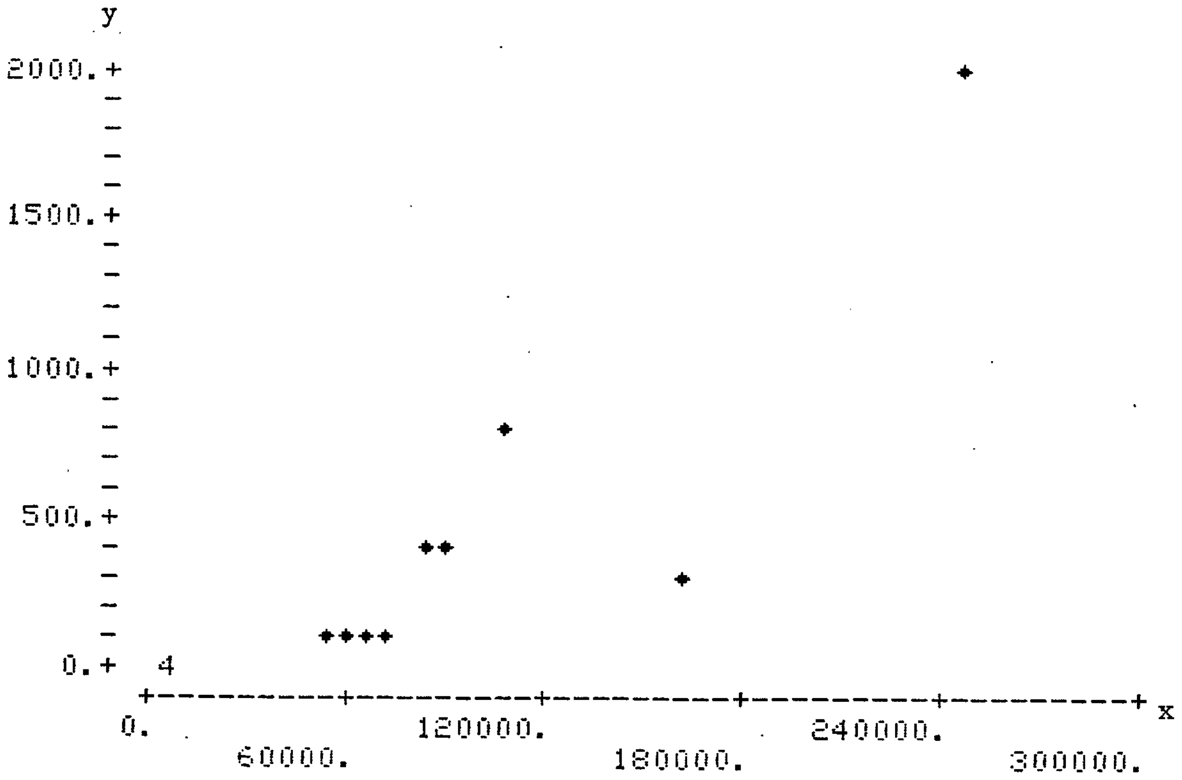


Fig. 4.12 Correlation of EDB and benzene in the exhaust emissions of an 850 cc engine equipped with a lead filter

Correlation factor = 0.855

Regression equation $y = -146 + 0.0065\ x_1$

R-squared = 73.2%

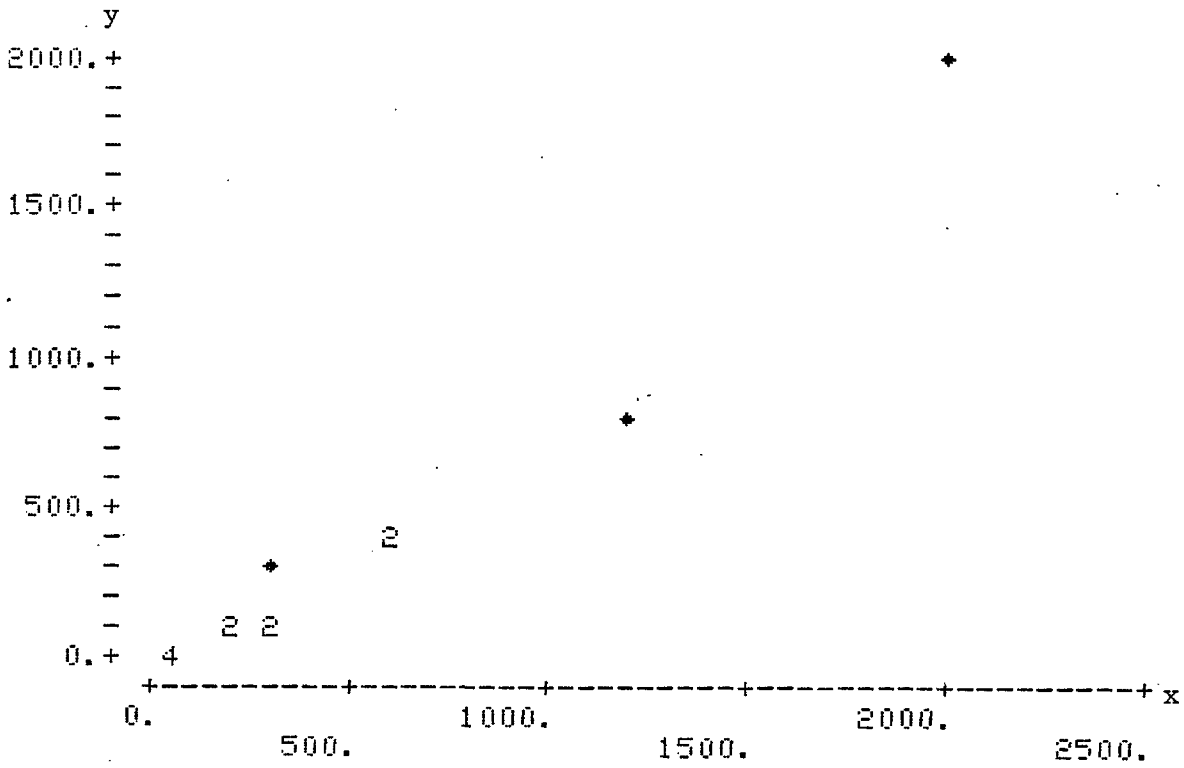


Fig. 4.13 Correlation of EDB and EDC in the exhaust emissions of an 850 cc engine equipped with a lead filter

Correlation factor = 0.983

Regression equation $y = -71.4 + 0.913\ x_1$

R-squared = 96.6%

by the engine equipped with a lead filter.

The lead filter appeared to have very little influence upon carbon monoxide emissions (less than 10% variation) whereas oxides of nitrogen appeared to be lower (up to 23%) in the case with the lead filter.

4.4 General Discussion

From the investigation of the raw exhaust emissions, correlation of individual compounds such as C_7/C_6, C_6/EDB and EDC/EDB appeared very high and consistent.

Variations in the concentrations of individual compounds were very similar to the trends demonstrated by the general air pollutants (THC, CO, NOx) and in good agreement with the trends observed in ambient air samples from the street side sampling locations.

It is more difficult to understand the variations in the ratios of individual components such as toluene to benzene, benzene to EDB and EDC to EDB, over the different driving cycle tests.

For the two engines studied (3 l and 0.85 l), mean C_7/C_6 ratios were 2.44 (σ_n = 0.32) and 2.94 (σ_n = 0.51), which suggests that such variations may be expected in street air samples, even more when the variety of vehicles in circulation is taken into account.

It is clear that the commonly reported ratio of toluene to benzene (2.4 : 1), as indicative of traffic pollution, is the result of a wide range of emissions by different vehicles plus evaporative losses, and an evaluation of these two factors separately is not yet feasible.

However, the same ratio C_7/C_6 in petrol was found to be approximately 4:1, which is in good agreement with the petrol composition stated by the refineries (2). Therefore it is evident (tables 4.2 and 4.5) that proportionally more toluene is consumed during the internal combustion process,resulting in lower C_7/C_6 ratios (mean 2.44 and 2.94) particularly at the higher combustion temperatures (1.89 and 2.44).

The C_7/C_6 ratios found in Exhibition Road, the traffic tunnel (2.45 and 2.60) and those found in the Airedale Valley (2.56, 2.68 and

2.86) lie however in between those obtained from the two engines studied. The high correlation factors for benzene and toluene in the raw exhaust emissions (0.988 and 0.951, mean 0.969), are in very good agreement with that from the Exhibition Road measurements (0.966), which shows an equally normal distribution of both the compounds into the atmosphere.

The C_6/EDB ratio in petrol, through the period of study, varied between 200 and 250. Mean ratios obtained from the emissions of the engines studied were however higher (285 and 313) with a wide range of variation (111 to 522). The much lower C_6/EDB ratios found in Exhibition Road and the traffic tunnel (97.7 and 108) indicate higher relative concentrations of EDB in street air than in the exhaust emissions.

This may be a consequence of the physical and chemical characteristics of the individual compounds, which gave rise to non-uniform distribution in air and their subsequent dispersion. This suggests that sampling at different heights from the ground may yield a different ratio.

Taking into account factors such as stability and the possibility of further reactions of the compounds under study and the evaporative losses involved, the problem appears to become even more complex. This is particularly important in the case of EDC and affects the EDC/EDB ratios and consequently their correlation factors.

On a weight by weight basis EDC and EDB in petrol have a ratio 1:1. The mean ratios found in the exhaust emissions of the two engines studied (3 1 and 0.85 1) were 4.54 and 1.61 respectively (mean 3.07), with a great variation (0.89 to 6.26). Mean values greater than 1 are expected taking into account the lower efficiency of EDC as a lead scavenger. The greater variation shows how the emission of EDC is closely dependent upon the engine and the driving mode.

The EDC/EDB ratios found in the street air samples were 2.52 (σ_n = 0.96) which is not far from the mean ratio obtained from the raw exhaust (3.07). Great differences were observed for the correlation factors of the two compounds, which can be seen easily in figures 3.13, 4.4 and 4.9. In the raw exhaust (fig. 4.4 and 4.9) a good linear correlation is indicated (factors 0.944 and 0.962) whereas in street air (fig. 3.13) all the points are scattered and the poor correlation is given by the factor 0.430. The high reactivity and inherent instability of EDC in the atmosphere is deemed to be the main reason for this, but nevertheless further investigation could elucidate more points which cannot be readily explained by the available data.

However, the great variations found in ratios and correlation factors of the exhaust emissions of the two engines studied explain well the variations of the same ratios and factors observed in street air, indicating that even greater variations may be expected.

The use of EDC and EDB as lead scavengers or preferably only EDB, is a question of cost, which did not appear to play any role in its choice for the aviation fuel where the absolutely highest possible efficiencies are required.

The mandatory use of lead filters will only be invoked for their activity on lead emissions. Its trapping efficiency for the other pollutants studied here, is dependent on how many cold and how many hot starts the engine does over a period of time. The gama alumina acts as a good trap only at higher temperatures and because of the great surface area involved the warming up process takes a long time, which allows higher emissions of the pollutants of concern in the exhaust gases, during this period.

4.5 Conclusions

(a) Aromatic hydrocarbons and halocarbons found as ambient air pollutants, owe their existence to the incomplete combustion of these species during the internal combustion process and not only to evaporative losses, since these compounds were readily found as constituents of the raw exhaust gases under all the modes of engine operation.

(b) Correlation factors found between individual compounds in the raw exhaust gases were higher than those found in the street air samples.

(c) Variations in the ratios between individual compounds observed in street air samples were related first to the effects of the different engines contributing to these compounds and second to further alterations in their distribution in the atmosphere, caused by the individual physical and chemical characteristics of each particular compound.

(d) A cold start of the engine released higher concentrations of general and individual pollutants (up to 2.4 times) than those released by a hot start of the engine, with the exception of the oxides of nitrogen.

(e) The particular characteristics of the engine and the mode of operation influence directly the concentration of the pollutants in the emission gases. Therefore the establishment of an appropriate driving cycle, to test the newly manufactured vehicles according to the existing regulations, is of great importance and this driving cycle must accurately reproduce the driving patterns of each particular country.

(f) The U.S. Federal driving cycle appeared to be closest to the real situation on the roads in central London, more so than the ECE and the constant speed driving tests.

(g) A dilution of 1:100 has been found for the exhaust emissions of the U.S. Federal test in the atmosphere, whereas a dilution of 1:1000 was found for the ECE and constant speed tests, in order to obtain concentrations of the pollutants comparable to those found in an urban situation.

(h) EDB was found to be more efficient as a lead scavenger than EDC.

(i) Replacing a standard exhaust of a vehicle with a lead filter resulted in up to 25% (at high temperatures) of the hydrocarbons and halocarbons being trapped.

(j) The use of a dynamometer to study the generation of vehicle associated air pollutants in relation to fuel composition, engine characteristics and mode of operation, provided a good method of undertaking a comparable evaluation of the factors involved.

4.6 References

1. Simanaitis, D.J., Automotive Engineering, August 1977.
2. The Associated Octel Company Limited, Personal communication.

CHAPTER 5 : AN AIRPORT CASE STUDY

5.1 Introduction

In the last two decades the introduction of jet aircraft employing low bypass turbofan engines at airports located in or near population centres, has brought increasing public attention to aircraft generated atmospheric pollution. As airport aircraft activity has increased, the emission of visible exhaust smoke (plume) and the attendent noise generated by jet engines has been viewed by the public with increasing concern.

In the U.S. the Environmental Protection Agency (EPA) has indicated the necessity of regulating aircraft emission of the combustion associated air pollutants (carbon monoxide, total hydrocarbons and oxides of nitrogen) (1).

A large number of studies have been undertaken to evaluate pollution from jet aircraft at airports in the U.S., such as the study in the vicinity of J.F. Kennedy Airport in New York (2), and Los Angeles International Airport in California (3). Studies have also been undertaken at Orly, Paris (4), Tokyo and Osaka International Airport, Japan (5). These studies have shown that in general, aircraft movements contribute only a small fraction to the air pollution in the vicinity of an airport.

The aircraft industry began research into the control of exhaust emissions from aircraft, with the major emphasis on smoke, which led to the investigation of changes in fuel additives and design, to reduce the smoke production by turbine engines.

Particular attention was paid to the amount of time spent by the aircraft in taxying, which injected into the atmosphere the largest amounts of pollutants, and the combustion efficiency of the aircraft engine running at idle (6).

A study undertaken at Dulles International Airport (7), was concerned with the effect of Concorde emissions on air quality at the vicinity of the airport. This study showed insignificant concentrations of pollutants within 1500 ft (457 m) from the aircraft.

In the U.K. a study was undertaken by J. Parker (8) at Heathrow Airport. This study comprised measurements of pollutant concentrations (smoke, deposited matter, THC, CO and some oxides of nitrogen) and also calculation of the total pollutant emission from the airport complex. The results demonstrated that the airport did not contribute "unduly" to local pollution, and that a major contribution resulted from the road traffic.

In a later study in the vicinity of Heathrow Airport (1974-76), undertaken by the Public Health Engineering Laboratory, Imperial College (9), high levels of non-methane hydrocarbons (>0.24 ppm) were detected at all sites on the airport perimeter as a result of aircraft movements. At the "outer sites" pollutant levels were generally low and caused predominantly by the road traffic.

Studies of air pollution in the vicinity of airports reported this far, include measurements of only general air pollutants and in some cases calculation of total emissions, and their final conclusion was that both aircraft movement and vehicle traffic into and around the airport are responsible for the air pollution of the area, with road traffic being usually the major contributor. The problem of source identification however remained unresolved, and in view of this an attempt was made during this study undertaken in the vicinity of Gatwick Airport.

The study involved the measurement of the ground levels of air pollutants around the airport which would permit the evaluation of the airport as a complex source of air pollution, pending a public enquiry. The study included the accumulation of air quality data at six sites around the airport.

5.2 The Mobile Laboratory

The nature of the study required measurements of the pollutants at six sites visited in rotation. A mobile laboratory had to be designed, which facilitated the monitoring work around the airport.

Criteria for the design of such a laboratory were:

(i) To offer all the facilities for a complete air pollution study, including all the equipment required for continuous analysis.

(ii) To be easily movable with a total weight of less than 3 tonnes, which would allow the use of a relatively light vehicle for towing.

Plate 4 : General view of the mobile laboratory

Plate 5 : Inside view of the mobile laboratory

Applying these criteria the mobile laboratory consisted of:

(1) The main laboratory room, with benches along the two sides.

(2) A smaller room providing working and living facilities.

(3) Separate store, housing the necessary gas cylinders, built between the chassis and the housing body. Flammable gases were stored separately in a side cupboard for safety reasons.

Into the laboratory were installed:

(a) AQC chromatograph.

(b) NOx analyzer.

(c) Lead analysis system (air soaking pump through a particular inlet and air flow meter).

(d) Two gas chromatographs with the necessary accessories and a permeation oven.

(e) A data logger enabling the storage of all outputs from the analyzers.

(f) Chart recorders (single, two and three channel).

(g) Meteorological data monitoring control box, linked to an externally mounted pole, supporting wind vane and anemometer.

A general view of the mobile laboratory is given in plate 4. An inside view is shown in plate 5.

5.3 Experimental Work

5.3.1 Sampling and Analytical Techniques for the Pollutants Measured

Total hydrocarbons, non-methane hydrocarbons, carbon monoxide, oxides of nitrogen (NO, NO_2,NOx) and lead as particulate matter, were measured on a continuous basis utilizing the analytical techniques described in Chapter 2. Air samples for the determination of the gaseous pollutants were drawn through a teflon tube inlet mounted on a pole 3 m above the ground level. Particulate lead was trapped on a filter connected to a separate inlet.

Additional work involved measurements of individual hydrocarbons and halocarbons at each site. The sampling procedures and analytical techniques employed for the measurement of these species are described in Chapter 2.

5.3.2 Programme of Work

The study involved the continuous monitoring and collection of air quality data over a period of six months (May to October 1979). The choice of the six sites was based upon criteria designed to cover in a regular way, the perimeter of the airport as permitted by the availability of electric supplies.

The locations of the sites are shown in fig. 5.1 and a brief description of the immediate surroundings of each is included in table 5.1.

Measurements were made continuously for one week at each site before moving to the next location on a Friday. The programme of visits is included in table 5.2. Ideally the cycle around the six

Table 5.1 : Description of Monitoring Sites

Site No.	Descriptions of surroundings, local sources of pollutants
2	Gatwick Park Hotel. Site to S of car park, Terminal area ∿1½ km S, A23 trunk road ∿200 m to E, Charlwood Road ∿100 m to N.
3	Charlwood. Site close to minor roads on SE corner of village
4	Sub-station. Site at SW corner of airfield, minor road ∿10 m to S, runway ∿350 m to N.
5	Beehive. Site in car park of Beehive building, minor roads 50-100 m to W, S, A23 trunk road ∿150 m to N.
6	AA Hut, in long-term car park, A23 road ∿150 m to N.
7.	Brickworks. Site under flight path ∿800 m E of end of runway. Occasional motor traffic using yard.

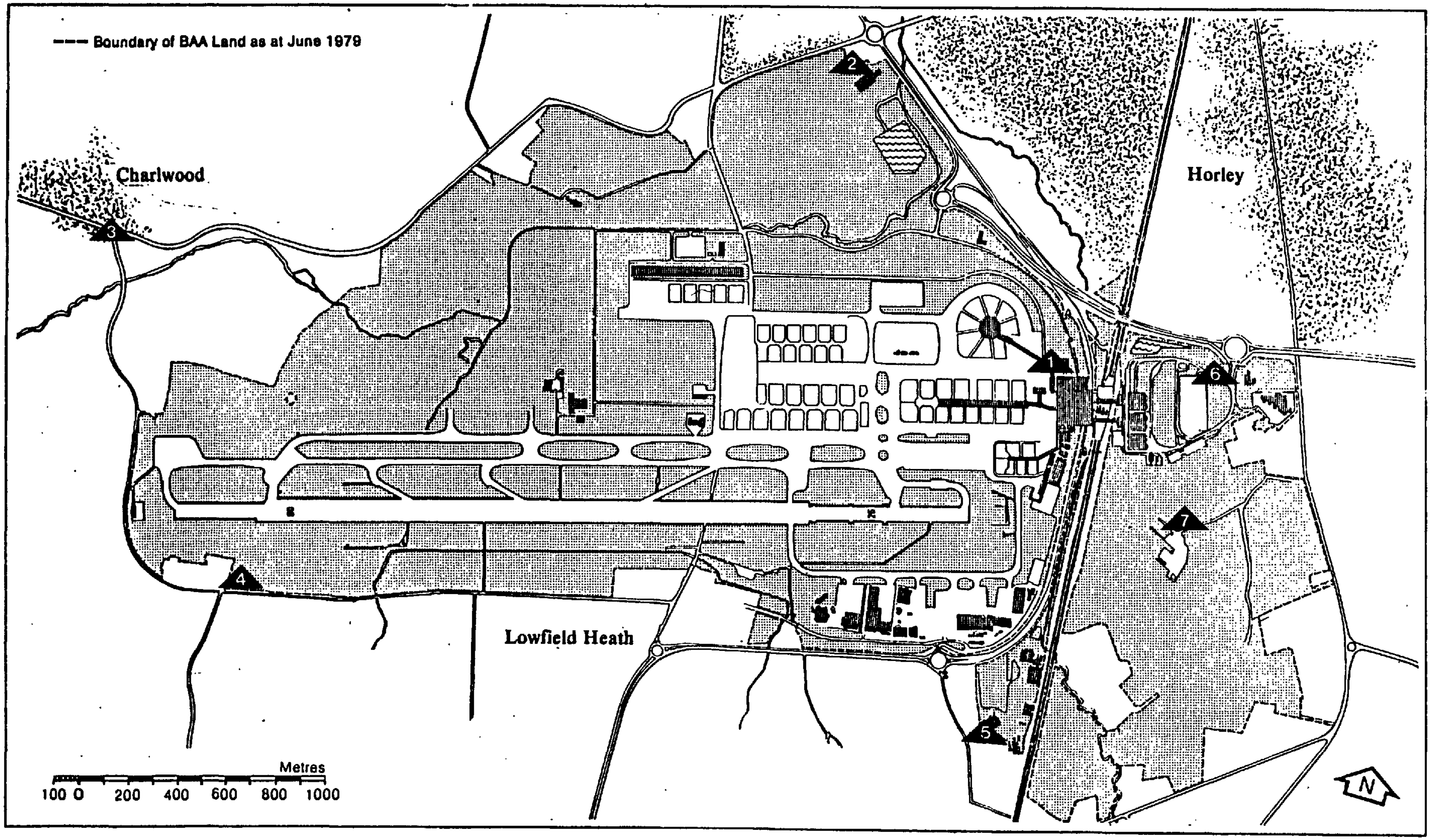


Fig. 5.1 Location of monitoring sites at Gatwick Airport

Table 5.2 : Programme of work at the six Gatwick sites

	Week commencing	Site Number & Name	
1.	30 April	AA Caravan (set up)	(6)
2.	4 May		
3.	11 May	Substation	(4)
4.	18 May	Charlwood	(3)
5.	25 May	Gatwick Park	(2)
6.	1 June	Brickworks	(7)
7.	8 June	AA Caravan	(6)
8.	15 June	Beehive	(5)
9.	13 July	Charlwood	(3)
10.	20 July	Gatwick Park	(2)
11.	27 July	Brickworks	(7)
12.	3 August	Beehive	(5)
13.	10 August	AA Caravan	(6)
14.	17 August	AA Caravan	(6)
15.	24 August	Charlwood	(3)
16.	31 August	Substation	(4)
17.	7 September	Substation	(4)
18.	14 September	Gatwick Park	(2)
19.	21 September	Beehive	(5)
20.	28 September	Beehive	(5)
21.	5 October	Brickworks	(7)
22.	12 October	Brickworks	(7)
23.	19 October	Charlwood	(3)
24.	26 October	Gatwick Park	(2)
25.	2 November	Substation	(4)

sites should have been rapid. This was not always feasible given the distances involved and inevitably there are some gaps in the data (approximately 5 h).

Sampling for analyses of individual compounds was carried out during the routine visits to the sites for the maintenance of the monitoring equipment.

5.4 Results and Discussion

5.4.1 General Pollutants

Concentrations of the general pollutants were calculated as hourly mean and in this form they were used for further computation. Summaries of the data (arithmetic means) found over the monitoring periods at each site are included in tables 5.3 to 5.7 togerther with the 50th, 90th and 99th percentiles of the distribution of hourly means for the gaseous pollutants measured.

Table 5.3 : Concentrations of CO measured at the six sites (ppm)

Site	Arithmetic Mean	Percentiles of hourly means		
		50th	90th	99th
2	0.2	0.1	0.4	0.9
3	0.9	0.5	2.0	4.0
4	0.3	0.2	0.7	1.3
5	0.4	0.3	0.9	2.2
6	1.0	0.7	2.1	4.7
7	0.3	0.2	0.8	1.6

Table 5.4 : Concentrations of NO measured at the six sites (pphm)

Site	Arithmetic Mean	Percentiles of hourly means		
		50th	90th	99th
2	1.5	1.3	2.2	7.1
3	1.5	0.9	2.6	7.3
4	2.0	1.6	2.6	4.8
5	2.8	1.2	8.8	18.6
6	3.1	1.9	6.7	16.0
7	1.1	0.7	2.0	4.4

Table 5.5 : Concentrations of NO_2 measured at the six sites (pphm)

Site	Arithmetic Mean	Percentiles of hourly means 50th	90th	99th
2	1.5	1.2	2.4	4.5
3	1.3	1.1	2.0	2.8
4	1.5	1.2	2.1	3.2
5	1.5	1.2	2.5	4.3
6	2.3	1.8	3.7	6.9
7	1.8	1.4	3.2	6.0

Table 5.6 : Concentrations of total hydrocarbons measured at the six sites (ppm)

Site	Arithmetic Mean	Percentiles of hourly means 50th	90th	99th
2	2.1	2.0	2.6	3.5
3	2.3	2.2	3.0	3.5
4	2.4	2.3	2.9	3.4
5	2.0	1.9	2.7	3.3
6	2.0	1.8	2.4	3.4
7	1.7	1.6	1.8	2.0

Table 5.7 : Concentrations of non-methane hydrocarbons measured at the six sites (ppm)

Site	Arithmetic Mean	Percentiles of hourly means 50th	90th	99th
2	0.5	0.3	1.1	1.9
3	0.4	0.3	0.7	1.2
4	0.7	0.6	1.0	1.3
5	0.3	0.2	0.5	0.9
6	0.7	0.5	1.4	2.0
7	0.2	0.1	0.2	0.3

Overall concentrations of all pollutants were low in comparison to those found at a central London off-street site and markedly lower than those measured at a London kerbside site (table 5.8) (10).

Table 5.8 : Summary of gaseous pollutants (total hydrocarbons (THC), carbon monoxide (CO) and oxides of nitrogen (NO, NO_2)) measured in London off-street and London kerbside

Pollutant and site	Percentiles of hourly means 50	90	99
THC (ppm)			
London off-street	3.0	6.0	10.0
London kerbside	4.6	8.7	16.5
CO (ppm)			
London off-street	2.4	4.8	7.9
London kerbside	3.9	8.5	14.1
NO (pphm)			
London off-street	2.9	8.4	17.5
London kerbside	5.5	22.8	54.0
NO_2 (pphm)			
London off-street	2.8	6.7	12.8
London kerbside	2.8	6.7	12.8

For carbon monoxide, the U.S. Federal Regulations (11) state that an 8 h mean of 9 ppm or an hourly mean of 35 ppm is not to be exceeded more than once per year. During the period of monitoring the values recorded at Gatwick were well below these standards.

In the case of nitrogen dioxide the World Health Organization criterion (12) of an hourly mean of 10-17 parts per hundred million (pphm) should not be exceeded more than once per month. These levels were never exceeded during the period of measurement at all sites.

The nitrogen dioxide standard in the United States (11) is expressed as an annual average of 5 pphm, not to be exceeded and although the measuring period did not extend over a year, the average concentrations of nitrogen dioxide at monitoring sites 6 and 7 over the six month measurement period were 2.3 and 1.8 pphm respectively, with 99th percentiles of 6.9 and 6.0 pphm respectively, so that it would seem most unlikely that the United States standard would be exceeded. The nitrogen dioxide concentrations at the other sites (2-5) however, were even lower than those at the sites 6 and 7.

The U.S. Federal standard for non-methane hydrocarbons (0.24 ppm, 6 am - 9 am average) was exceeded at all the Gatwick sites over the period of this study.

The results of the lead measurements at the Gatwick six sites (table 5.9) compared to those found at five urban U.K. sites (table 5.10 (13) were very similar, with the highest levels recorded at site 5. The lead levels found however, did not exceed the United States standards (14).

Table 5.9 : Summary of lead measurements at the six sites

Site	Lead concentration (ng m^{-3}) (arithmetic average over monitoring period)
2	200
3	447
4	373
5	588
6	333
7	290

Table 5.10 : Lead concentrations measured at other sites in the U.K.

Site	Lead concentration (ng m^{-3})
Five sites mean 1976/7	510*
Five sites mean 1977/8	380*
U.S. Standard	1500**

* Mean annual average of sites in Stoke, Leeds, Belfast and Coventry

** Applies to an average over a calendar quarter

Although pollutant levels recorded at all the sites were on average low, some variations were observed between the sites. Occasional higher NO concentrations were observed at the AA hut (site 6) and the Beehive (site 5) and the 99th percentiles were the highest recorded. This is not surprising in view of the fact that both sites are located near roads and car parks where motor vehicles would be significant sources of NO. The highest carbon monoxide concentrations (mean) were measured at site 6 (AA hut) and site 3 (Charlwood), which also exhibited the highest upper percentiles of all the sites. In both cases car traffic was deemed to be the source since site 6 was subject to the heaviest vehicle traffic of all the sites studied, whilst site 3 was in a lay-by near a road, albeit a minor one.

Total hydrocarbon concentrations were of comparable magnitude at all the sites, since the major proportion was naturally generated methane.

The non-methane hydrocarbon concentrations showed rather more variability among the sites, with sites 2, 4 and 6 exhibiting the highest levels. For site 6 it was clear that motor vehicles were the source indicated by the good agreement of the high CO and NO concentrations at this particular site.

At site 2 (Car Park Hotel) the highest levels of NMHC were observed when the wind was from the north-west which would tend to rule out the airport as being the source of these high levels. The source of these relatively high NMHC levels at sites 2 and 4 were deemed not to originate from any combustion process since no concomitant increase in CO and NOx concentrations was observed.

A further summary of the results of monitoring at the six sites around Gatwick is given in fig. 5.2. This shows the time series of daily mean concentrations for the gaseous pollutants at the various sites, for the monitoring period June to September, together with the daily aircraft movement (ACM) (for the same period). It is evident that, overall, the AA hut (site 6) exhibited the highest levels.

The higher than average concentrations observed at the Beehive (site 5) during the last week of this period coincided with some activity in the car park associated with the removal of some Portakabins.

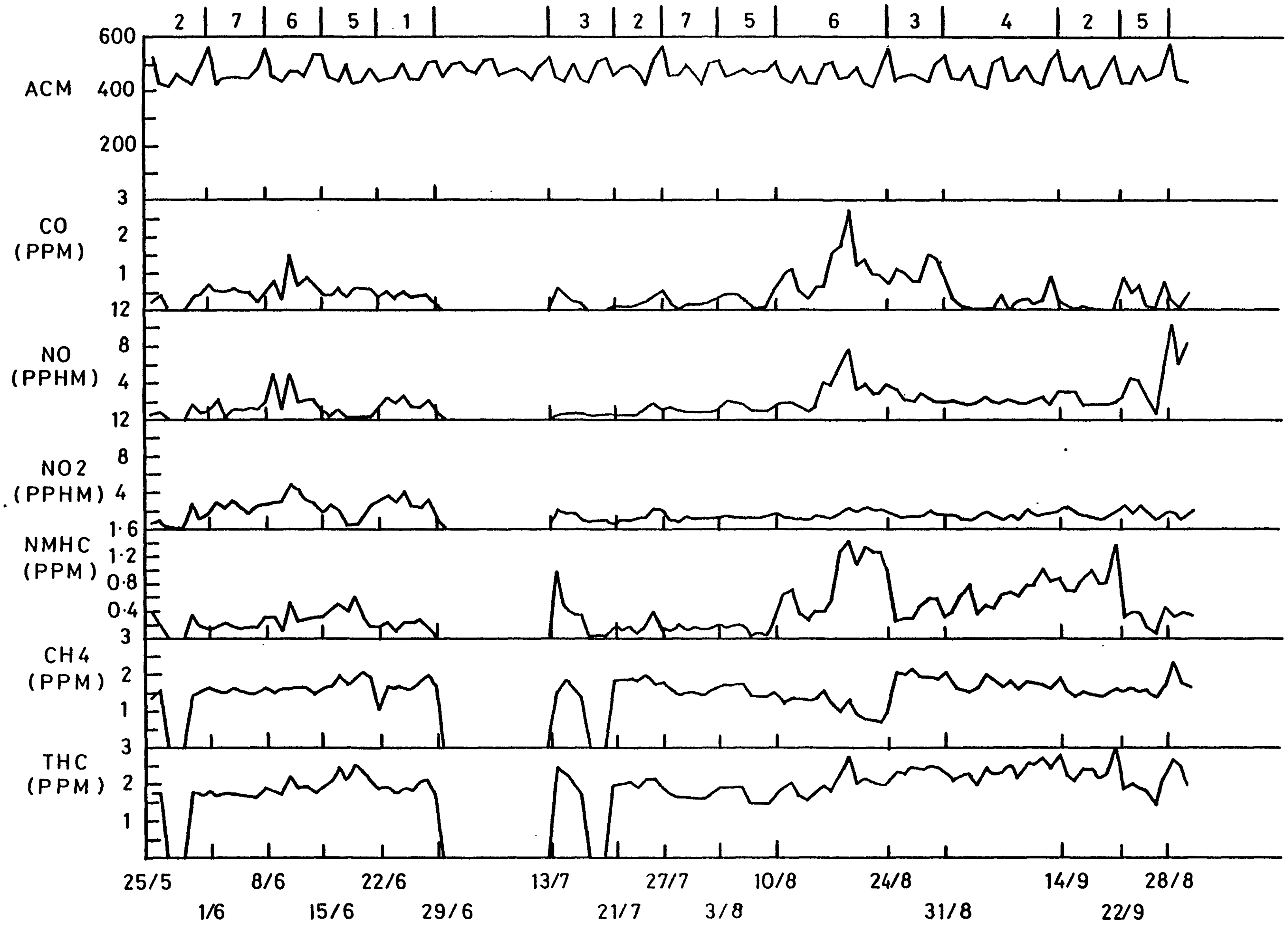


Fig 5·2 Air quality at the six sites vs. daily aircraft movements (ACM)

Figure 5.2 also indicates that there was little or no correlation between total aircraft movements and pollutant concentrations at the six sites.

Table 5.11 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7), m+p-xylene and EDB) at the Gatwick site 2 (Car Park Hotel)

$\mu g\ m^{-3}$

Date	Hour	C_6	C_7	m+p xyelene	EDB	C_7/C_6	C_6/EDB
14/ 9/79	15.00-15.30	14.0	3055	10.0	0.12	218	117
	15.30-16.00	13.2	2830	15.0	0.12	214	110
	16.00.16.30	16.4	2889	29.0	0.14	176	117
	16.30-17.00	16.0	2865	16.0	0.14	179	114
17/ 9/79	14.00-14.30	6.4	117	23.0	0.06	18.3	107
	14.30-15.00	15.0	2920	16.0	0.13	195	115
	15.00-15.30	12.0	2999	16.0	0.11	250	109
7/10/79	13.30-14.00	3.4	6.4	3.2	traces	1.88	-
	14.00-14.30	2.0	4.7	2.6	traces	2.35	-
	14.30-15.00	2.7	5.7	2.8	traces	2.11	-
1/11/79	13.00-13.30	5.4	9.3	5.7	traces	1.72	-
	13.30-14.00	8.1	9.6	4.6	traces	1.18	-
	14.00-14.30	6.8	15.0	3.0	traces	2.21	-
4/11/79	14.30-15.00	5.9	15.7	15.6	traces	2.66	-
	15.00-15.30	11.2	37.6	30.4	traces	3.36	-

C_7/C_6 $\bar{x} = 84.5$ $\sigma_n = 100$

C_6/EDB $\bar{x} = 112.7$ $\sigma_n = 3.7$

5.4.2 Individual Pollutants

Detailed results for the individual pollutants measured (76 analyses) are included in Appendix C (hydrocarbons 1-16, EDB 17, EDC 18).

Table 5.11 includes results for individual compounds measured at site 2 (Gatwick Car Park Hotel).

In this table some exceedingly high values for toluene are shown, compared to those of benzene, xylene and EDB. The high toluene concentrations occurred on 14 and 17 September and did not appear on sampling occasions after these dates. These high toluene concentrations correlated well with the observations of high total hydrocarbons and it is assumed that the uncertain origin of these higher peaks was a source emitting toluene, which was perceptible under certain prevailing winds (north-west).

Statistical analysis of the results in table 5.11 gave a C_7/C_6 ratio $\bar{x} = 84.5$ which according to early results reported here excludes vehicle generated pollution as the cause. On the other hand the C_6/EDB mean ratio was found $\bar{x} = 112.7$ which indicates that benzene and EDB originated from internal combustion engines. The overall levels of individual pollutants were very low, compared to those at an urban site (London), with the exception of the toluene peaks at the times they appeared. These low levels of individual pollutants could easily have been caused by the limited volume of traffic in the car park and on the near-by road. EDC however, was not detected at this site, which may indicate a contribution from the airport, since only EDB is used as an additive in aviation fuel.

Figure 5.3 shows the correlation of EDB and benzene at this site, in a regression analysis, with EDB plotted against the benzene concentrations. A good correlation factor of 0.995 is given, which is significantly higher than has been found in a street air situation.

Table 5.12 includes results for individual compounds measured at site 3 (Charlwood).

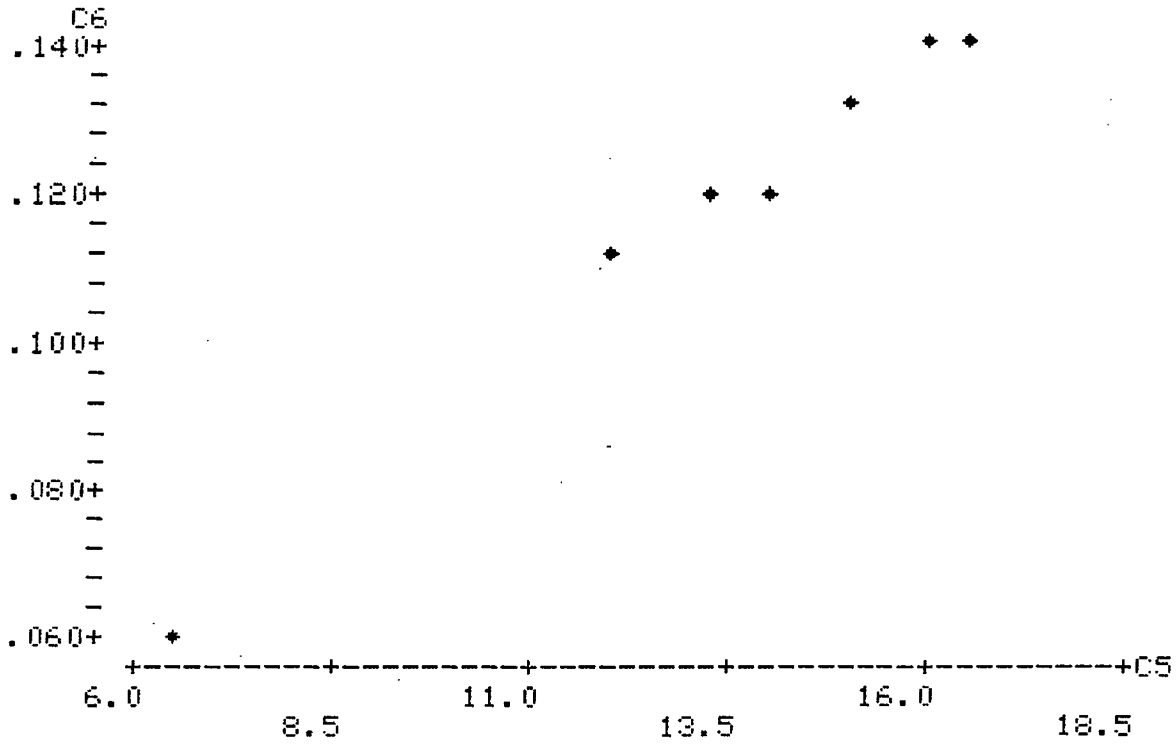


Fig. 5.3 Correlation of EDB and benzene at site 2 (Car Park Hotel)

Correlation factor = 0.995

Regression equation $y = 0.0103 + 0.0080\ x_1$

R-squared = 99.1%

Table 5.12 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7), m+p-xylene and EDB) at the Gatwick site 3 (Charlwood) $\mu g\ m^{-3}$

Date	Hour	C_6	C_7	m+p xylene	EDB	C_7/C_6	C_6/EDB
21/ 8/79	14.30-15.00	9.6	16.0	13.0	0.110	1.67	87
	15.00-15.30	7.5	13.7	9.0	0.074	1.83	101
	15.30-16.00	5.5	10.8	10.0	0.060	1.96	98
7/10/79	11.00-11.30	17.6	37.0	30.5	0.160	2.10	110
	11.30-12.00	3.4	8.5	6.2	traces	2.50	-
	12.00-12.30	6.9	13.4	8.2	0.060	1.94	115
	12.30-13.00	6.3	12.1	11.0	0.050	1.98	122
12/10/79	13.00-13.30	5.8	12.1	10.6	0.050	2.09	116
	13.30-14.00	5.4	12.4	10.1	traces	2.30	-
	14.00-14.30	7.4	14.8	12.0	0.070	2.00	106
	14.30-15.00	6.2	13.8	15.9	0.054	2.23	115

C_7/C_6 $\bar{x}$ = 2.05 σ_n = 0.22

C_6/EDB $\bar{x}$ = 107.8 σ_n = 10.3

Concentrations at site 3 were also found to be very low, in comparison to any urban situation. The results obtained statistically for the C_7/C_6 and C_6/EDB ratios, indicate relatively lower toluene concentrations. Nevertheless, it is evident that the pollutants could have easily originated from internal combustion sources.

The correlation of benzene to toluene and EDB to benzene are shown in fig. 5.4 and 5.5 with factors of 0.980 and 0.918 respectively.

The situation at site 4 (substation) is presented in table 5.13.

High toluene concentrations were recorded at this site as at site 2, which again was in good agreement with higher concentrations of NMHC recorded at this site. Statistical analysis produced a C_7/C_6 mean ratio of 12.94 which indicates that the contribution of the alternative source (except road traffic and aircraft movement) at this site

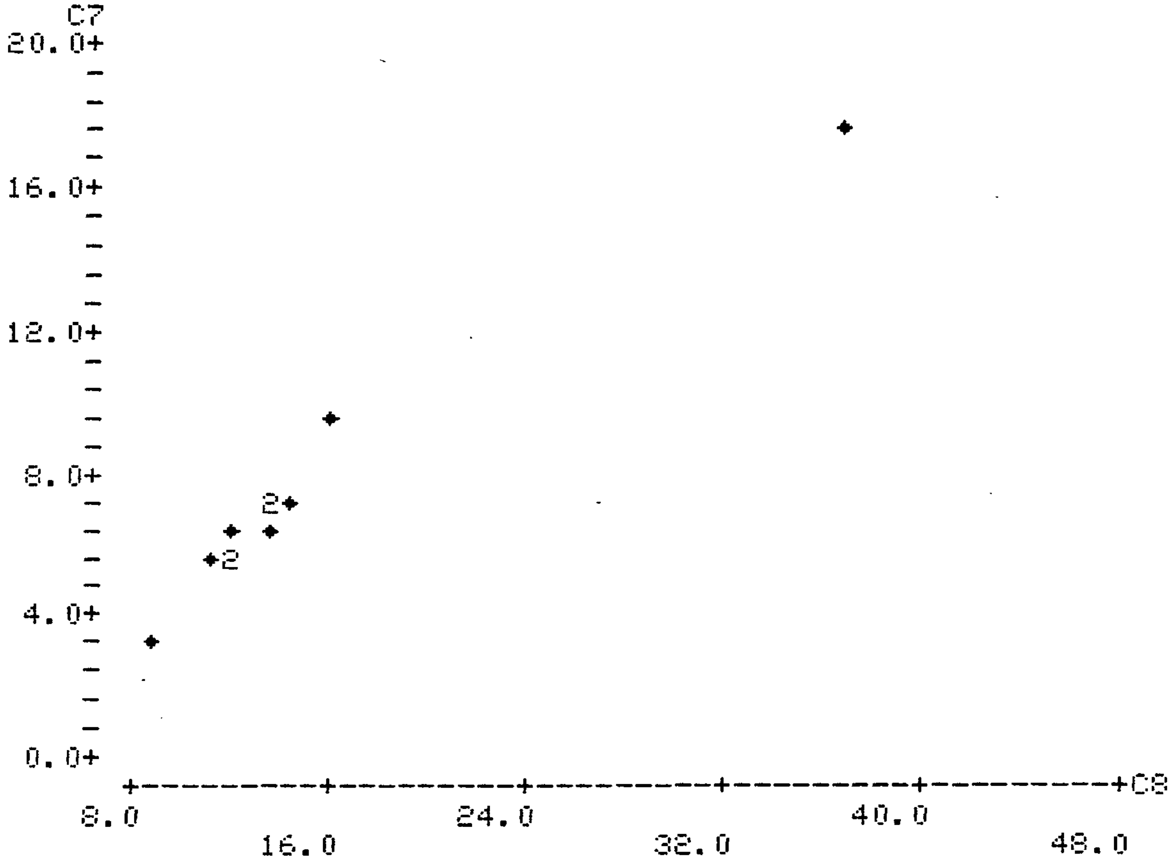


Fig. 5.4 Correlation of benzene and toluene at site 3 (Charlwood)

Correlation factor = 0.980

Regression equation $y = 0.199 + 0.481\ x_1$

R-squared = 96.0%

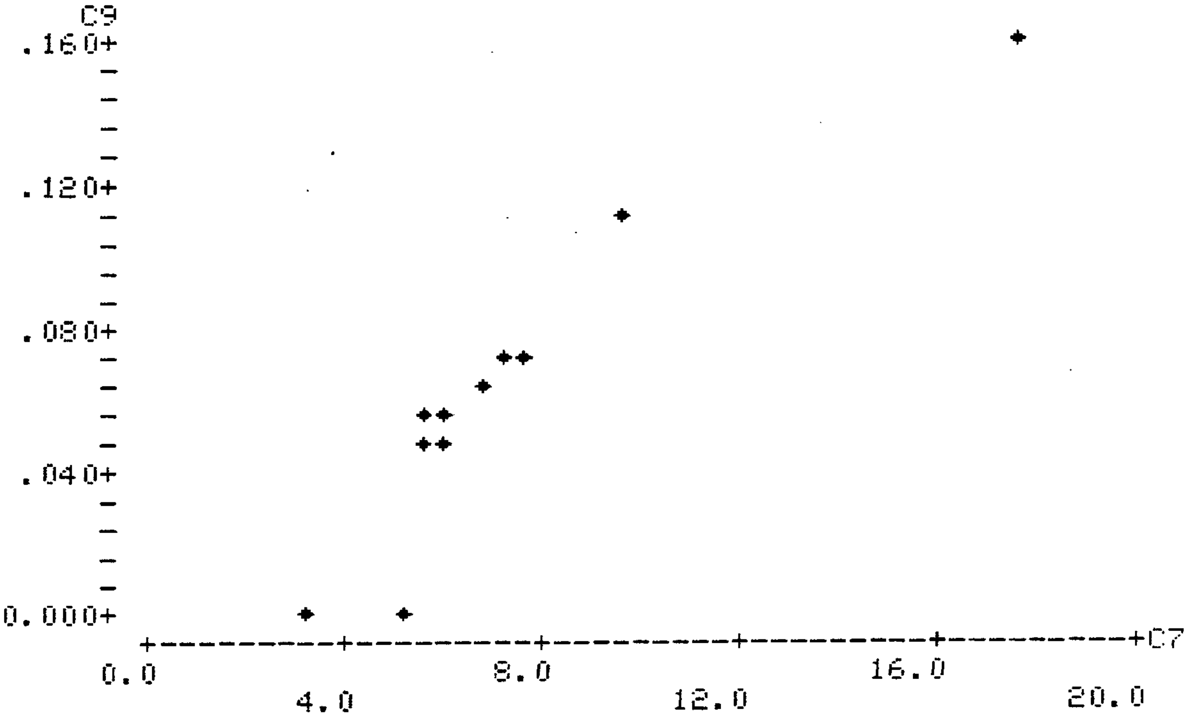


Fig. 5.5 Correlation of EDB and benzene at site 3 (Charlwood)

Correlation factor = 0.918

Regression equation $y = -0.0199 + 0.0111\ x_1$

R-squared = 84.3%

Table 5.13 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7), m+p-xylene and EDB) at the Gatwick site 4 (Substation) $\mu g\ m^{-3}$

Date	Hour	C_6	C_7	m+p xylene	EDB	C_7/C_6	C_6/EDB
3/ 9/79	16.00-16.30	4.0	102	2.7	traces	25.5	-
	16.30-17.00	2.6	92.5	5.0	0.014	35.6	186
	17.00-17.30	2.0	100	5.0	traces	50.0	-
5/ 9/79	16.00-16.30	1.5	11.1	10.4	0.030	7.40	50
	16.30-17.00	2.4	9.1	traces	traces	3.79	-
	17.00-17.30	2.8	7.9	traces	0.027	2.82	104
	17.30-18.00	4.0	10.8	traces	0.040	2.70	100
7/ 9/79	15.30-16.00	1.4	22.0	13.0	0.014	15.71	100
	16.00-16.30	1.3	12.7	2.9	0.011	9.77	118
	16.30-17.00	3.2	18.0	8.4	0.030	5.62	107
	17.00-17.30	2.8	24.0	7.3	0.018	8.57	156
10/ 9/79	15.00-15.30	5.1	22.9	10.0	0.060	4.49	85
	15.30-16.00	8.3	34.6	9.2	0.064	4.17	130
	16.00-16.30	5.9	29.7	15.4	0.090	5.03	66

C_7/C_6 $\bar{x} = 12.94$ $\sigma_n = 13.8$

C_6/EDB $\bar{x} = 109.2$ $\sigma_n = 36.6$

was lower than that at site 2 ($C_7/C_6 = 84.5$). The C_6/EDB mean ratio (109.2) lies very close to those found in areas of dense traffic, which indicates that these two compounds were produced by internal combustion engines (vehicle or aircraft). Since the location of this particular site was close to the end of the runway the origin was probably aircraft.

The correlation of EDB and benzene at this site, given by the regression analysis was 0.756 whereas a factor of only 0.026 was obtained for the correlation of benzene and toluene.

Table 5.14 includes the results obtained at the Beehive (Site 5). Statistical analysis yielded a C_7/C_6 mean ratio of 3.19

Table 5.14 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7), m+p-xylene and EDB) at the Gatwick site 5 (Beehive) $\mu g\ m^{-3}$

Date	Hour	C_6	C_7	m+p xylene	EDB	C_7/C_6	C_6/EDB
24/ 9/79	15.00-15.30	4.3	11.3	5.0	0.020	2.63	215
	15.30-16.00	6.7	17.9	8.5	0.040	2.67	167
	16.00-16.30	7.0	16.9	9.7	0.040	2.41	175
	16.30-17.00	4.6	12.3	7.9	0.040	2.67	115
28/ 9/79	14.00-14.30	4.8	17.2	9.8	0.030	3.58	160
	14.30-15.00	5.1	13.8	7.4	0.050	2.71	102
	15.00-15.30	3.1	18.4	9.4	0.030	5.94	103
	15.30-16.00	7.7	20.2	13.0	0.080	2.62	96
1/10/79	13.30-14.00	9.1	22.7	12.7	0.070	2.49	130
	14.00-14.30	6.7	18.7	10.6	0.067	2.79	100
	14.30-15.00	3.6	14.6	11.5	0.028	4.06	128
	15.00-15.30	4.3	16.2	10.0	0.037	3.76	116

C_7/C_6 $\bar{x}$ = 3.19 σ_n = 0.98

C_6/EDB $\bar{x}$ = 133.9 σ_n = 35.7

which indicates higher concentrations of toluene than those measured in urban location. The C_6/EDB mean ratio (133.9) could be indicative of internal combustion sources with EDB concentrations slightly lower than expected. A poorer correlation factor for EDB and benzene was found by regression analysis (0.803) whereas a factor of 0.685 was obtained for the correlation of benzene and toluene.

Site 6 (AA hut) was subject to the highest motor vehicle traffic of all the sites. Data for this site are presented in table 5.15, which also includes EDC measurements since this was the only site where EDC was detected. This site exhibited typical traffic pollution with similar concentration levels and characteristics to those found in urban locations.

The C_7/C_6 mean ratio (2.48) is very close to that found at the Exhibition Road site (2.45) and the same can be said for the C_6/EDB ratio (109.5 compared to 97.7 in Exhibition Road and 108 in the

Table 5.15 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7) EDB and EDC) at Gatwick site 6 (AA hut)

$\mu g\ m^{-3}$

Date	Hour	C_6	C_7	EDB	EDC	C_7/C_6	C_6/EDB	EDC/EDB
3/10/79	14.00-14.30	26	51	0.22	0.22	1.96	118	1.0
	14.30-15.00	16	34	0.15	-	2.13	107	-
	15.00-15.30	12	37	0.09	-	3.08	133	-
7/10/79	15.30-16.00	15	35	0.13	-	2.33	115	-
	16.00-16.30	19	46	0.17	0.20	2.42	112	1.18
	16.30-17.00	17	42	0.15	-	2.47	113	-
12/10/79	15.00-15.30	19	46	0.18	0.22	2.42	105	1.22
	15.30-16.00	18	45	0.18	0.19	2.50	100	1.06
	16.00-16.30	18	46	0.18	-	2.56	100	-
	16.30-17.00	16	41	0.15	-	2.56	107	-
	17.00-17.30	15	42	0.16	-	2.80	94	-

C_7/C_6 $\bar{x} = 2.48$ $\sigma_n = 0.28$

C_6/EDB $\bar{x} = 109.5$ $\sigma_n = 10.1$

EDC/EDB $\bar{x} = 1.12$ $\sigma_n = 0.09$

traffic tunnel). Correlation of benzene to toluene is shown in fig. 5.6 with a factor of 0.814 and the correlation of EDB and benzene is shown in fig. 5.7 with a correlation factor 0.914.

Results from the last site 7 (Brickworks) are shown in table 5.16. Statistical analysis gave a mean C_7/C_6 ratio of 4.62 which indicates higher toluene concentrations compared to those resulting from a typical site polluted by road traffic. The C_6/EDB mean ratio (121.3) is indicative of internal combustion engine pollution although the flow of vehicles was very limited. This particular site was lying beneath the usual landing path of the aircraft. The correlation derived by a regression analysis gave a factor of 0.317 for benzene to toluene and a factor of 0.801 for EDB to benzene.

So far, from the data obtained in this study at the six sites,

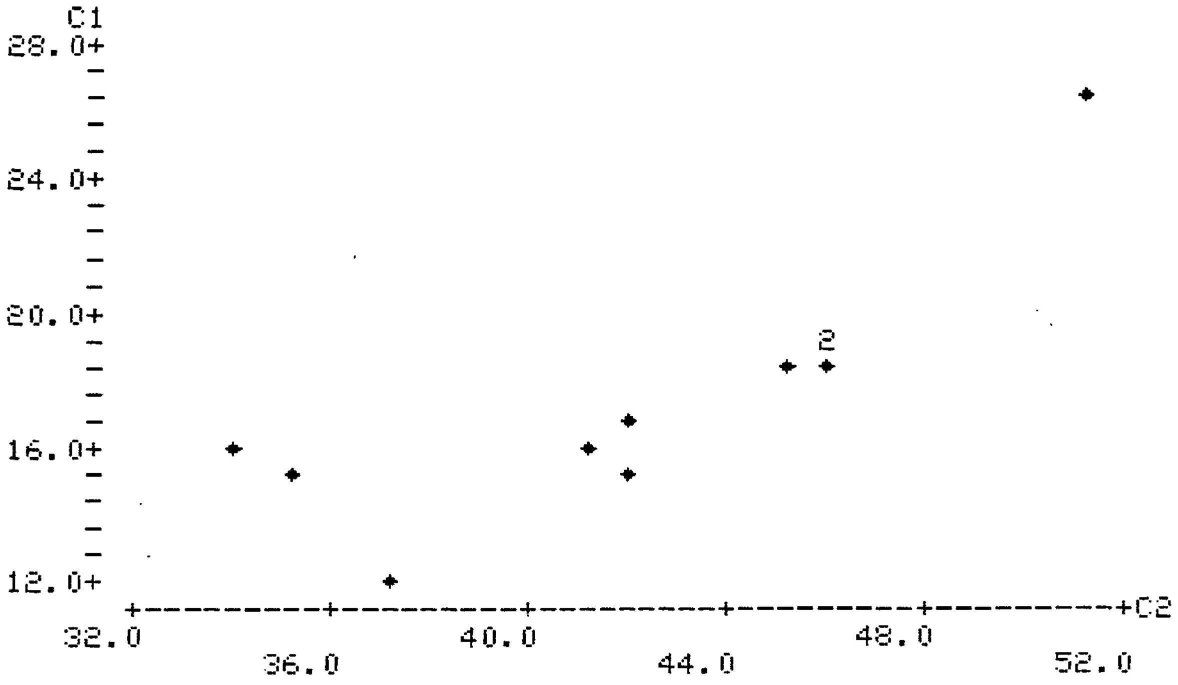


Fig. 5.6 Correlation of benzene and toluene at site 6 (AA hut)

Correlation factor = 0.814

Regression equation $y = -5.73 + 0.546\ x_1$

R-squared = 66.2

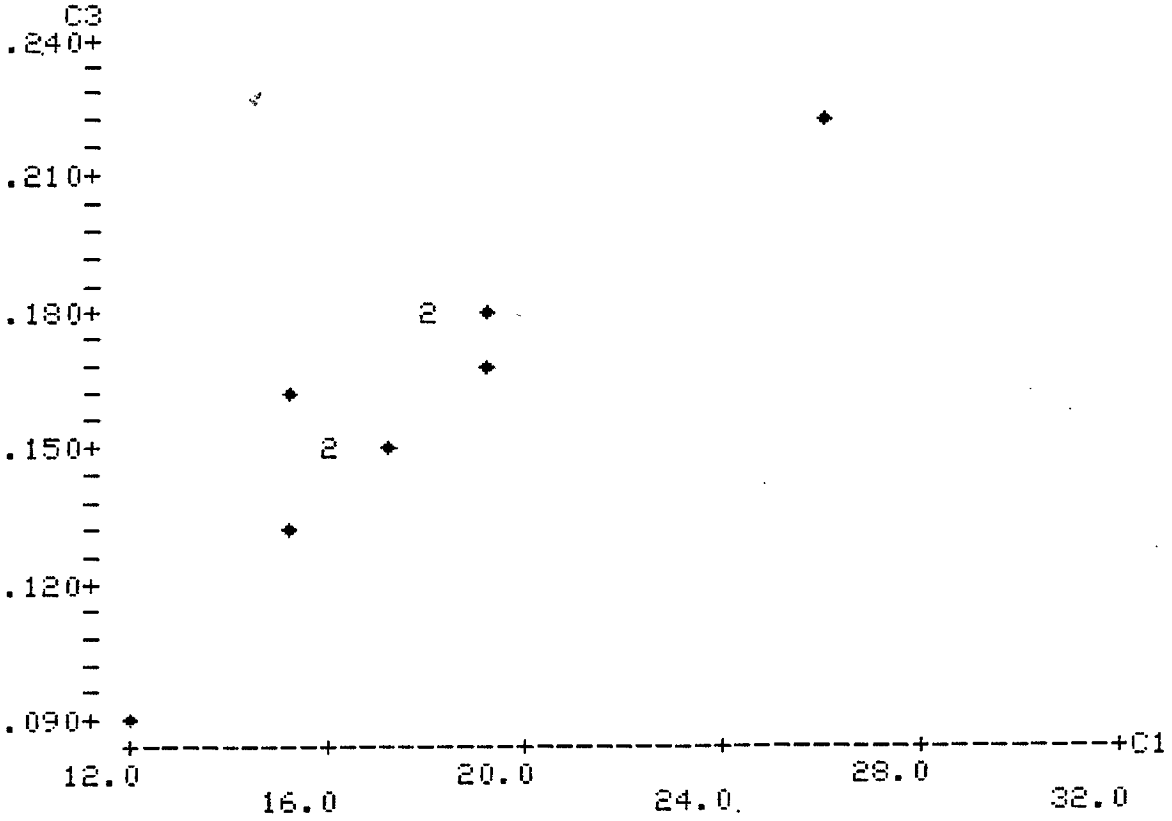


Fig. 5.7 Correlation of EDB and benzene at site 6 (AA hut)

Correlation factor = 0.914

Regression equation $y = 0.0108 + 0.0086 x_1$

R-squared = 83.6%

Table 5.16 : Concentrations of individual pollutants (benzene (C_6), toluene (C_7), m+p-xylene and EDB) at the Gatwick site 7 (Brickworks)

$\mu g\ m^{-3}$

Date	Hour	C_6	C_7	m+p xylene	EDB	C_7/C_6	C_6/EDB
5/10/79	14.00-14.30	9.7	16.3	5.2	0.076	1.68	128
	14.30-15.00	3.1	14.8	6.7	traces	4.77	-
	15.00-15.30	4.4	8.7	4.8	0.028	1.98	157
	15.30-16.00	3.8	8.2	4.3	0.035	2.16	108
9/10/79	11.30-12.00	7.7	12.0	5.9	0.080	1.56	96.3
	12.00-12.30	7.3	48.9	12.6	0.067	6.70	109
	12.30-13.00	6.4	34.5	12.8	0.060	5.39	107
	15.30-16.00	5.1	48.4	9.0	traces	9.49	-
	16.30-17.00	9.2	43.5	11.0	0.080	4.73	115
10/10/79	13.00-13.30	6.0	35.4	12.0	0.050	5.90	120
	13.30-14.00	6.7	39.2	8.3	0.057	5.85	118
	15.30-16.00	6.2	29.0	16.8	0.040	4.68	155
	16.00-16.30	5.9	30.8	11.6	traces	5.22	-

C_7/C_6 $\bar{x} = 4.62$ $\sigma_n = 2.20$

C_6/EDB $\bar{x} = 121.3$ $\sigma_n = 19$

the identification of pollution sources other than vehicle and aircraft was feasible, but it was not possible to differentiate between the relative contribution of vehicle traffic and the aircraft movements.

A further investigation into this aspect involved analyses of the fuels used by the aircraft (aviation fuels) in comparison to the previously studied motor fuels. This was limited, however, by the availability of only two types of aviation fuel at the depot unit of the airport. Clearly, aircraft coming from other airports could be utilizing other types of fuel. The two available types of aviation fuel were:

(i) Shell Jet for aircraft with jet engines. This fuel did not contain any lead, EDB or EDC.

(ii) Shell 100 L AVGAS for aircraft with internal combustion engines, containing 0.25 g l^{-1} TEL and 0.25 g l^{-1}EDB.

Detailed analyses of the two fuel types are included in Appendix C, together with a typical motor fuel analysis. A C_7/C_6 ratio = 6.3 was calculated from the Shell Jet fuel analysis and a C_7/C_6 ratio = 15 from the Shell Avgas.

These higher C_7/C_6 ratios could give an explanation for the higher C_7/C_6 ratios found at sites 5 and 7 (Beehive and Brickworks) which, it may be assumed, were the most affected by aviation generated pollution.

The development of profiles for the hydrocarbons studied has enabled more information about the prevailing situation to be obtained.

Figure 5.8 shows the profiles of the sixteen hydrocarbons (1-16) against their concentrations in the two types of aviation fuels. Figure 5.9 shows the profiles of hydrocarbons from a typical petrol analysis and a typical Exhibition Road sample.

From the sixteen hydrocarbons under study four peaks characterise the profile of a petrol analysis. Two major ones, 2 and 4 (toluene and m+p-xylene respectively), and two minor ones, 8 and 11 (m+p-Ethyl-toluene and 1,2,4 Trimethyl-benzene respecitvely).

The toluene peak is also the one which dominates the profile produced from the Shell 100 L Avgas aviation fuel, with a minor contribution by peak number 4.

Hydrocarbons 2 and 4 (toluene and m+p-xylene) in Shell Jet, represent only a very small proportion of its components, whereas the two major peaks are the 7 and 12 (N-propyl-benzene and 1,2,3 Trimethylbenzene respectively).

In fig.5.9 it is clearly shown that the characteristic peaks of petrol are also obtained from the analysis of an air sample taken from an area of dense traffic (Exhibition Road).

From figs 5.10, 5.11 and 5.12 which include profiles of the hydrocarbons sampled at each site it is evident that hydrocarbons at the six sites during the respective sampling periods were caused by the following:

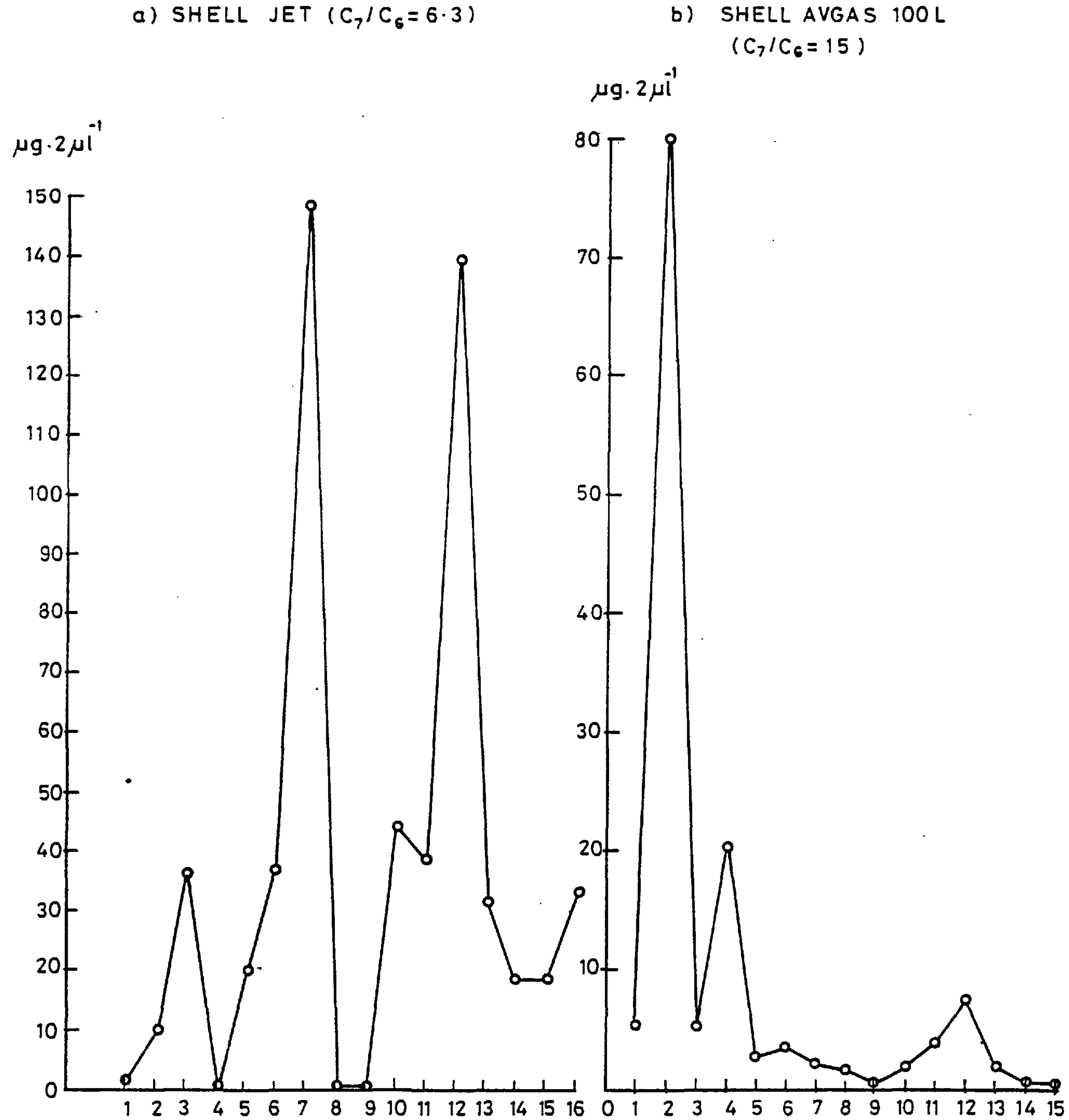


Fig 5·8 Profiles of individual hydrocarbons (1-16) from the analyses of aviation fuels

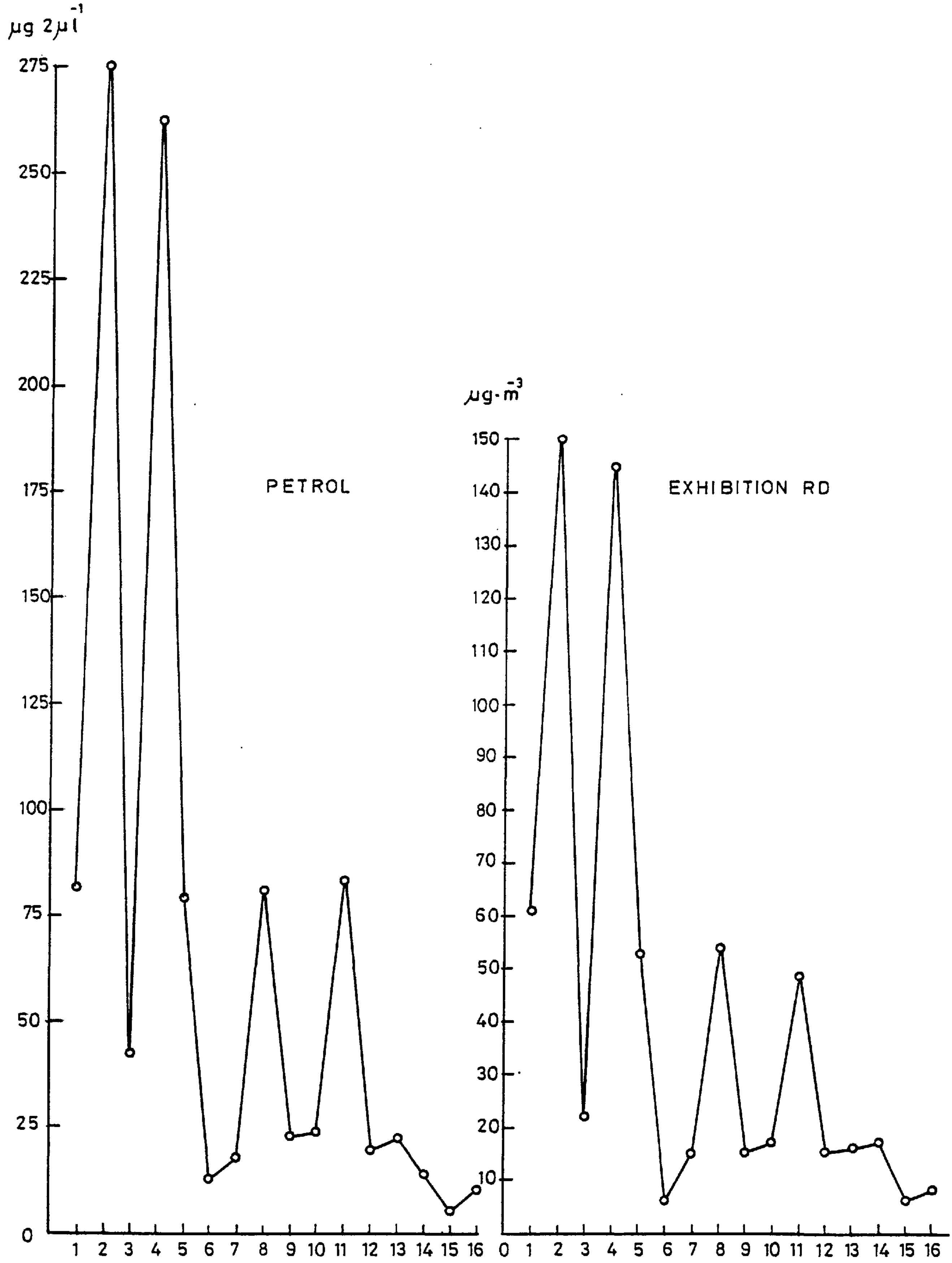


Fig 5·9 Profiles of individual hydrocarbons (1-16) from a petrol analysis and a street air sample analysis

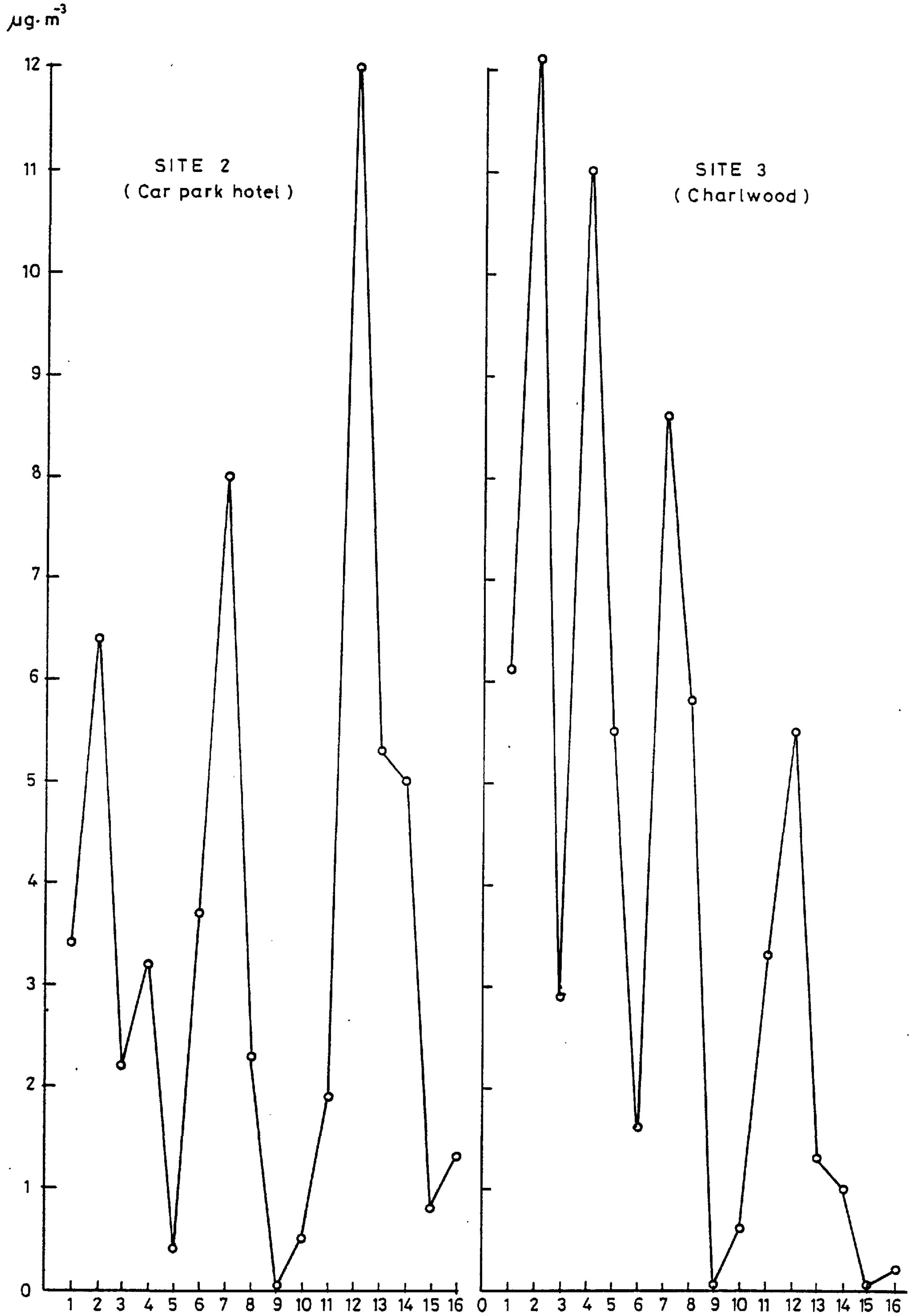


Fig 5·10 Profiles of individual hydrocarbons (1-16) from air sample analyses at Gatwick sites 2 and 3

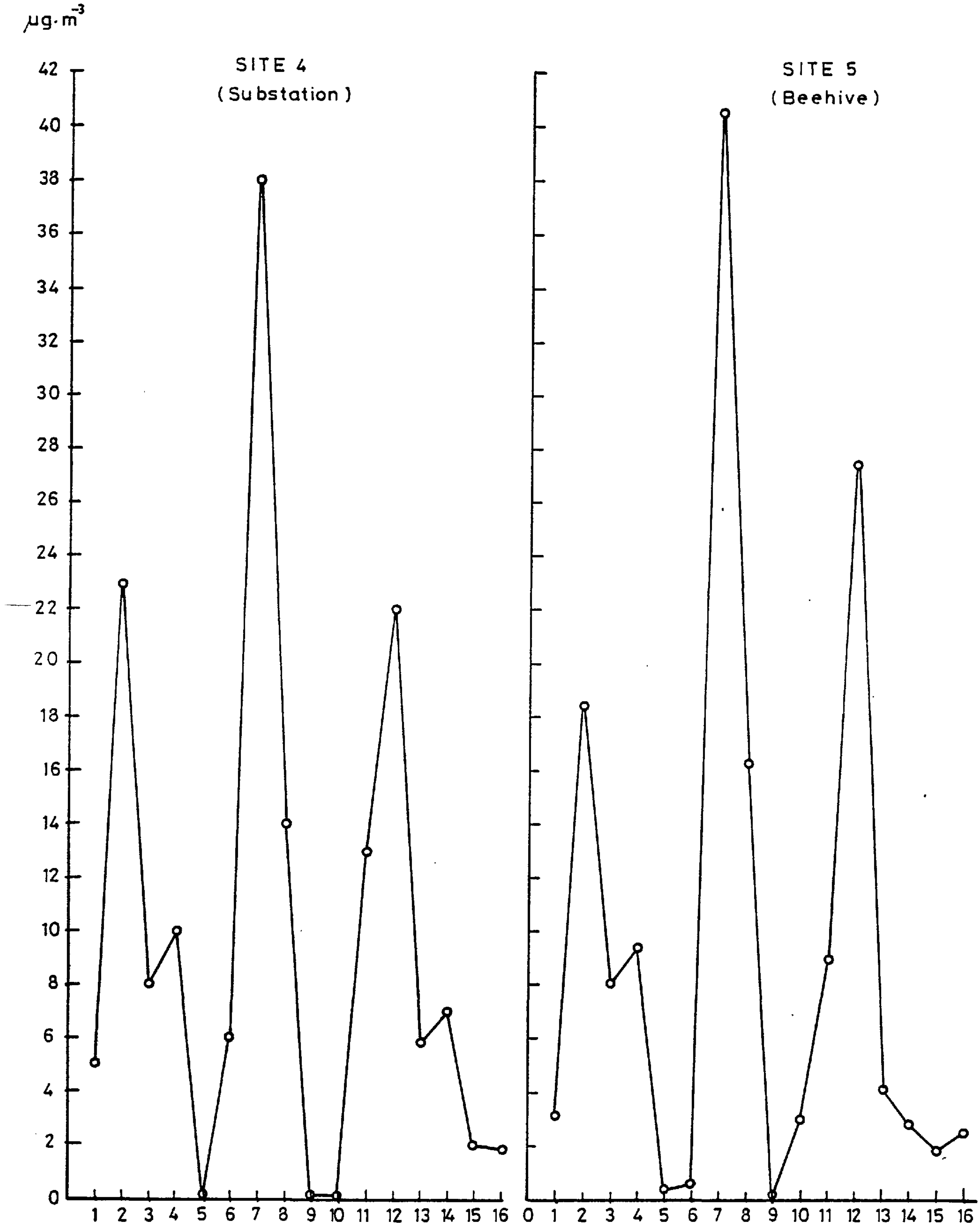


Fig 5·11 Profiles of individual hydrocarbons (1-16) from air sample analyses at Gatwick sites 4 and 5

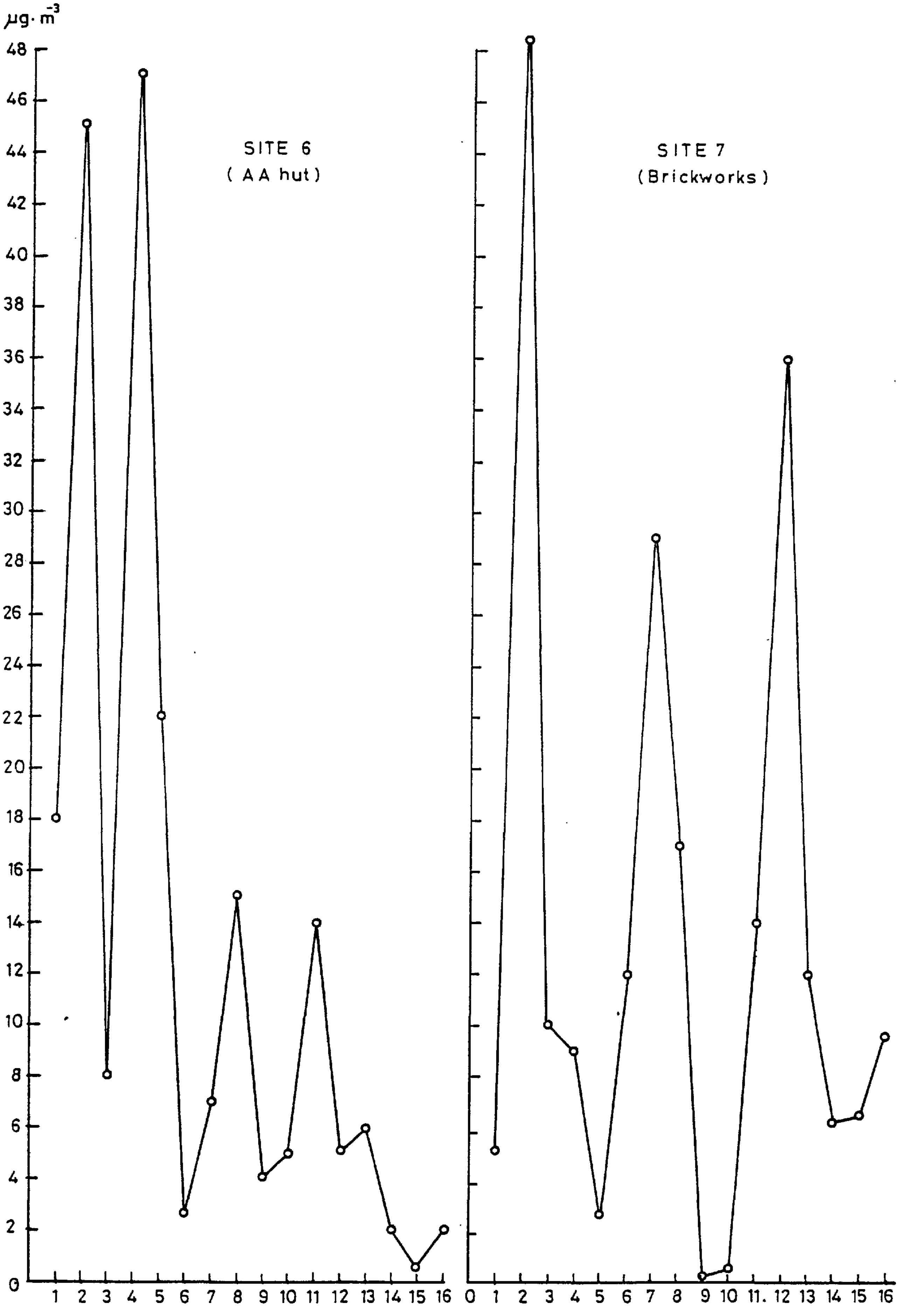


Fig 5·12 Profiles of individual hydrocarbons (1-16) from air sample analyses at Gatwick sites 6 and 7

(a) Predominantly by road traffic at site 6 (AA hut).

(b) Mainly by road traffic with a minor contribution by aircraft movements at site 3 (Charlwood).

(c) Mainly by aircraft movement with a minor contribution by road traffic at sites 2, 4 and 5 (Car Park Hotel, Substation and Beehive).

(d) Predominantly by aircraft movement with only a minor contribution from traffic at site 7 (Brickworks).

These conclusions should not be taken as implying that the six sites were always subject to the pollution source as shown in fig. 5.10, 5.11 and 5.12.

The situation existing at each time must be considered to be the result of the different factors prevailing at that time, such as frequency of aircraft movements, vehicle traffic, prevailing wind and dispersion of pollutants.

However, it is clearly shown that at certain times both aviation and vehicle generated pollution was reaching all of the sites in the vicinity of the airport with the exception of site 6 (AA hut) which was subject to road traffic pollution to such an extent that any contribution from the aircraft movement was insignificant.

5.5 Conclusions

(a) The monitoring study has shown that concentrations of gaseous pollutants measured around Gatwick Airport were on average low in comparison with some other U.K. urban areas and with ambient air quality guidelines adopted in other countries.

(b) Where comparisons may be made, none of the air quality standards or guidelines referring to the health effects of the gaseous pollutants measured in this study, have been exceeded. The U.S. standard for NMHC, promulgated with a view to reducing ozone concentrations, was exceeded at all sites.

(c) Comparison of the results of the monitoring study with data from Central London shows that concentrations of THC, CO, NO and NO_2 were lower at the Gatwick sites than at a kerbside site or background site in London. Exceptions were site 6 (AA hut) subject to high road traffic and site 5 (Beehive), where the upper percentiles of NO were comparable with those of the London background site, but lower than the London kerbside site.

(d) Lead concentrations were such that the U.S. standard was not exceeded, measured concentrations at Gatwick being comparable with those found in typical U.K. urban areas.

(e) During periods of significantly higher than average pollutant concentrations, wind data suggest that both airport and non-airport emissions could (at different times) be the sources of the elevated levels, which were caused primarily under poor dispersion conditions (low wind).

(f) The use of individual hydrocarbons and their ratios in the different types of fuels used by aircraft and vehicle, enabled the partial identification of sources and their relative contribution to this complex air pollution problem.

(g) The contribution of both aircraft movements and vehicle traffic was identified at all sites at certain times.

(h) From the six sites only site 6 (AA hut) was apparently subject to high levels of pollution caused predominantly by road traffic.

(i) A contribution from a toluene source, not involving combustion process, was identified, the influence of which was perceptible at two sites under certain wind conditions (north west to south east).

(j) On the basis of the results obtained during this study, the airport cannot be considered to be a significantly more important contributor to average ground level concentrations of the pollutants studied than other sources.

5.6 References

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APPENDICES A, B, C

Key to Hydrocarbons and Halocarbons for Appendices A, B, C

Number	Compound
1	Benzene
2	Toluene
3	Ethyl-benzene
4	m+p-Xylene
5	o-Xylene
6	Iso-propyl-benzene
7	N-propyl-benzene
8	m+p-Ethyl-toluene
9	1,3,5 Trimethyl-benzene
10	o-Ethyl-toluene
11	1,2,4 Trimethyl-benzene
12	1,2,3 Trimethyl-benzene
13	m-Diethyl-benzene
14	p-Diethyl-benzene
15	o-Diethyl-benzene
16	Dimethyl-ethyl-benzene
17	1,2 Dibromoethane
18	1,2 Dichloroethane

APPENDIX A Measurements of hydrocarbons and halocarbons in Exhibition Road $\mu g\ m^{-3}$

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
25/1/79 08.00- 8.30	32	88	13	88	39	9	12	45	13	19	44	19	19	23	10	-		
09.00-09.30	25	70	9	66	26	5	5	31	10	11	33	11	10	15	5	8		
10.00-10.30	17	59	8	59	23	7	8	33	8	13	32	18	17	19	9	13		
11.00-11.30	19	38	6	39	16	5	7	25	8	11	26	15	16	16	8	13		
12.00-12.30	16	43	6	44	16	6	8	29	10	13	34	16	16	19	10	15		
13.00-13.30	18	33	5	38	14	7	9	28	9	14	31	19	19	20	9	15		
14.00-14.30	28	60	9	49	28	11	13	35	12	18	38	23	21	25	12	19		
26/1/79 08.30-09.00	37	93	15	93	39	13	12	37	19	21	48	27	33	15	12	-		
09.00-09.30	46	101	16	95	50	12	20	42	12	23	55	28	26	17	12	-		
09.30-10.00	37	78	10	65	24	6	6	30	9	14	37	12	24	10	10	17		
10.00-10.30	35	66	8	55	21	3	6	27	6	11	30	12	16	10	6	-		
17.00-17.30	69	175	28	175	77	18	20	65	19	28	78	31	35	32	17	-		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
26/1/79 17.30-18.00	43	113	19	118	52	15	11	58	19	26	69	20	-	-	-	-		
18.00-18.30	38	102	18	102	54	21	23	43	14	25	57	45	28	21	13	-		
18.30-19.00	33	88	16	98	45	14	21	42	15	21	66	32	29	16	10	-		
27/1/79 08.30-09.00	26	82	9	65	21	2	7	26	9	10	23	6	-	-	-	-		
09.00-09.30	29	75	14	83	36	12	12	31	10	15	37	15	17	17	11	-		
09.30-10.00	32	80	15	87	36	10	15	31	11	26	44	13	19	8	8	-		
10.00-10.30	50	127	22	129	52	14	19	59	16	24	59	19	-	-	-	-		
28/1/79 14.45-15.15	43	83	12	79	30	5	4	24	6	6	22	5	6	6	4	3		
14.15-14.45	45	102	12	80	31	3	6	32	9	11	26	7	10	6	9	6		
29/1/79 08.30-09.00	45	113	15	100	40	9	9	37	10	14	32	10	-	-	-	-		
09.00-09.30	57	138	19	122	52	14	19	41	14	20	39	18	29	24	13	-		
09.30-10.00	69	145	19	111	54	16	12	40	13	18	38	25	23	12	10	-		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
29/1/79 10.00-10.30	59	133	15	95	44	15	11	36	10	16	32	33	19	10	10	-		
30/1/79 08.00-08.30	49	143	22	140	62	17	20	53	21	28	47	21	25	26	14	-		
09.00-09.30	74	148	23	142	62	15	18	52	18	26	66	22	35	18	15	17		
09.30-10.00	80	157	23	147	68	17	18	55	16	24	51	26	27	15	13	-		
10.00-10.30	51	122	19	116	57	14	14	44	14	22	42	27	24	11	13	-		
17.00-17.30	58	145	25	148	64	15	18	57	13	26	68	24	29	13	19	7		
17.30-18.00	77	195	31	193	79	16	20	69	20	26	58	23	31	15	13	-		
18.00-18.30	73	224	30	187	68	7	10	58	10	14	45	12	20	10	8	7		
18.30-19.00	73	145	25	145	64	19	20	53	14	29	50	42	30	15	12	-		
31/1/79 08.00-08.30	58	119	17	107	44	11	12	36	11	15	49	19	16	9	13	11		
09.00-09.30	62	151	23	154	53	7	9	51	11	13	42	11	-	-	-	-		
10.00-10.30	43	114	18	115	44	12	14	38	12	18	47	17	19	10	10	12		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
31/1/79 11.00-11.30	36	86	13	82	33	9	11	29	9	12	27	12	20	7	11	10		
12.00-12.30	51	89	15	88	36	10	12	31	9	13	36	13	14	9	8	11		
13.00-13.30	24	56	9	55	19	3	4	17	6	5	17	6	8	3	7	-		
14.00-14.30	66	151	24	143	65	16	16	51	15	22	50	26	-	-	-	-		
15.00-15.30	64	120	17	110	42	7	6	36	8	9	25	5	8	6	12	-		
16.00-16.30	50	128	20	129	58	19	18	51	16	23	64	25	32	13	17	18		
17.00-17.30	56	134	22	136	65	18	18	50	16	23	62	44	27	13	16	23		
18.00-18.30	57	137	23	134	66	18	17	52	12	22	46	28	28	17	15	-		
19.00-19.30	85	196	30	183	77	18	29	59	19	30	73	24	30	20	16	20		
6/3/79 09.00-09.30	46	104	30	124	48	24	41	58	36	46	50	94	39	31	45	27	0.50	1.60
10.00-10.30	26	59	9	57	23	8	13	23	8	18	28	16	23	9	12	14	0.23	0.67
12/3/79 09.30-10.00	38	82	11	82	28	4	5	29	7	7	23	4	8	6	7	7	0.46	0.88

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
12/3/79 12.00-12.30	25	54	7	51	18	2	3	16	5	5	15	3	1.7	0.2	0.5	3	0.24	0.68
15.30-16.00	28	57	8	50	17	2	3	17	5	5	15	3	4	3	3	6	0.33	0.50
16.30-17.00	38	88	12	79	23	3	5	25	7	6	19	5	7	5	3	6	0.24	0.55
13/3/79 09.00-09.30	61	150	22	145	53	6	15	54	15	17	48	15	16	17	6	8	0.63	1.56
09.30-10.00	45	107	16	103	38	7	7	38	10	10	31	7	9	11	6	11	0.43	0.61
10.00-10.30	56	129	21	122	43	6	11	44	11	11	35	7	13	10	2	5	0.47	0.94
16.30-17.00	54	122	20	121	40	4	8	39	9	9	34	12	9	9	4	4	0.51	1.44
17.00-17.30	45	127	19	120	41	6	9	42	10	11	34	6	9	9	4	4	0.56	1.35
17.30-18.00	38	103	17	109	36	5	8	37	9	9	30	7	11	9	4	6	0.55	1.08
15/3/79 08.45-09.15	43	97	13	92	30	3	5	30	8	8	38	4	5	4	4	6	0.41	2.14
09.15-09.45	43	89	12	84	31	5	4	27	6	8	27	5	5	5	4	3	0.44	1.27
09.45-10.15	35	76	10	68	21	2	4	24	6	7	34	6	4	4	3	3	0.34	0.96

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
15/3/79 16.30-17.00	27	59	8	64	18	2	3	19	4	6	17	3	2	4	3	4	0.26	0.69
17.00-17.30	49	114	17	104	38	5	7	32	9	11	33	5	7	6	4	3	0.45	1.23
17.30-18.00	44	97	15	91	34	6	9	32	9	12	35	11	11	10	5	7	0.34	1.96
16/3/79 09.15-09.45	58	129	17	117	41	5	9	40	10	12	35	9	10	11	3	6	0.60	2.02
09.45-10.15	40	98	13	86	28	2	6	31	8	10	26	7	9	8	4	5	0.45	1.57
22/5/79 16.30-17.00	33	80	14	78	29	5	7	34	8	12	31	9	14	11	7	6	0.29	-
17.00-17.30	59	137	21	127	48	13	10	48	12	17	58	17	17	9	14	13	0.63	-
17.30-18.00	55	130	20	117	44	7	7	42	10	15	49	23	14	8	13	9	0.60	-
23/5/79 09.00-09	15	47	9	46	22	6	6	32	9	14	34	15	15	12	8	11	0.15	-
09.30-10.00	7	19	4	17	6	1	2	6	2	2	5	5	4	4	3	3	0.07	-
24/5/79 08.30-09.00	6	16	2	11	4	1	1	4	1	1	3	2	0.7	1	0.8	0.7	0.10	-
09.00-09.30	52	125	19	110	43	9	10	42	10	15	39	16	14	12	4	4	0.48	-

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
24/5/79 09.30-10.00	48	120	21	105	48	17	19	43	13	20	39	28	31	16	11	15	0.47	-
16.45-17.15	96	258	43	237	96	27	26	79	25	32	78	32	32	33	13	23	1.26	-
17.15-17.45	53	122	18	100	38	4	8	34	8	11	33	11	17	6	5	12	0.53	-
17.45-18.15	61	146	21	118	38	6	7	38	10	15	45	14	17	11	7	8	0.54	-
25/5/79 08.30-09.00	9	25	4	23	8	1	2	8	2	3	10	3	7	4	2	7	0.12	-
09.00-09.30	34	79	13	76	27	4	5	26	6	7	28	5	8	4	3	3	0.30	-
09.30-10.00	24	59	10	54	18	2	3	17	4	4	16	3	4	3	2	2	0.25	-
27/5/79 13.00-13.30	15	26	6	26	10	2	2	12	3	4	8	2	3	3	2	1	0.17	-
13.30-14.00	33	61	10	50	17	2	5	20	5	7	18	5	8	8	5	7	0.31	-
14.00-14.30	18	41	7	32	11	2	2	12	3	4	11	6	5	3	1.5	3	0.19	-
14.30-15.00	36	78	16	72	35	14	11	32	11	17	31	21	17	9	7	13	0.40	-
28/5/79 13.00-13.30	6	14	3	13	5	1	2	5	1.1	1	3	0.4	1.7	2.5	1.7	2	0.12	-

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
28/5/79 13.30-14.00	35	79	12	65	22	2	4	22	5	6	21	7	7	6	2	4	0.39	-
29/5/79 08.45-09.15	31	75	11	61	22	3	5	21	5	6	19	8	7	5	2	3	0.26	-
09.15-09.45	32	73	12	64	23	4	4	23	5	6	20	8	6	5	2	3	0.28	-
09.45-10.15	23	69	10	56	21	5	5	22	6	9	21	16	12	9	4	8	0.19	-
16.15-16.45	39	94	15	68	23	5	7	22	6	6	20	14	8	4	3	3	0.45	1.08
16.45-17.15	51	127	20	114	39	3	8	39	10	12	36	12	11	8	2	4	0.61	1.35
17.15-17.45	20	48	7	41	14	3	3	15	4	6	17	12	7	8	4	4	0.33	0.75
17.45-18.15	36	77	11	66	24	6	8	24	6	9	28	15	11	8	4	7	0.56	0.62
30/5/79 08.15-08.45	27	70	11	65	23	2	5	23	5	7	25	6	11	7	2	6	0.30	0.86
08.45-09.15	34	88	13	77	26	2	5	27	6	7	25	7	12	11	2	11	0.38	0.70
09.15-09.45	32	78	12	67	24	5	4	23	6	6	21	6	5	5	1	2	0.39	0.48
31/5/79 08.30-09.00	41	101	16	91	35	9	9	34	10	15	43	30	13	4	4	8	0.45	1.12

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
31/5/79 09.00-09.30	62	153	24	128	58	21	17	52	16	23	63	36	24	21	11	20	0.63	0.96
09.30-10.00	47	113	18	105	41	12	10	44	11	16	48	24	17	14	7	11	0.44	0.67
21/8/79 09.00-09.30	23	76	10	58	23	6	5	27	6	7	25	9	8	11	6	5	0.24	-
09.30-10.00	25	78	11	60	21	3	3	21	5	6	20	3	6	6	3	3	0.22	-
10.00-10.30	15	52	8	33	15	3	2	12	3	4	11	2	4	4	2	2	0.15	-
17.00-17.30	35	80	14	70	42	9	50	32	8	12	57	20	25	13	11	10	0.43	1.08
17.30-18.00	30	90	16	83	43	5	41	31	6	9	56	9	9	11	6	6	0.23	0.87
18.00-18.30	22	62	13	61	26	4	44	28	6	7	33	4	6	8	4	2	0.23	0.92
23/8/79 09.00-09.30	24	65	15	65	36	16	19	35	14	19	29	10	13	17	13	15	0.20	-
09.30-10.00	18	50	11	54	26	12	13	32	9	17	38	9	12	12	9	5	0.19	-
17.30-18.00	43	97	15	97	39	3	4	29	6	8	30	5	3	3	3	2	0.35	1.10
18.00-18.30	31	70	10	65	22	3	3	22	4	7	46	2	4	7	5	3	0.31	0.92

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
24/8/79 09.00-09.30	19	70	11	56	16	2	3	23	5	7	22	5	8	5	4	3	0.17	-
09.30-10.00	19	64	10	74	18	4	3	17	4	5	17	4	4	10	5	5	-	-
10.00-10.30	18	89	13	49	25	6	4	18	4	6	15	2	6	5	3	3	0.24	-
28/8/79 09.00-09.30	43	95	18	89	35	11	11	49	14	23	46	23	21	16	10	12	0.58	0.90
09.30-10.00	32	79	13	61	20	4	6	23	6	8	23	14	13	7	2	4	0.31	0.69
10.00-10.30	28	68	11	62	31	3	7	20	5	6	20	6	5	4	2	3	0.29	0.62
10.30-11.00	27	72	13	57	22	7	4	18	6	8	16	8	2	2	1	2	0.27	-
16.30-17.00	68	147	23	142	65	8	36	59	9	17	68	12	20	17	6	4	0.69	1.14
17.00-17.30	39	91	15	92	40	10	18	34	6	7	34	10	6	4	2	2	0.42	0.65
17.30-18.00	39	92	15	85	36	7	17	34	5	10	34	10	9	9	3	4	0.37	0.62

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
18/10/79																		
14.30-15.00	20	59	21	60	24	6	4	13	3	4	13	6	5	6	3	3		
15.00-15.30	30	69	13	70	38	5	8	21	6	8	20	7	8	7	4	3		
22/10/79 16.00-16.30	18	46	9	44	25	14	11	35	–	18	23	24	26	25	12	16		
16.30-17.00	21	53	9	35	19	15	11	30	–	21	19	14	19	17	9	10		
17.00-17.30	26	63	15	50	28	16	12	32	–	20	36	25	38	27	19	22		
17.30-18.00	23	58	13	71	33	22	16	39	–	25	43	26	29	24	17	16		
18.00-18.30	25	59	14	67	46	22	15	33	–	27	42	26	33	30	9	14		
23/10/79 08.30-09.00	23	56	11	51	30	11	12	20	11	19	25	18	29	23	15	20		
09.00-09.30	23	58	12	55	29	17	11	35	–	20	40	26	34	28	18	23		
09.30-10.00	15	40	11	44	21	16	15	28	–	19	20	18	28	21	13	16		
10.00-10.30	14	29	2	18	8	2	2	10	–	6	8	9	6	7	3	3		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
23/10/79 16.00-16.30	29	68	12	57	34	21	15	42	-	19	33	26	41	33	14	15		
16.30-17.00	38	84	13	81	38	19	16	47	-	19	55	25	45	29	9	14		
17.00-17.30	55	122	15	116	47	14	16	59	-	21	46	22	32	28	18	21		
17.30-18.00	42	95	16	97	47	23	22	49	-	28	52	23	26	29	14	20		
24/10/79 08.30-09.00	21	59	11	58	31	19	15	46	-	22	31	19	40	33	13	18		
09.00-09.30	31	71	16	88	44	25	20	62	-	29	58	31	35	31	16	19		
09.30-10.00	31	76	13	87	37	17	12	53	-	21	50	27	34	25	16	22		
10.00-10.30	51	125	15	105	30	6	8	49	-	15	45	18	20	21	10	17		
16.30-17.00	42	100	29	105	49	33	26	65	-	35	39	32	40	34	17	26		
17.00-17.30	52	123	20	119	57	30	24	37	21	31	42	46	41	37	14	21		
17.30-18.00	45	107	18	105	56	25	25	40	19	29	44	28	38	33	23	29		
25/10/79 09.30-10.00	27	76	9	61	26	10	11	42	-	17	36	30	23	21	12	18		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
25/10/79 10.00–10.30	25	53	6	38	12	2	3	16	–	3	10	3	3	5	3	4		
16.30–17.00	96	209	33	227	104	52	44	125	47	82	116	66	80	93	31	50		
17.00–17.30	102	253	52	265	141	75	65	149	36	104	140	125	87	108	44	80		
17.30–18.00	123	290	59	298	155	80	83	144	70	99	151	108	127	129	41	61		
26/10/79 08.45–09.15	53	125	23	127	74	39	30	74	34	56	72	78	51	65	32	33		
09.15–09.45	39	98	29	98	48	14	25	80	–	47	59	53	35	29	18	25		
09.45–10.15	48	113	32	99	35	23	26	44	21	51	53	73	–	–	–	–		
29/10/79 09.00–09.30	55	133	25	135	67	39	29	56	27	43	67	43	69	58	30	33		
09.30–10.00	31	76	16	84	45	21	21	44	11	24	47	34	40	40	21	23		

General pollutants (Total hydrocarbons, methane, non methane hydrocarbons, carbon monoxide and oxides of nitrogen) measured at Exhibition Road

Hours	THC ppm	Methane ppm	NMHC ppm	CO ppm	NOx pphm
06-07	2.6	2.3	0.3	0.7	15
07-08	3.0	2.3	0.7	1.3	28
08-09	3.3	2.3	1.0	2.0	28
09-10	3.2	2.3	0.9	1.8	25
10-11	3.0	2.3	0.7	1.6	23
11-12	2.6	2.1	0.5	1.0	18
12-13	2.5	2.0	0.5	1.0	15
13-14	2.8	2.1	0.7	1.1	18
14-15	3.5	2.3	1.2	1.7	20
15-16	3.8	2.3	1.5	2.0	25
16-17	4.0	2.4	1.6	2.5	32
17-18	4.0	2.4	1.6	2.4	28
18-19	3.5	2.3	1.2	2.2	18
19-20	3.0	2.3	0.7	2.0	15
20-21	2.8	2.2	0.6	1.4	13
21-22	2.7	2.2	0.5	1.3	12
22-23	3.0	2.4	0.6	1.5	16
23-24	3.2	2.4	0.8	1.7	18
24-01	3.0	2.5	0.5	1.3	14
01-02	2.9	2.5	0.4	0.5	6
02-03	2.8	2.5	0.3	0.4	5
03-04	2.7	2.5	0.2	0.3	3
04-05	2.7	2.5	0.2	0.4	6
05-06	2.7	2.4	0.3	0.5	8

APPENDIX A Measurements of hydrocarbons by the kerb (A), 10 m from the kerb (B) and 20 m from the kerb (C) in Exhibition Road ($\mu g\ m^{-3}$)

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
19/3/79 (A) 09.00-09.30	61	150	22	145	53	6	15	54	15	17	48	15	16	17	6	8		
(B)	38	103	17	109	36	5	8	37	9	9	30	7	11	9	4	6		
(C)	38	82	11	82	28	4	5	29	7	7	23	4	8	6	7	7		
19/3/79 (A) 09.30-10.00	46	96	14	96	35	10	10	32	11	11	31	13	14	14	9	8		
(B)	33	83	11	86	29	6	7	28	8	10	27	10	11	10	6	7		
(C)	29	72	10	70	25	5	6	25	7	9	25	9	11	9	6	6		
28/8/79 (A) 16.30-17.00	68	147	23	142	64	8	19	59	9	17	68	12	19	17	6	4		
(B)	31	64	18	77	31	5	16	24	5	6	22	11	5	5	3	3		
(C)	26	60	11	67	26	3	13	24	4	6	26	20	11	12	4	8		
28/8/79 (A) 17.00-17.30	39	91	15	93	40	10	18	34	6	7	34	10	6	4	2	2.5		
(B)	34	76	13	92	32	6	15	27	5	6	27	15	8	7	5	4		
(C)	27	62	11	64	25	3	11	22	3	5	23	3	2	0.7	2.5	2.2		

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
28/8/79 (A) 17.30-18.00	137	343	54	365	121	26	49	104	31	33	120	40	40	26	6	15		
(B)	92	224	33	212	67	10	22	60	14	16	62	19	7	13	4	4		
(C)	39	92	15	85	36	7	17	34	5	8	34	10	9	9	3	3.5		
29/10/79 (A) 09.00-09.30	55	131	25	135	67	39	29	56	27	43	67	43	69	58	30	33		
(B)	25	62	11	63	32	25	22	31	15	29	35	29	33	28	15	27		
(C)	21	51	7	47	21	16	16	22	10	17	20	20	24	23	14	15		
29/10/79 (A) 09.30-10.00	31	76	16	84	45	21	21	44	11	21	47	34	40	32	21	23		
(B)	22	49	11	47	22	12	13	21	12	14	27	22	31	27	16	17		
(C)	19	42	7	41	20	8	9	22	14	18	24	18	21	22	14	16		

APPENDIX A Measurements of hydrocarbons and halocarbons in the traffic tunnel

μg m^{-3}

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
2/2/79 02.00-02.30	21	61	7	43	15	3	5	14	5	7	20	16	8	9	8	-	0.20	
2/2/79 02.30-03.00	59	138	13	75	27	6	11	24	7	9	29	9	14	13	11	-	0.52	
6/2/79 15.30-15.45	411	1175	169	1047	473	53	66	307	83	86	262	61	-	-	-	-	3.88	-
15.45-16.00	628	1626	225	1530	627	72	94	480	115	136	416	109	169	93	61	82	6.48	-
16.00-16.15	690	1768	273	1700	692	80	110	563	137	163	501	175	181	107	70	-	7.64	-
9/2/79 18.00-18.10	329	1014	158	898	400	72	88	279	64	110	269	86	98	45	58	-	3.79	-
18.10-18.20	478	1169	260	1355	544	90	105	371	100	122	336	126	138	97	94	77	5.02	-
18.20-18.30	491	1247	198	1165	555	92	104	412	104	143	400	351	278	109	104	-	4.68	-
18.35-18.45	298	1040	300	1188	500	112	153	420	126	155	425	183	234	259	100	-	2.52	-
18.45-18.55	292	1025	163	985	431	108	129	364	114	137	368	145	-	-	-	-	2.64	-
20/2/79 15.10-15.20	374	1115	179	1027	442	70	101	387	111	133	364	148	148	74	45	54	3.48	-
15.30-15.40	287	860	150	920	389	94	124	379	105	134	354	162	160	82	69	-	2.48	-

APPENDIX A

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
20/2/79 15.50-16.00	276	652	98	625	228	18	50	273	72	82	280	119	114	62	65	66	3.50	-
16.00-16.10	229	612	99	614	256	49	75	261	80	93	258	158	125	70	67	78	2.80	-
16.20-16.30	323	890	134	805	382	110	148	416	120	271	425	307	258	117	155	-	2.68	-
23/2/79 13.40-13.50	250	630	110	664	291	55	182	257	93	199	242	113	187	107	92	110	2.11	-
14.20-14.30	293	716	118	761	367	65	92	296	82	110	273	127	133	75	64	73	3.15	-
15.00-15.10	366	846	137	870	345	61	75	326	89	125	301	134	142	90	63	76	3.94	-
26/2/79 13.40-13.50	213	510	84	533	215	48	54	209	61	86	207	125	121	74	56	66	1.88	-
14.20-14.30	216	522	85	523	216	44	50	198	58	81	190	109	108	80	63	74	1.98	-
15.00-15.10	265	618	107	655	272	60	63	244	104	93	222	106	168	94	74	79	2.93	-
27/2/79 17.20-17.30	530	1141	169	1082	420	82	106	419	120	127	329	113	180	95	72	114	3.21	-
17.50-18.00	677	1385	208	1315	511	61	86	441	119	162	428	132	148	78	64	68	5.18	-
18.20-18.30	972	2136	325	2040	773	84	131	679	163	194	584	187	215	142	117	106	8.21	-
18.50-19.00	555	1194	203	1395	523	69	110	557	139	166	541	189	212	116	85	127	4.22	-

APPENDIX A Measurements of hydrocarbons and halocarbons in Airedale Valley
$\mu g\ m^{-3}$

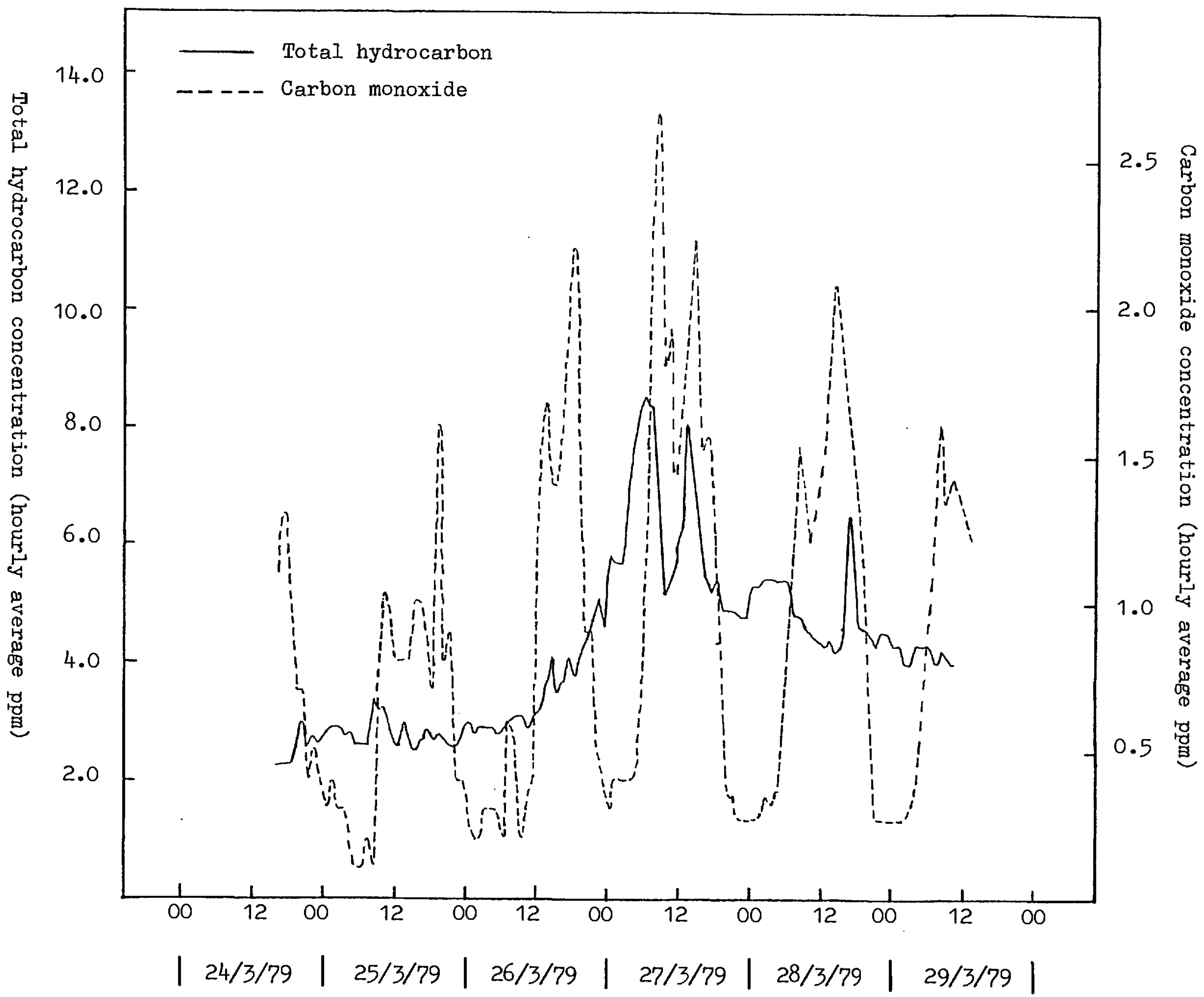
Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Shipley																		
6/4/79 08.30-09.00	16	51	11	53	26	6	5	20	7	13	35	21	14	3	4	7	-	-
09.00-09.30	19	56	10	56	18	2	4	23	8	15	33	13	19	9	7	10	-	-
16.30-17.00	16	44	8	44	17	1	3	18	5	5	15	11	5	3	3	-	-	-
17.00-17.30	15	42	7	40	15	4	4	17	4	6	19	15	8	4	6	5	0.12	-
7/4/79 11.00-11.30	40	116	21	116	47	5	9	49	12	15	45	22	24	15	10	16	0.37	-
11.30-12.00	27	84	14	85	34	6	11	37	10	13	33	26	17	12	8	12	0.30	-
16.00-16.30	22	50	9	50	18	4	7	24	6	11	24	18	18	10	6	9	0.20	-
16.30-17.00	13	39	7	38	15	3	3	16	4	3	11	2	3	1.8	1	1	0.15	-
8/4/79 10.00-10.30	15	40	7	38	13	2	3	13	4	4	12	9	5	3	2	5	0.23	
9/4/79 09.30-10.00	15	45	10	55	20	3	4	20	5	8	19	8	5	3	2	3	0.13	
10/4/79 09.30-10.00	37	116	21	109	41	6	8	42	9	11	34	11	15	8	6	6	0.48	

APPENDIX A

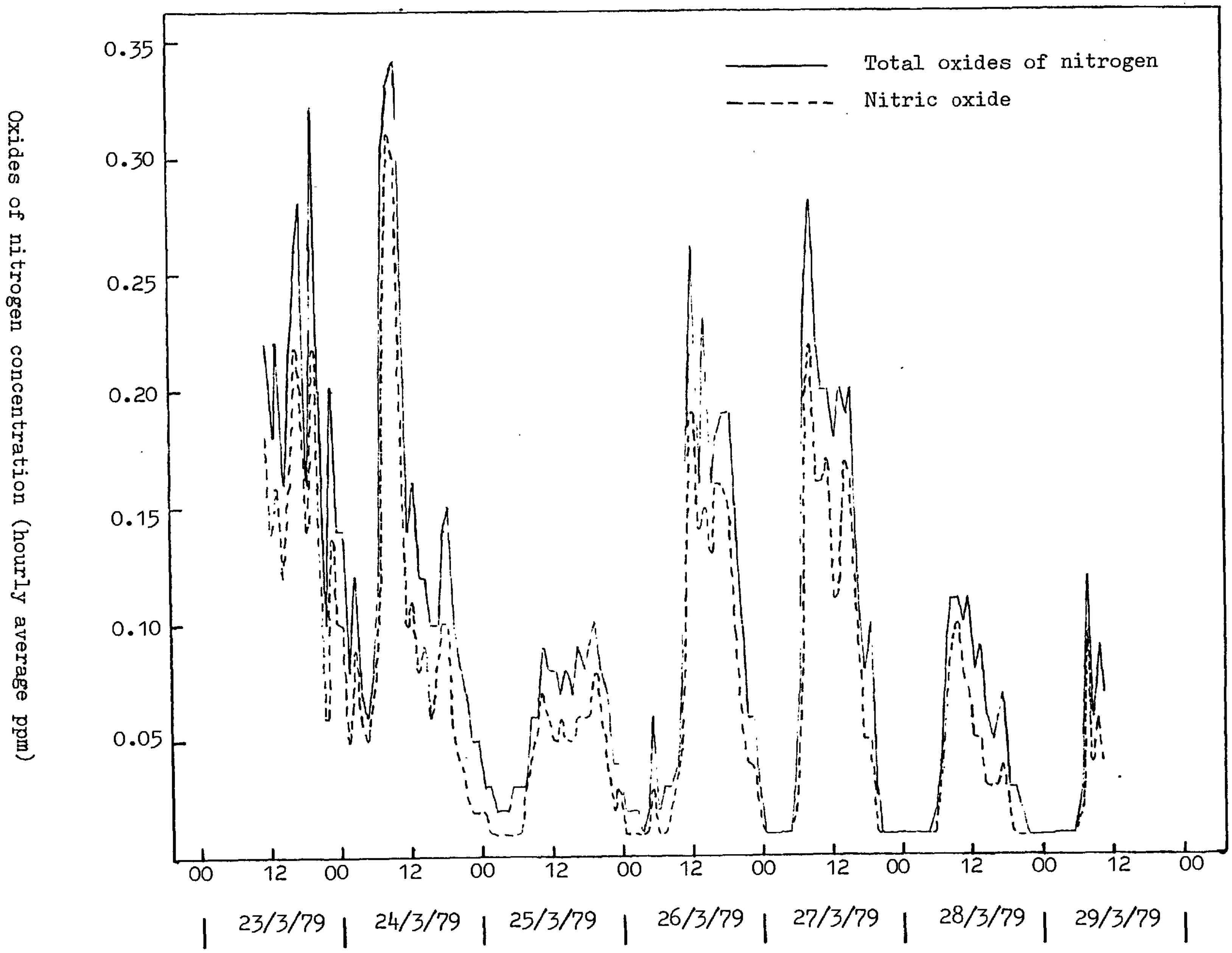
Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Keighley																		
9/4/79 08.00-08.30	16	44	7	38	15	3	7	16	3	5	11	9	6	8	2	3	0.15	-
10/4/79 08.00-08.30	42	110	18	99	43	7	10	44	9	16	36	22	16	8	11	11	0.42	-
Bingley																		
9/4/79 09.00-09.30	24	62	10	60	23	5	4	24	5	5	18	9	10	14	7	7	0.30	-
10/4/79 09.00-09.30	50	117	23	112	49	11	13	48	14	23	42	27	21	10	15	17	0.59	-
Shipley SW hill																		
6/4/79 18.00-18.30	74	390	15	72	31	14	15	40	12	17	36	22	32	2.2	14	20	-	-
Windermere lake																		
9/4/79 16.00-16.30	5	13	2	12	4	0.5	1.3	5	1.2	1	5	3	1	1.8	1	1	0.1	-
Remote field																		
9/4/79 17.30-18.00	2	5	0.9	4	1	0.7	0.4	1.9	0.4	0.5	2	1.1	1.5	1.2	1.2	1.4	0.009	

Table 1 : Summary of pollutant data for site 1 (Keighley) in Airedale Valley

Date Pollutant	23/3 FRI	24/3 SAT	25/3 SUN	26/3 MON	27/3 TUE	28/3 WED	29/3 THUR	Period Mean
(ppm) CARBON MONOXIDE								
Av.conc.07.00-19.00		1.2	0.7	1.1	2.1	1.6	1.3	1.3
Av.conc. 24 hours		0.8	0.6	0.8	0.9	0.9		0.9
Max.hourly mean		1.3 (17.00-18.00)	1.6 (19.00-20.00)	2.2 (18.00-19.00)	2.6 (09.00-10.00)	2.2 (16.00-17.00)	1.7 (08.00-09.00)	1.9
Max.peak value		2.3 (18.25)	2.8 (14.20)	9.6 (18.55)	7.6 (09.04)	5.3 (16.43)	2.9 (07.36)	5.1
(ppm) TOTAL HYDROCARBONS								
Av.conc.07.00-19.00		2.3	2.8	3.2	6.3	4.9	4.2	3.9
Av.conc. 24 hours		2.2	2.8	3.6	5.9	4.8		3.5
Max.hourly mean		2.9 (18.00-19.00)	3.4 (08.00-09.00)	5.1 (22.00-23.00)	8.5 (06.00-07.00)	6.3 (17.00-18.00)	4.3 (05.00-06.00)	5.1
Max.peak value		3.1 (16.05)	11.9 (19.00)	5.7 (06.50)	9.1 (17.23)	8.2 (17.23)	5.3 (07.40)	7.2
(ppm) OXIDES OF NITROGEN								
Av.conc.07.00-19.00	0.21	0.19	0.07	0.15	0.18	0.08	0.09	0.14
Av.conc. 24 hours	0.20	0.14	0.06	0.10	0.10	0.04		0.11
Max.hourly mean	0.32 (19.00-20.00)	0.34 (09.00-10.00)	0.10 (19.00-20.00)	0.26 (12.00-13.00)	0.28 (08.00-09.00)	0.11 (09.00-10.00)	0.12 (07.00-08.00)	0.22
Max.peak value	1.5 (14.40)	0.76 (07.40)	0.42 (08.15)	1.60 (12.07)	0.86 (08.45)	0.84 (07.30)	0.65 (07.38)	0.95
(ppm) NITRIC OXIDE								
Av.conc.07.00-19.00	0.17	0.14	0.05	0.12	0.14	0.06	0.06	0.11
Av.conc. 24 hours	0.17	0.10	0.04	0.07	0.08	0.03	0.03	0.07
Max.hourly mean	0.22 (19.00-20.00)	0.31 (09.00-10.00)	0.08 (19.00-20.00)	0.19 (12.00-13.00)	0.22 (08.00-09.00)	0.10 (09.00-10.00)	0.10 (07.00-08.00)	0.17
Max.peak value	1.30 (14.35)	0.72 (07.38)	0.41 (08.13)	1.96 (12.08)	0.84 (08.40)	0.86 (08.39)	0.66 (07.33)	0.96
($\mu g\ m^{-3}$) LEAD 24 hours (18.00-18.00)	5.1	1.9	3.2	3.7	1.4	2.0		2.9



CARBON MONOXIDE AND TOTAL HYDROCARBON LEVELS: KEIGHLEY

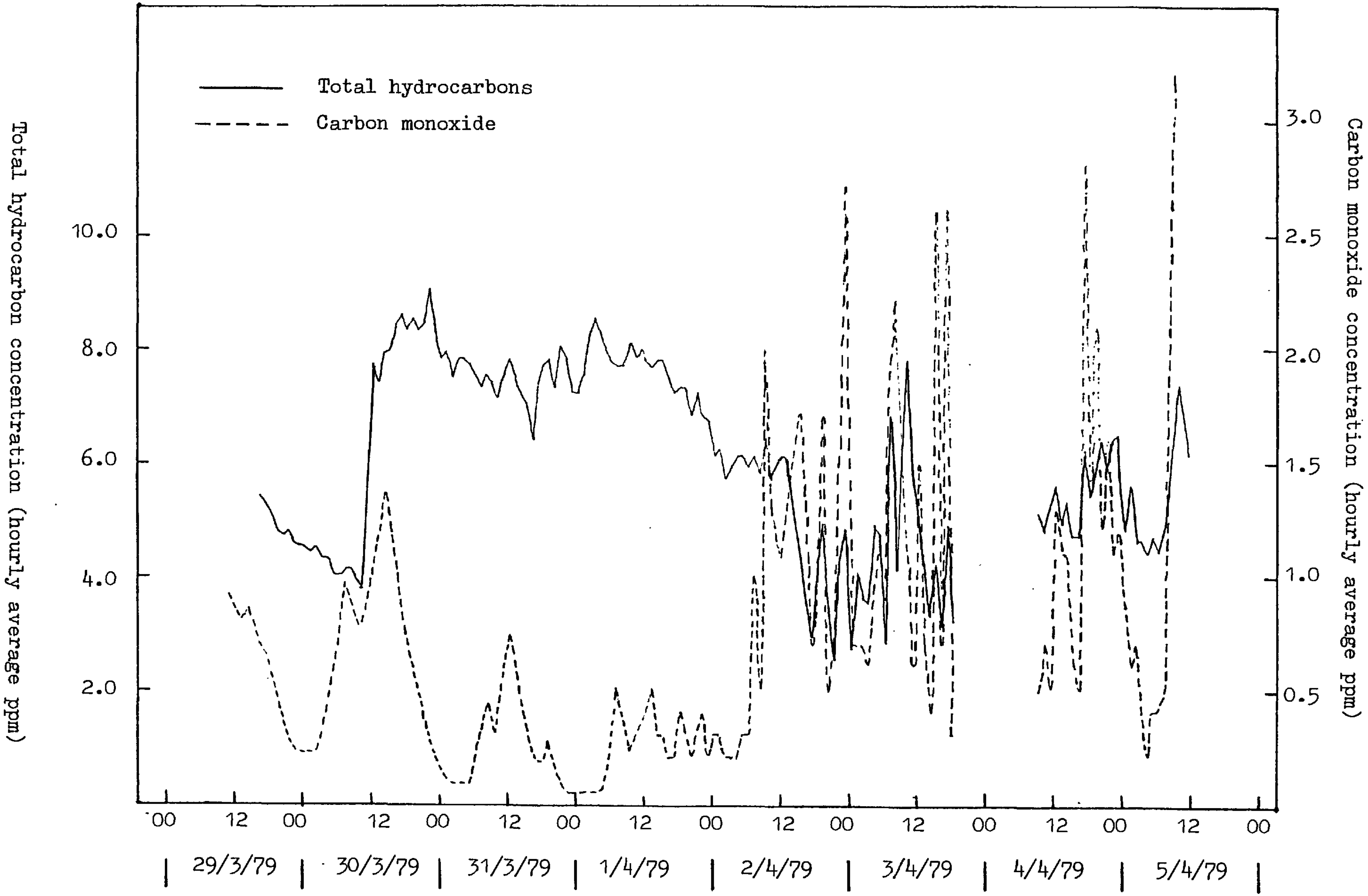


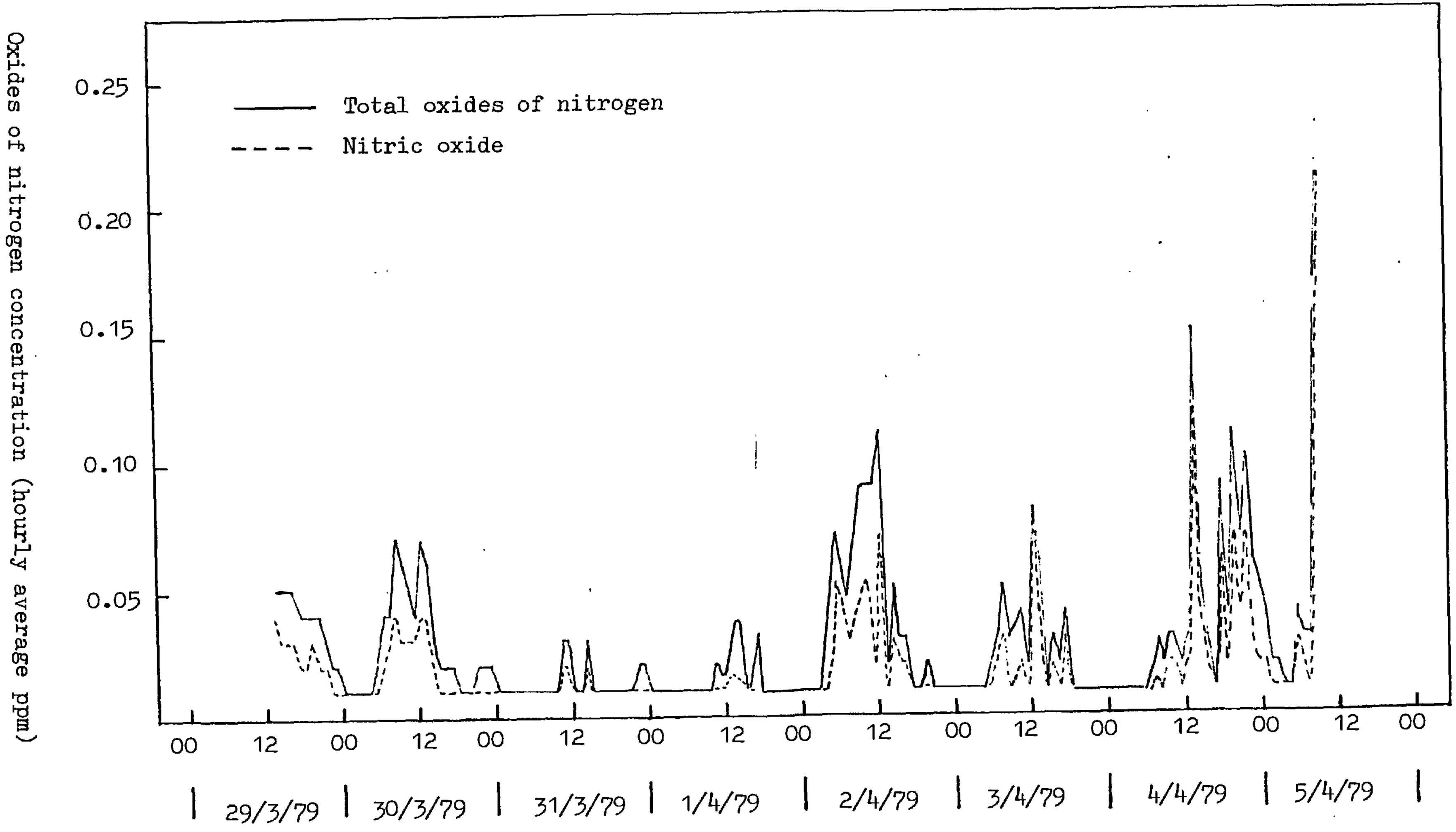
OXIDES OF NITROGEN LEVELS: KEIGHLEY

Table 2 : Summary of pollutant data for site 2 (Bingley) in Airedale Valley

Date	30/3	31/3	1/4	2/4	3/4	4/4	5/4	Period
Pollutant	FRI	SAT	SUN	MON	TUE	WED	THUR	Mean
(ppm) CARBON MONOXIDE								
Av.conc.07.00-19.00	0.7	0.3	0.3	1.4	1.3	1.1	2.1	1.0
Av.conc. 24 hours	0.6	0.2	0.3	1.0	1.1	1.2		0.7
Max.hourly mean	1.4 (17.00-18.00)	0.7 (16.00-15.00)	0.5 (13.00-14.00)	2.7 (12.00-13.00)	2.6 (17.00-18.00)	2.8 (17.00-18.00)	3.2 (09.00-10.00)	2.0
Max.peak value	2.9 (17.52)	4.2 (12.26)	1.7 (18.40)	11.3 (23.50)	20.0 (11.10)	10.0 (18.00)	8.2 (08.50)	8.3
(ppm) TOTAL HYDROCARBONS								
Av.conc.07.00-19.00	7.3	7.3	7.7	5.0	4.7	5.2	5.3	6.1
Av.conc. 24 hours	7.2	7.5	7.6	5.1	4.4	5.5		6.2
Max.hourly mean	9.0 (22.00-23.00)	8.0 (21.00-22.00)	8.5 (03.00-04.00)	6.4 (09.00-10.00)	7.8 (10.00-11.00)	6.5 (23.00-24.00)	5.7 (08.00-09.00)	7.4
Max.peak value	16.8 (22.50)	12.0 (22.20)	10.6 (03.50)	14.5 (12.35)	12.7 (11.00)	9.5 (23.50)	8.8 (08.45)	12.1
(ppm) OXIDES OF NITROGEN								
Av.conc.07.00-19.00	0.04	0.02	0.01	0.05	0.04	0.05	0.14	0.05
Av.conc. 24 hours	0.03	0.01	0.01	0.04	0.03	0.06		0.03
Max.hourly mean	0.07 (08.00-09.00)	0.03 (10.00-11.00)	0.02 (10.00-11.00)	0.11 (12.00-13.00)	0.08 (12.00-13.00)	0.15 (13.00-14.00)	0.25 (09.00-10.00)	0.12
Max.peak value	0.56 (22.55)	0.24 (11.45)	0.17 (10.25)	0.80 (11.57)	0.32 (13.05)	0.08 (12.40)	0.88 (08.45)	0.54)
(ppm) NITRIC OXIDE								
Av.conc.07.00-19.00	0.03	0.01	0.01	0.03	0.02	0.03	0.12	0.04
Av.conc. 24 hours	0.02	0.01	0.01	0.02	0.02	0.04		0.02
Max.hourly mean	0.04 (08.00-09.00)	0.02 (11.00-12.00)	0.02 (10.00-11.00)	0.07 (12.00-13.00)	0.08 (12.00-13.00)	0.12 (13.00-14.00)	0.21 (09.00-10.00)	0.08
Max.peak value	0.54 (22.50)	0.25 (11.40)	0.14 (10.18)	0.96 (11.53)	0.34 (17.35)	0.96 (12.55)	0.86 (08.40)	0.58
($\mu g\ m^{-3}$) LEAD								
24 hours(18.00-18.00)	2.9	1.2	0.7	1.5	4.0	3.5	4.0	2.5

CARBON MONOXIDE AND TOTAL HYDROCARBON LEVELS: BINGLEY

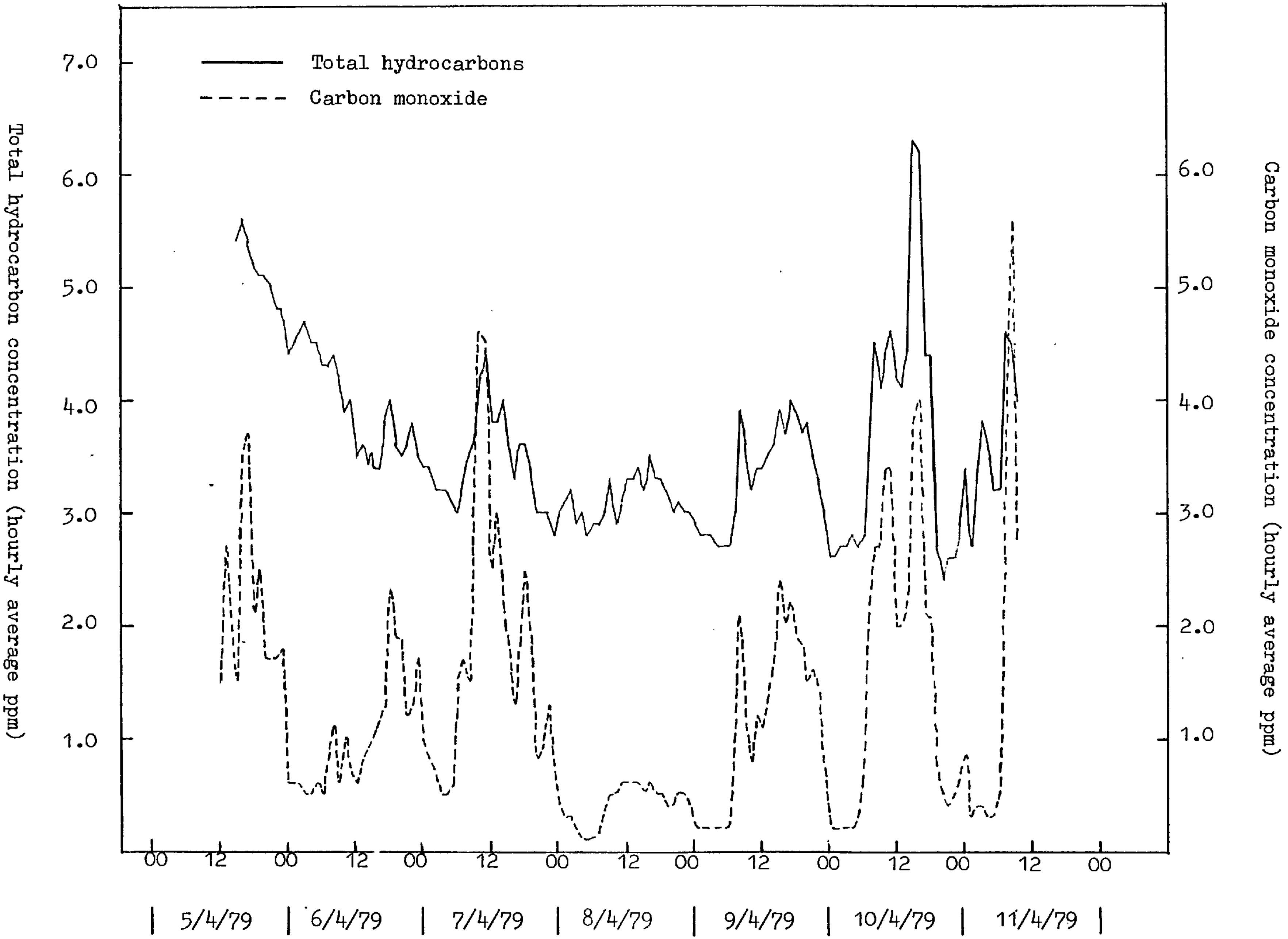




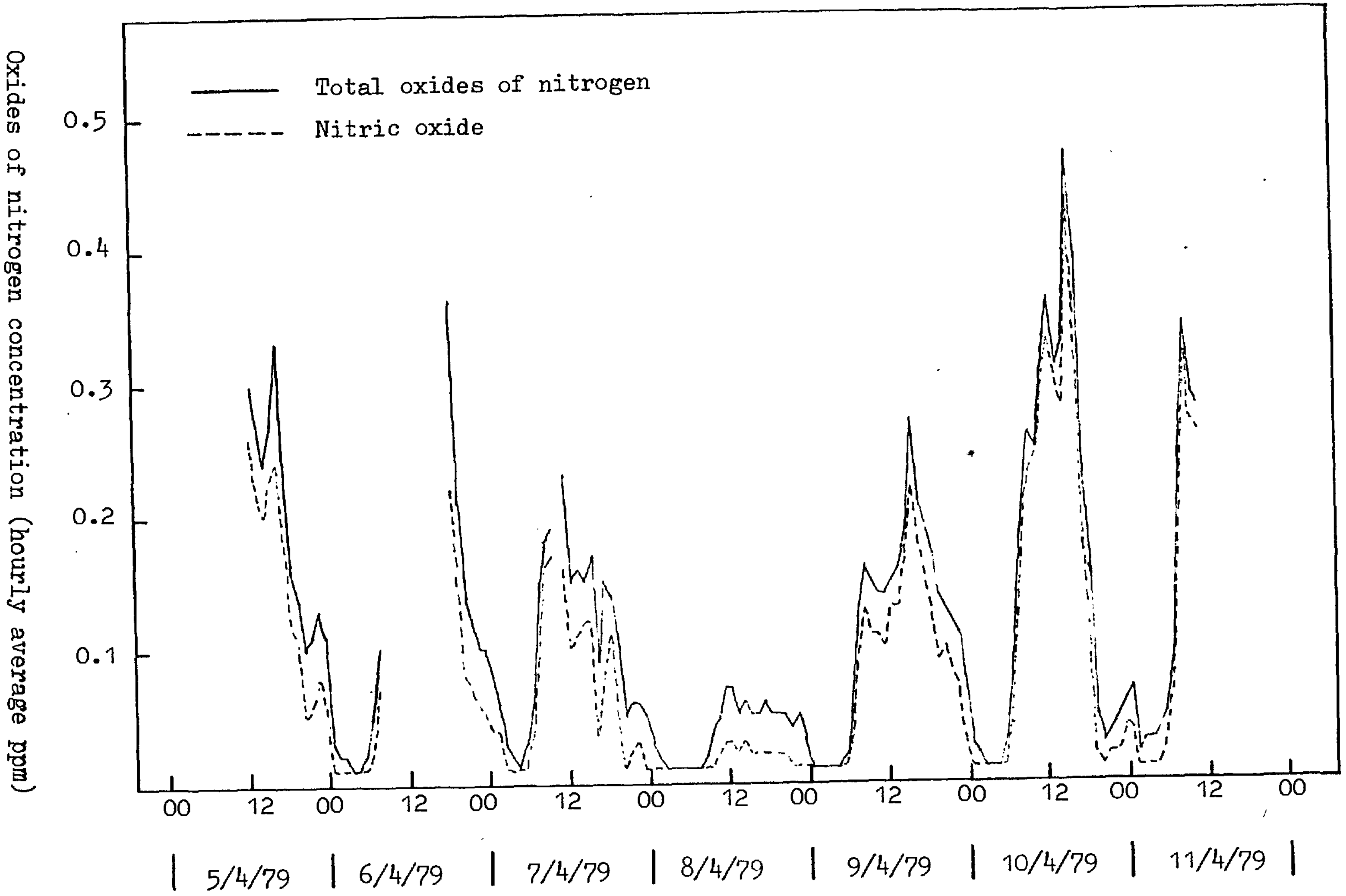
OXIDES OF NITROGEN LEVELS: BINGLEY

Table 3 : Summary of pollutant data for site 3 (Shipley) in Airedale Valley

Date	5/4	6/4	7/4	8/4	9/4	10/4	11/4	Period
Pollutant	THUR	FRI	SAT	SUN	MON	TUE	WED	Mean
(ppm) CARBON MONOXIDE								
Av.conc.07.00-19.00	2.5	1.0	2.6	0.5	1.6	2.7	3.7	2.1
Av.conc. 24 hours		0.9	1.7	0.4	1.1	1.6		1.1
Max.hourly mean	3.7 (17.00-18.00)	2.3 (18.00-19.00)	4.6 (10.00-11.00)	0.6 (11.00-12.00)	2.4 (15.00-16.00)	4.0 (16.00-17.00)	5.6 (08.00-09.00)	3.3
Max.peak value	8.7 (16.55)	8.5 (16.50)	21.0 (11.35)	1.4 (14.05)	7.0 (21.30)	11.0 (10.25)	15.2 (08.15)	10.4
(ppm) TOTAL HYDROCARBONS								
Av.conc.07.00-19.00	5.5	4.0	3.7	3.1	3.6	4.6	4.4	4.1
Av.conc. 24 hours		3.9	3.4	3.2	3.3	3.6		3.5
Max.hourly mean	5.6 (16.00-	4.7 (03.00-	4.4 (11.00-	3.5 (16.00-	4.0 (17.00-	6.3 (15.00-	4.6 (07.00-	4.7
Max.peak value	6.8 (19.55)	6.8 (09.25)	5.5 (11.30)	3.9 (16.15)	5.1 (16.25)	10.0 (16.05)	6.7 (08.20)	6.4
(ppm) OXIDES OF NITROGEN								
Av.conc.07.00-19.00	0.26	0.23	0.16	0.05	0.17	0.29	0.29	0.21
Av.conc. 24 hours		0.08	0.10	0.04	0.11	0.16		0.10
Max.hourly mean	0.33 (16.00-17.00)	0.36 (18.00-19.00)	0.23 (11.00-12.00)	0.07 (11.00-12.00)	0.27 (15.00-16.00)	0.47 (15.00-16.00)	0.34 (08.00-09.00)	0.30
Max.peak value	1.34 (12.07)	0.59 (19.00)	0.76 (09.27)	0.51 (14.18)	0.74 (15.25)	0.95 (17.57)	0.64 (09.15)	0.79
(ppm) NITRIC OXIDE								
Av.conc.07.00-19.00	0.21	0.15	0.10	0.02	0.14	0.27	0.27	0.17
Av.conc. 24 hours		0.06	0.07	0.02	0.09	0.14		0.08
Max.hourly mean	0.26 (12.00-13.00)	0.22 (18.00-19.00)	0.17 (09.00-10.00)	0.03 (11.00-12.00)	0.22 (15.00-16.00)	0.44 (15.00-16.00)	0.34 (08.00-09.00)	0.24
Max.peak value	1.36 (12.04)	0.56 (18.55)	0.84 (09.22)	0.50 (14.14)	0.64 (15.20)	1.04 (17.53)	0.62 (07.10)	0.79
($\mu g\ m^{-3}$) LEAD								
24 hours(18.00-18.00)	2.1	3.1	0.5	2.4	4.4	3.9		2.7



CARBON MONOXIDE AND TOTAL HYDROCARBON LEVELS: SHIPLEY



OXIDES OF NITROGEN LEVELS: SHIPLEY

APPENDIX B Measurements of hydrocarbons and halocarbons in the exhaust emissions of a 3 l engine under different driving tests ($\mu g\ m^{-3}$)

	EEC Cold Start		EEC Hot Start		ECE/CVS	
	bag 1	bag 2	bag 1	bag 2	bag 1	bag 2
1	147402	81279	98107	90332	5592	5442
2	320446	201312	210789	195624	15827	13925
3	18739	14495	11330	10687	1312	960
4	183005	129932	110167	96582	12058	8836
5	74435	54333	32943	24962	3247	2475
6	1875	1336	1607	843	90	172
7	2168	1795	2746	1318	205	222
8	9047	8013	5840	5450	1058	677
9	4500	3988	3207	2783	488	383
10	2963	2587	2644	1908	309	298
11	7655	6888	5446	5083	1024	713
12	2364	2210	2550	2492	280	308
13	2032	1823	3402	2966	196	178
14	2234	1456	3653	3287	164	301
15	713	574	1305	1044	-	-
16	1136	939	769	317	77	184
17	562	292	234	200	25	14
18	3250	1616	1465	1180	132	66

APPENDIX B

	US Federal	Constant Speed				
		Idle	20 mph	30 mph	40 mph	50 mph
1	6063	236575	151678	179650	60000	48454
2	15754	665582	411642	508440	123400	91338
3	1187	51001	26366	35848	9700	7506
4	10822	428658	237336	337682	74100	55603
5	3007	111696	93470	93827	24400	20489
6	131	3936	505	6065	447	403
7	162	6339	3451	7016	993	785
8	827	41631	18152	26434	7342	6268
9	442	16148	9547	13309	2797	2239
10	352	8957	5966	9035	1978	1668
11	808	37458	18998	24640	5916	4931
12	356	5648	5714	2758	2638	2242
13	189	2897	3067	1582	1430	1199
14	204	2778	2218	1225	1594	1408
15	-	-	-	118	-	-
16	83	1422	992	741	679	633
17	48	878	618	669	180	98
18	97	3988	2000	2253	800	339

APPENDIX B Measurements of hydrocarbons and halocarbons in the exhaust emissions of an 850 cc engine under different driving tests (µg m^{-3})

	ECE Cold Start	ECE Hot Start	ECE/CVS		US Federal	
	bag 1	bag 2	bag 1	bag 2	Cold Start	Hot Start
1	185800	107100	5850	4580	7512	7563
2	718100	333300	17837	12250	24475	24519
3	73000	33059	1989	1376	3115	3365
4	666000	274770	16187	10525	23736	24649
5	174500	76465	5094	3128	6693	7416
6	5482	1612	271	110	112	360
7	13796	6675	612	370	702	972
8	50862	33528	2874	1888	4611	5184
9	16988	12017	1036	582	1359	1715
10	13600	8128	839	480	1029	1517
11	39985	32036	3173	2265	4226	5029
12	4008	4078	851	428	655	1338
13	1767	1659	460	291	386	849
14	1216	1415	348	244	286	773
15	766	719	149	126	74	383
16	102	846	214	123	118	649
17	1360	533	26	34	29	22
18	1215	735	38	38	71	65

APPENDIX B

	US Federal		Constant Speed			
	Dilution air	Idle	20 mph	30 mph	40 mph	50 mph
1	74	173200	56271	58628	60179	56938
2	186	396600	129380	143028	160929	139018
3	16	35606	9650	11184	17966	14826
4	81	239930	60981	69742	119431	90925
5	33	68114	17448	20570	39265	29820
6	13	1289	398	366	870	560
7	15	4470	1139	1328	3228	2237
8	25	29044	7229	8323	23232	15006
9	5.5	8717	1905	2168	6348	3972
10	10	6799	1522	2015	4893	3680
11	26	21818	5177	5910	20435	11538
12	24	3816	809	982	4107	1573
13	23	1956	793	2477	2136	1120
14	20	2096	652	866	2007	797
15	9	1012	378	430	1168	899
16	11	-	110	482	1471	746
17	0.3	332	165	155	139	135
18	-	372	365	315	217	189

APPENDIX B Measurements of hydrocarbons and halocarbons in the exhaust emissions of an 850 cc engine, equipped with a lead filter (μg m^{-3})

	EEC Cold Start		ECE Hot Start		ECE/CVS	
	bag 1	bag 2	bag 1	bag 2	bag 1	bag 2
1	248180	108434	81985	91938	5173	6129
2	1000194	391678	280896	325842	17047	21065
3	110660	51191	33830	43335	2056	2716
4	1012619	461937	259850	317015	15322	19738
5	273315	133896	70058	88782	4571	5761
6	5439	3154	2779	2885	120	104
7	17197	10946	6218	10266	415	556
8	76337	58540	37301	58225	2682	3901
9	23027	18490	10878	16296	830	1144
10	16485	13675	8068	14486	617	924
11	90444	53164	31221	47097	2586	3685
12	6635	5939	4684	9688	406	855
13	1524	2902	2292	6380	202	316
14	1679	2049	1608	4376	179	279
15	1279	563	1083	2074	239	218
16	713	889	812	4648	142	442
17	1951	798	422	388	25	25
18	2022	1207	597	578	54	29

APPENDIX B

	US Federal		Constant Speed			
	Hot Start	Idle	20 mph	30 mph	40 mph	50 mph
1	8275	164941	55080	57596	63002	74714
2	29059	406286	160080	172516	178246	189179
3	3771	45319	16281	18501	21414	23409
4	29110	316545	105866	115720	130296	145089
5	8136	97392	31450	36112	46463	51873
6	376	2945	648	772	1849	1950
7	945	7803	2019	2312	4017	3520
8	6107	46591	14438	17214	22364	26475
9	1796	14092	3733	4274	6122	7390
10	1456	11517	3150	3815	6155	7221
11	7093	38131	10746	11394	16521	20441
12	1108	7160	1436	1742	2226	2448
13	709	4463	966	924	1532	1480
14	569	4106	728	493	905	1145
15	353	2124	861	554	1094	1316
16	539	2479	934	637	957	-
17	31	151	143	126	117	83
18	51	297	283	292	215	190

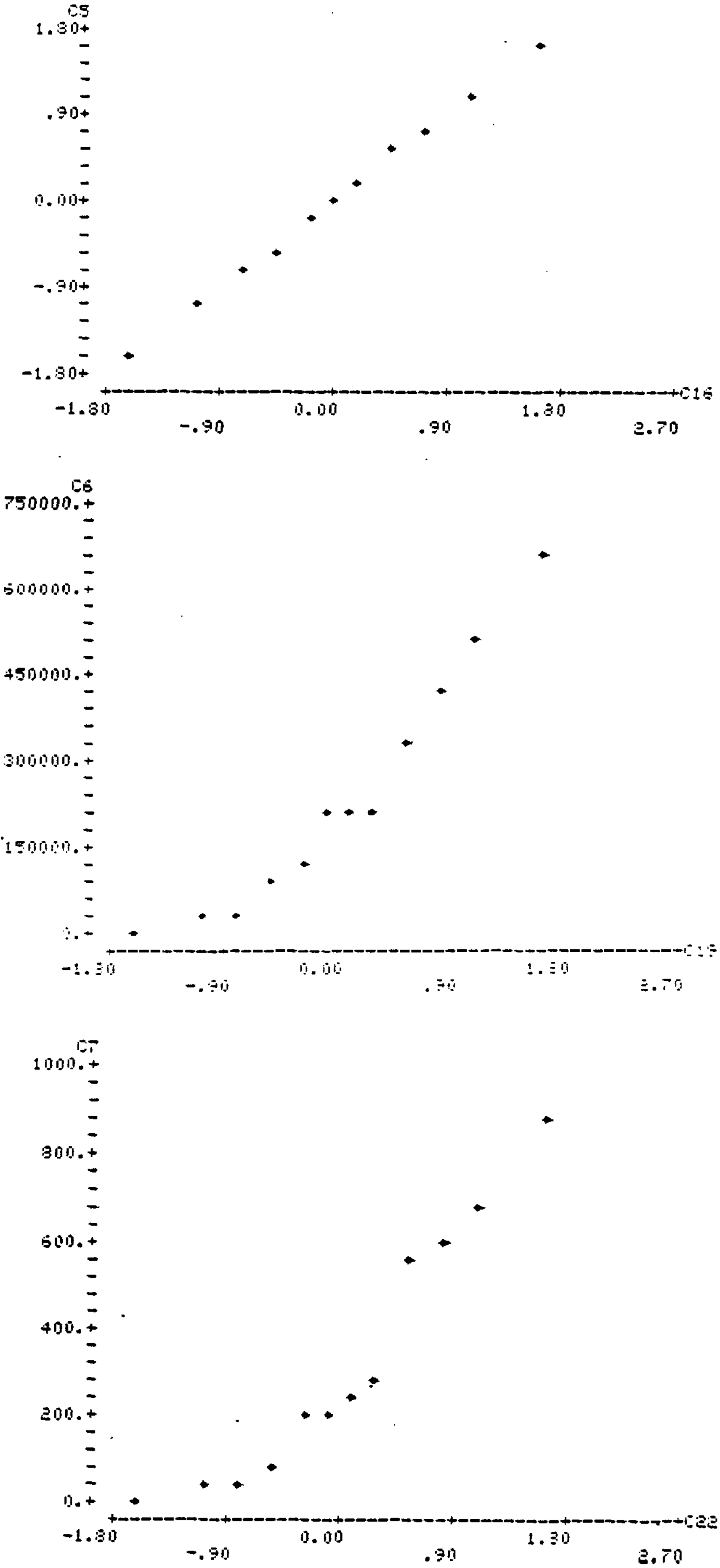


Fig. 1 Frequency distribution of benzene, toluene and EDB concentrations in the 3 l engine exhaust emissions.

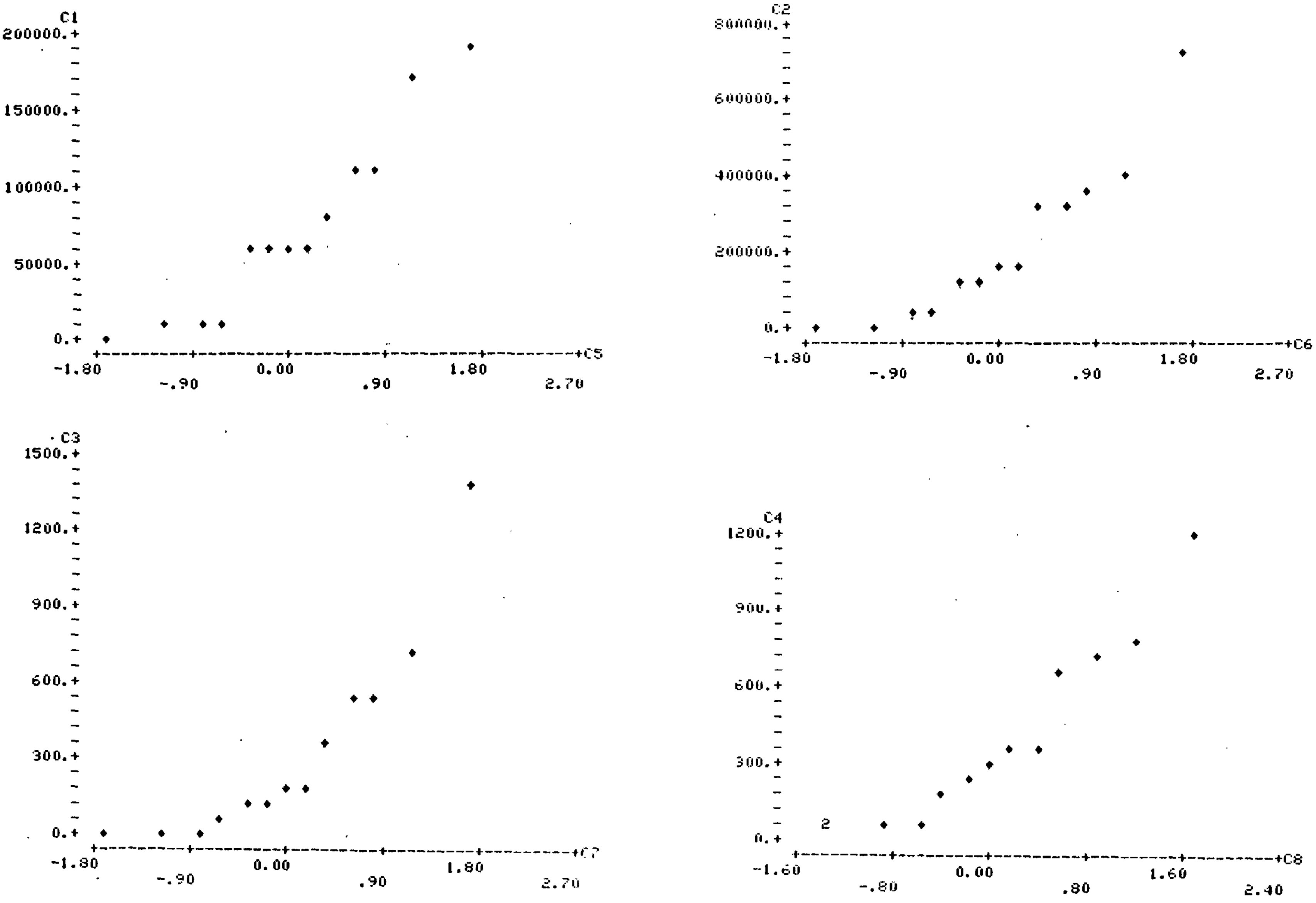


Fig. 2 Frequency distribution of benzene, toluene, EDB and EDC concentrations in the 0.85 l engine exhaust emissions.

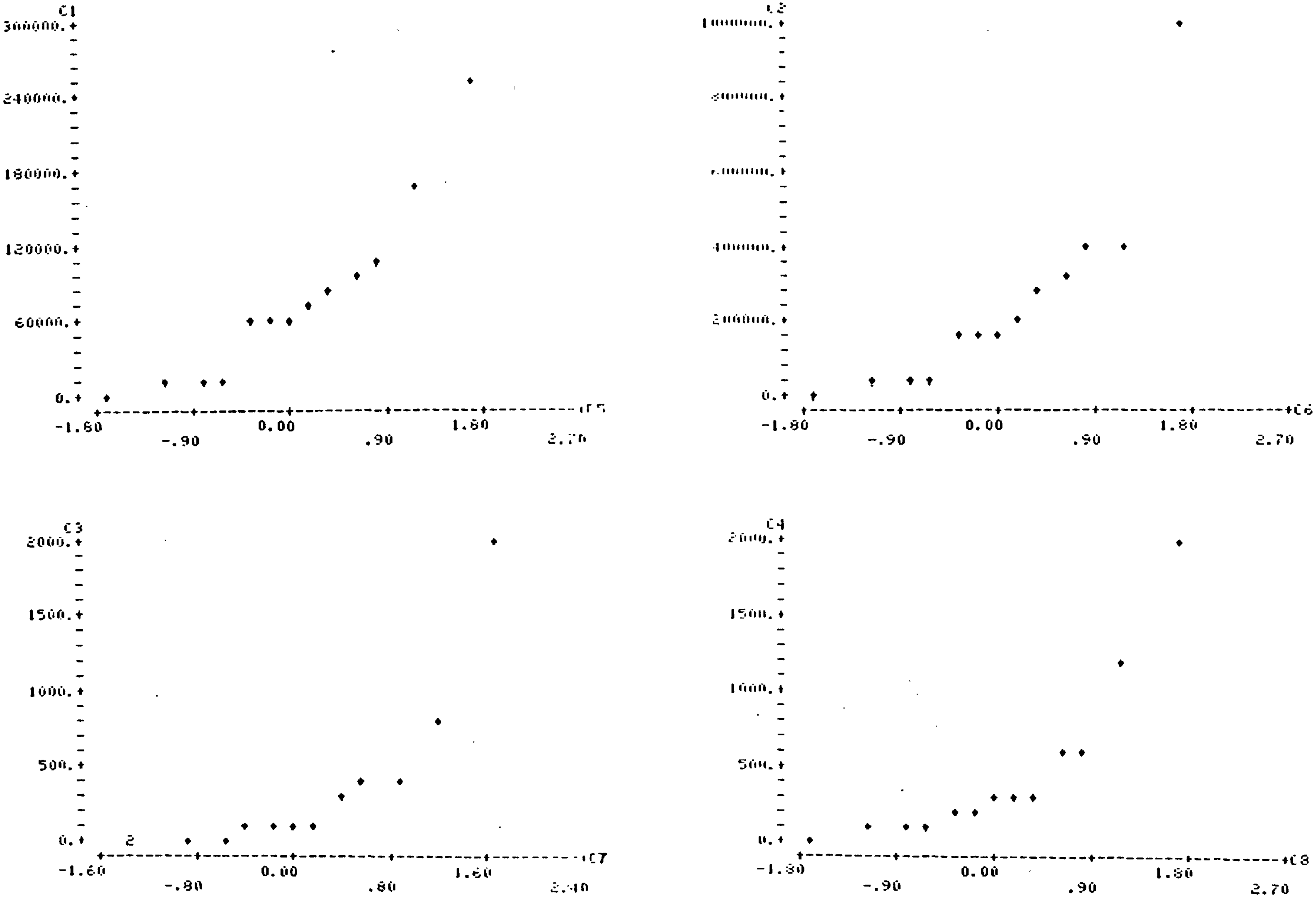
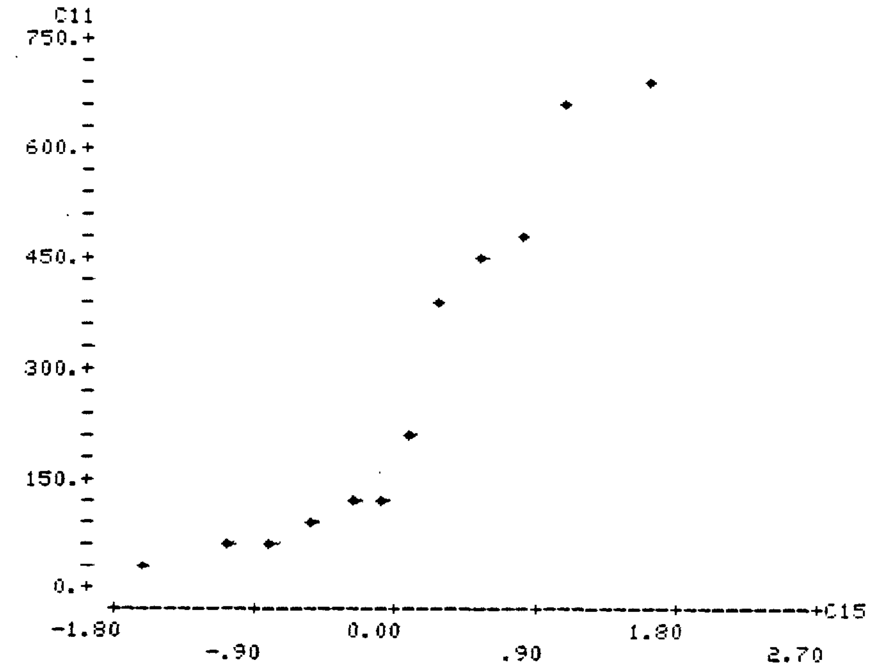


Fig. 3 Frequency distribution of benzene, toluene, EDB and EDC concentrations in the exhaust emissions of a 0.85 l engine equipped with a lead filter.



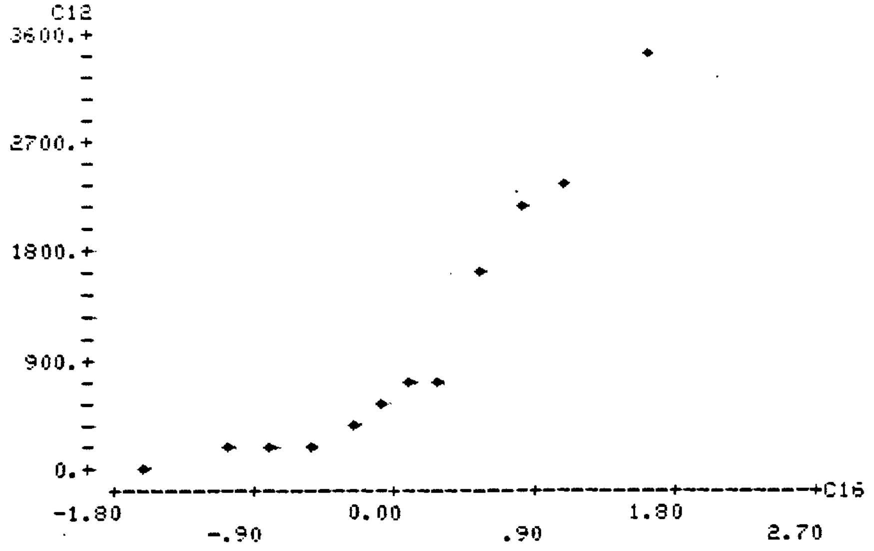


Fig. 4 Frequency distribution of EDB and EDC concentrations in the 1.6 l engine exhaust emissions.

APPENDIX C Measurements of hydrocarbons and halocarbons at Gatwick

Site 2 µg m^{-3}

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
14/9/79 15.00-15.30	14.0	3055	13	10	4	7	26	12	-	1.3	6	4	2.4	1.7	1.0	1.0	0.12	-
15.30-16.00	13.2	2830	15	15	6	28	42	15	-	-	24	52	36	25	-	3.3	0.12	-
16.00-16.30	16.4	2889	20	29	8.3	25	45	30	-	8	26	47	36	23	11	7	0.14	-
16.30-17.00	16.0	2865	20	16	2.0	15	53	17	4	6	24	45	27	16	8	15	0.14	-
17/9/79 14.00-14.30	6.4	117	26	23	9	61	123	27	5	18	15	65	18	10	7	8	0.06	-
14.30-15.00	15	2920	17	16	3.4	24	85	33	-	14	27	64	56	21	14	14	0.13	-
15.00-15.30	12	2999	16	16	1.3	22	83	30	-	7	38	39	24	15	12	14	0.11	-
7/10/79 13.30-14.00	3.4	6.4	2.2	3.2	0.4	3.7	8	2.6	-	0.5	1.9	12	5.3	5.0	0.8	1.3	-	-
14.00-14.30	2.0	4.7	2.1	2.6	-	1.5	7.6	2.0	-	0.3	1.5	5.3	-	0.4	-	-	-	-
14.30-15.00	2.7	5.7	2.3	2.8	-	3.2	7.5	2.1	-	-	2.0	6.6	-	2.2	-	-	-	-
1/11/79 13.00-13.30	5.4	9.3	2.0	5.7	-	8.6	43.5	10.4	-	4.0	8.9	21.3	-	-	-	-	-	-
13.30-14.00	8.1	9.6	1.7	4.6	-	4.6	12.6	11.3	5.0	9.6	15.1	12.8	-	-	-	-	-	-

APPENDIX C Site 2

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
4/11/79 14.00-14.30	6.8	15.0	1.7	3.0	-	3.5	2.8	8.0	-	-	11.4	2.3	-	-	-	-	-	-
15.00-15.30	11.2	37.6	11.4	30.4	13.0	15.0	16.6	26.3	-	32.0	16.2	19.9	25.9	18.5	-	14.6	-	-
14.30-15.00	5.9	15.7	2.5	15.6	5.9	9.1	21.0	16.0	-	12.0	18.7	24.1	17.9	15.3	8.2	0.8	-	-

APPENDIX C Measurements of hydrocarbons and halocarbons at Gatwick

Site 3 $\mu g\ m^{-3}$

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
21/8/79 14.30-15.00	9.6	16.0	3	13	7	2	4	41	5	9	29	14	19	10	9	6.7	0.11	-
15.00-15.30	7.5	13.7	2	9	3	0.7	0.5	3	0.7	0.9	3	1.6	5	3	1.3	1.4	0.074	-
15.30-16.00	5.5	10.8	-	10	4.5	2.2	3.6	3	0.8	1.5	6	8.2	-	-	-	-	0.056	-
7/10/79 11.00-11.30	17.6	37.0	5.5	30.5	9.7	2.6	7.7	10	1.4	1.7	8.0	10	2.1	1.2	0.5	0.6	0.16	-
11.30-12.00	3.4	8.5	2.4	6.2	1.5	2.1	6.8	3.4	-	0.9	2.8	4.1	1.8	1.0	-	0.5	-	-
12.00-12.30	6.9	13.4	3.8	8.2	3.3	3.9	11.8	4.7	-	0.8	3.3	3.0	0.4	1.1	-	0.5	0.06	-
12.30-13.00	6.1	12.1	2.9	11	5.5	1.6	8.6	5.8	-	0.6	3.6	5.5	1.3	1.0	-	0.2	0.05	-
12/10/79 13.00-13.30	5.8	12.1	3.4	10.6	4.6	2.2	8.7	8.8	-	2.6	5.8	5.9	2.7	3.8	3.4	4.4	0.05	-
13.30-14.00	5.4	12.4	3.1	10.1	3.8	3.1	7.4	5.8	-	0.9	5.0	7.1	1.8	2.9	1.3	1.7	-	-
14.00-14.30	7.4	14.8	3.9	12	5.4	1.7	8.0	14.9	-	11.7	15.8	11.3	4.5	6.0	4.2	3.6	0.07	-
14.30-15.00	6.2	13.8	2.5	15.9	5.5	0.9	8.0	9.1	-	6.1	11.3	12.4	12.9	6.4	1.8	1.4	0.054	-

APPENDIX C Measurements of hydrocarbons and halocarbons at Gatwick
Site 4 $\mu g\ m^{-3}$

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
3/9/79 16.00-16.30	4.0	102	3.2	2.7	1.7	4.4	17.1	4.3	-	-	3.0	12.8	-	-	-	-	-	-
16.30-17.00	2.6	92.5	2.8	5.0	-	1.1	11.3	13.6	-	-	10.7	18.9	6.8	-	-	-	0.014	-
17.00-17.30	2.0	100	2.7	5.0	0.4	1.4	17.8	4.2	-	-	3.6	35.5	-	0.6	-	-	-	-
5/9/79 16.00-16.30	1.5	11.1	4.7	10.4	4.9	1.7	13.7	11.1	2.8	0.7	8.6	12.7	7.9	0.3	0.2	0.4	0.03	-
16.30-17.00	2.4	9.1	2.2	-	-	1.1	17.5	2.9	-	-	5.3	13.0	-	-	0.1	-	-	-
17.00-17.30	2.8	7.9	4.4	-	-	0.8	14.4	3.0	-	-	5.0	11.0	-	-	-	-	0.03	-
17.30-18.00	4.0	10.8	6.4	-	-	2.8	18.0	2.1	-	-	1.8	18.8	-	-	-	-	0.04	-
7/9/79 15.30-16.00	1.4	22	0.1	13.0	1.5	9.3	35.7	2.0	-	-	1.8	16.4	-	0.8	-	-	0.014	-
16.00-16.30	1.3	12.7	0.1	2.9	-	5.0	43.5	1.4	-	-	0.8	22.4	-	-	-	-	0.011	-
16.30-17.00	3.2	18.0	5.2	8.4	-	6.4	154	5.3	-	-	8.4	48.7	-	0.6	-	-	0.03	-
17.00-17.30	2.8	24.0	6.2	7.3	-	2.2	39	2.9	-	0.25	1.8	20.6	-	-	-	-	0.018	-
10/9/79 15.00-15.30	5.1	22.9	8	10	-	6	38	14	-	-	13	22	5.8	7	2	1.8	0.06	-
15.30-16.00	8.3	34.6	7.0	9.2	-	2.5	35	5	-	-	3.4	17.5	3.8	1.9	1.3	2.0	0.064	-
16.00-16.30	5.9	29.7	8.7	15.4	3.6	4.0	77	14.3	-	-	8.3	9.5	2.8	3.9	1.2	1.3	0.09	-

APPENDIX C

Site 5

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
24/9/79 15.00-15.30	4.3	11.3	3.8	5.0	-	2.7	34.3	5.6	0.5	0.7	5.0	6.0	3.4	2.3	1.1	1.6	0.02	-
15.30-16.00	6.7	17.9	6.8	8.5	1.9	6.2	63	11.2	0.8	1.0	10.7	18.2	10	8.6	1.6	3.7	0.04	-
16.00-16.30	7.0	16.9	6	9.7	3.9	5.0	51	9.5	0.6	0.7	8.3	14.0	3.5	2.8	-	1.3	0.04	-
16.30-17.00	4.6	12.3	4.3	7.9	3.4	4.6	66	2.3	-	0.4	5.4	13.1	2.0	2.4	-	2.1	0.04	-
28/9/79 14.00-14.30	4.8	17.2	10.6	9.8	-	9.2	50	17	-	11	7.8	16.8	9.1	6.2	4.5	4.1	0.03	-
14.30-15.00	5.1	13.8	6.1	7.4	1.4	11.9	35.5	31.3	-	13.9	26.0	31.9	16.6	17.8	7.5	9.0	0.05	-
15.00-15.30	3.1	18.4	8.1	9.4	3.2	5.2	40.5	16.3	-	3.0	9	27.5	4.1	2.8	1.9	2.5	0.03	-
15.30-16.00	7.7	20.2	7.6	13.0	4.4	4.7	38.1	16.6	-	1.7	8.6	18.0	3.3	2.9	0.7	1.2	0.08	-
1/10/79 13.30-14.00	9.1	22.7	7.2	12.7	4.1	5.1	46.6	12.4	-	1.5	9.5	14.0	1.7	2.5	0.6	1.0	0.07	-
14.00-14.30	6.7	18.7	8.6	10.6	4.7	4.9	40.3	11.3	-	1.5	10.4	14.5	7.2	5.9	3.8	5.3	0.067	-
14.30-15.00	3.6	14.6	7.2	11.5	3.4	6.1	37	12.3	-	-	11.4	17.9	2.7	3.6	0.8	0.4	0.028	-
15.00-15.30	4.3	16.2	8	10	-	4.0	28	10	-	0.8	6.0	14	1.4	2.0	-	0.5	0.037	-

APPENDIX C

Site 6

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
3/10/79 14.00-14.30	26	51	9	50	18	8	8	24	6	10	28	15	14	13	7	5.5	0.22	0.22
14.30-15.00	16	34	6	30	9	3	4	14	3.3	5	17	18	10	10	3	7	0.15	-
15.00-15.30	12	37	6	34	13	1.2	2.6	11	2	2.5	9.4	5	3	3	0.7	0.7	0.09	-
7/10/79 15.30-16.00	15	35	5.8	35	15	3.4	6.5	11.6	3.2	4.6	10.8	5.2	2.9	2.8	1.9	0.9	0.13	-
16.00-16.30	19	46	7.1	41	16.5	4.8	5.1	16.5	2.4	13	12.5	9.2	2.9	2.2	1.2	1.1	0.17	0.20
16.30-17.00	17	42	6.7	41	15	2.9	14	14.4	3.2	4.4	14.3	7.8	4.7	4.4	1.6	1.1	0.15	-
12/10/79 15.00-15.30	19	46	8.3	51	13.4	7.9	11	22.6	5.5	9.0	25.7	18.8	16.7	5.7	3.1	6.7	0.18	0.22
15.30-16.00	18	45	8	47	22	2.6	7	15	4	5	14	5	6	2.0	0.5	2.0	0.18	0.19
16.00-16.30	18	46	8	48	17.6	2.3	11.8	20.7	5.6	8.1	22.4	10.2	19	11	6.3	11.2	0.18	-
16.30-17.00	16	41	7.2	42	16	4.7	4.9	13.4	2.1	2.7	10.9	2.5	2.3	2.1	0.5	1.2	0.15	-
17.00-17.30	15	42	7.6	42	14.4	2.3	10.9	13.5	2.3	2.9	11.6	2.3	3.9	3.1	2.3	2.1	0.16	-

APPENDIX C

Site 7

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
5/10/79 14.00-14.30	9.7	16.3	6.0	5.2	-	15.4	19	10.7	-	4.1	7.1	11.8	2.9	2.8	1.9	-	0.076	-
14.30-15.00	3.1	14.8	4.4	6.7	-	2.3	16.4	4.7	-	0.9	3.4	5.6	3.2	1.8	1.0	-	-	-
15.00-15.30	4.4	8.7	3.7	4.8	-	6.0	16.0	4.6	-	0.6	3.4	5.5	3.2	2.8	0.4	-	0.028	-
15.30-16.00	3.8	8.2	3.0	4.3	-	0.8	14.7	4.9	-	0.7	3.8	6.6	2.0	2.7	0.7	-	0.035	-
9/10/79 11.30-12.00	7.7	12	3.3	5.9	1.7	2.6	2.9	1.9	-	2.5	1.9	2.8	5.5	6.1	3.1	2.8	0.08	-
12.00-12.30	7.3	48.9	9.8	12.6	4.6	3.8	12.8	12.2	-	2.7	10	13.7	8.3	10.9	3.8	-	0.067	-
12.30-13.00	6.4	34.5	8.0	12.8	3.8	8.9	17.8	18.3	-	6.6	11.7	28.4	22.4	22.5	-	19.4	0.06	-
9/10/79 15.30-16.00	5.1	48.4	10	9.0	2.6	12	29	17	-	5.0	14	36	12	6.2	6.5	0.6	-	-
16.30-17.00	9.2	43.5	11	11	4.4	8.5	12.6	10.9	-	-	11.1	15.4	5.4	4.1	-	-	0.08	-
10/10/79 13.00-13.30	6.0	35.4	7.2	12	5.8	9.8	11.8	16.7	-	-	15.6	19.7	11.8	15.6	9.2	12.8	0.05	-
13.30-14.00	6.7	39.2	7.8	8.3	4.1	7.8	9.5	8.8	-	-	7.8	12.7	1.7	0.9	-	2.3	0.057	-
15.30-16.00	6.2	29.0	6.7	16.8	7.3	9.5	12.5	16.6	-	-	15	18.2	16.1	9.9	-	10.6	0.04	-
16.00-16.30	5.9	30.8	7.0	11.6	3.6	9.5	13.9	13.4	-	2.7	12.6	17.0	6.0	3.3	-	-	-	-

APPENDIX G Analyses of petrol and aviation fuels (ng 0.02 μl^{-1})

Date — Hour	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Petrol	830	2748	417	2629	785	124	182	803	228	230	830	193	224	138	52	104	4	4
Shell Jet	16	100	364	–	202	369	1488	–	–	444	387	1391	316	187	186	333	–	–
Shell 100L Avgas	53	800	52	202	25	32	20	13	–	16	37	73	16	4	3	–	5	–

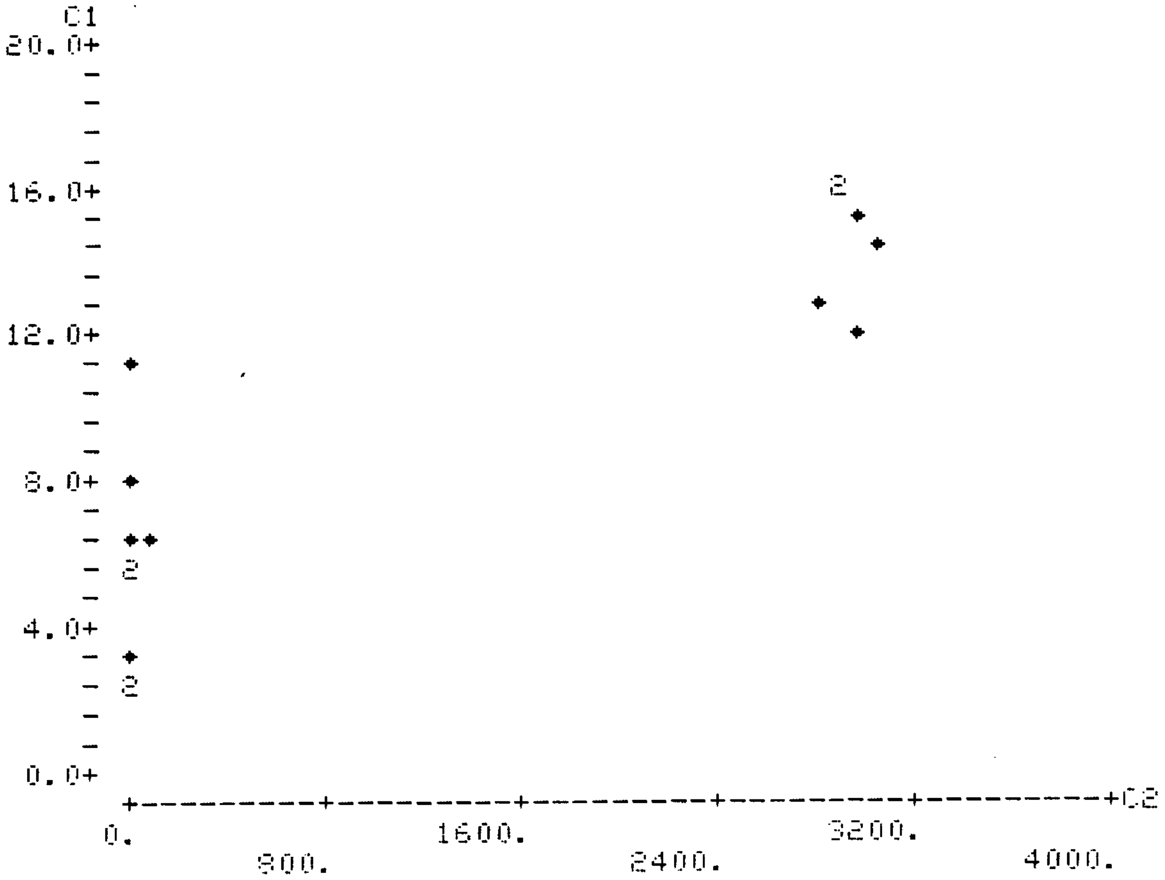


Fig. 1 Correlation of benzene and toluene at site 2 (Car Park Hotel)

Correlation factor = 0.878

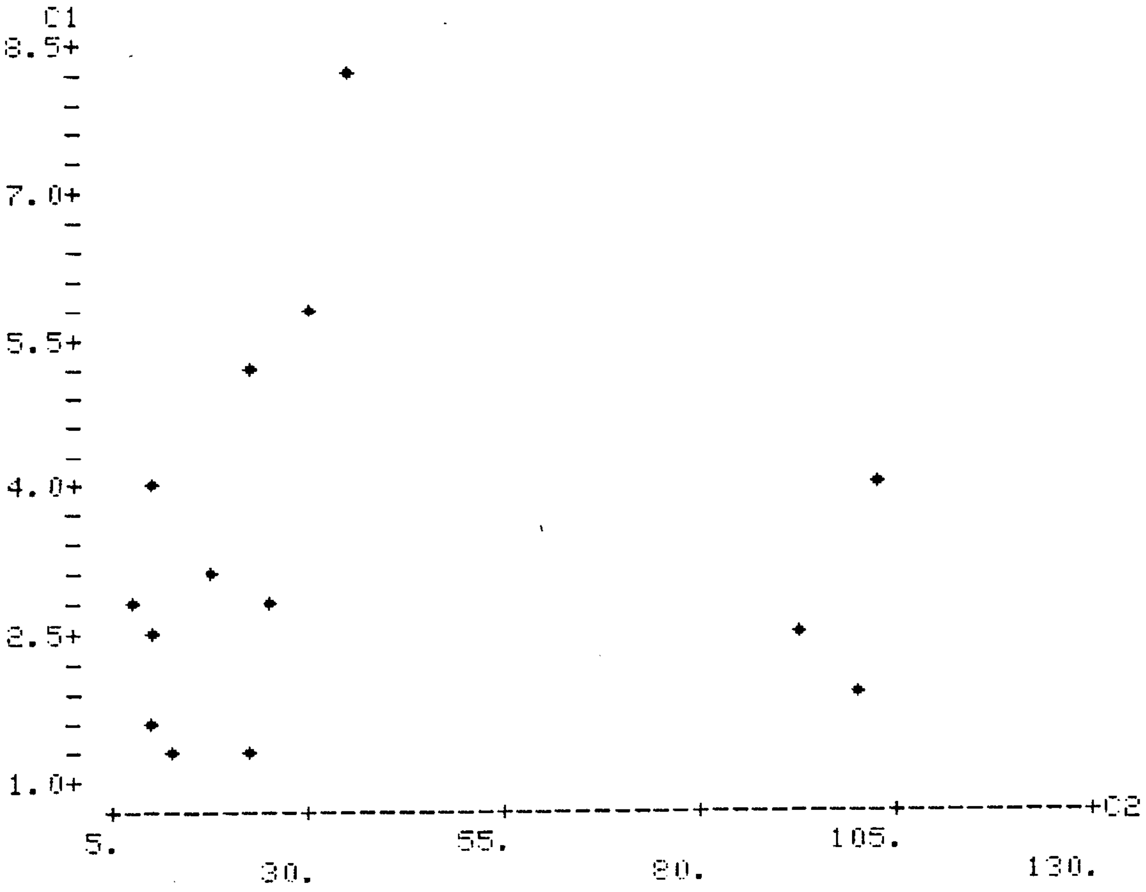


Fig. 2 Correlation of benzene and toluene at site 4 (substation)

Correlation factor = 0.026

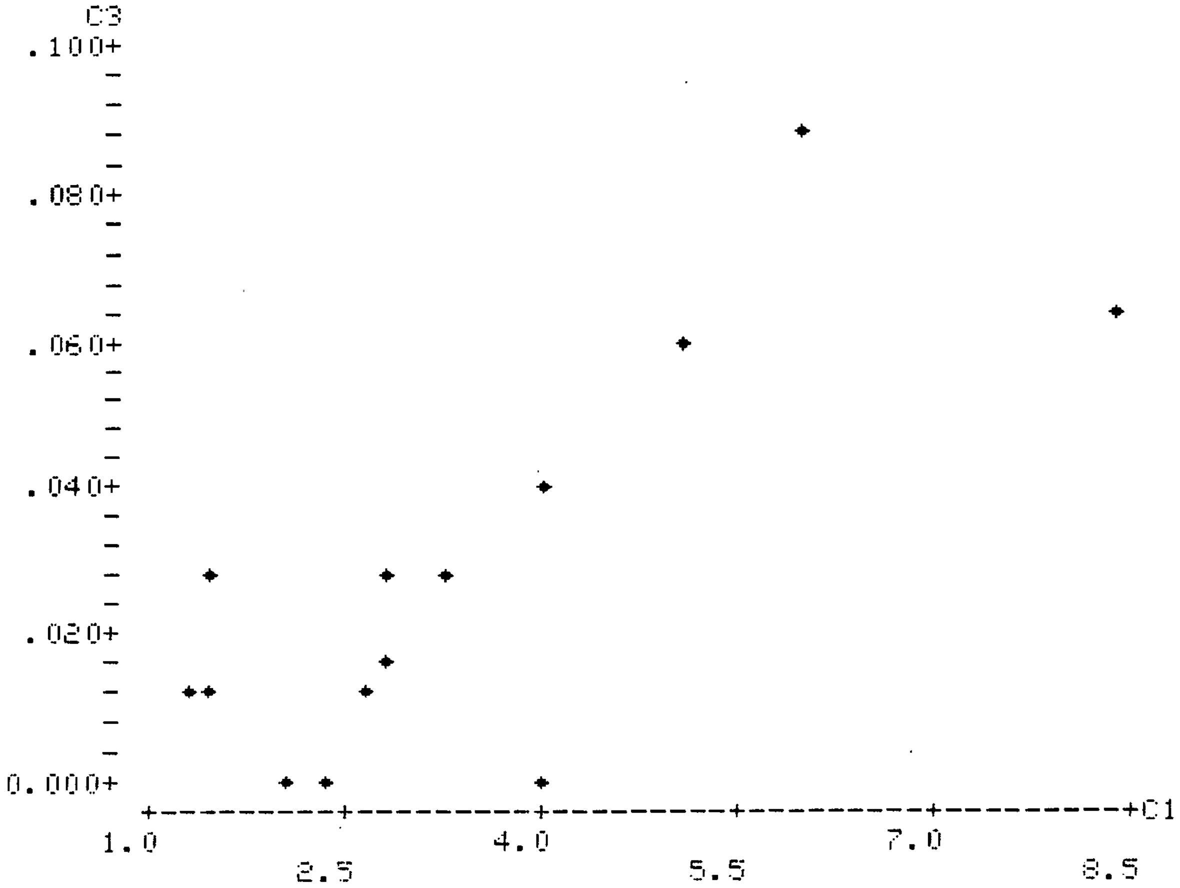


Fig. 3 Correlation of EDB and benzene at site 4 (substation)

Correlation factor = 0.756

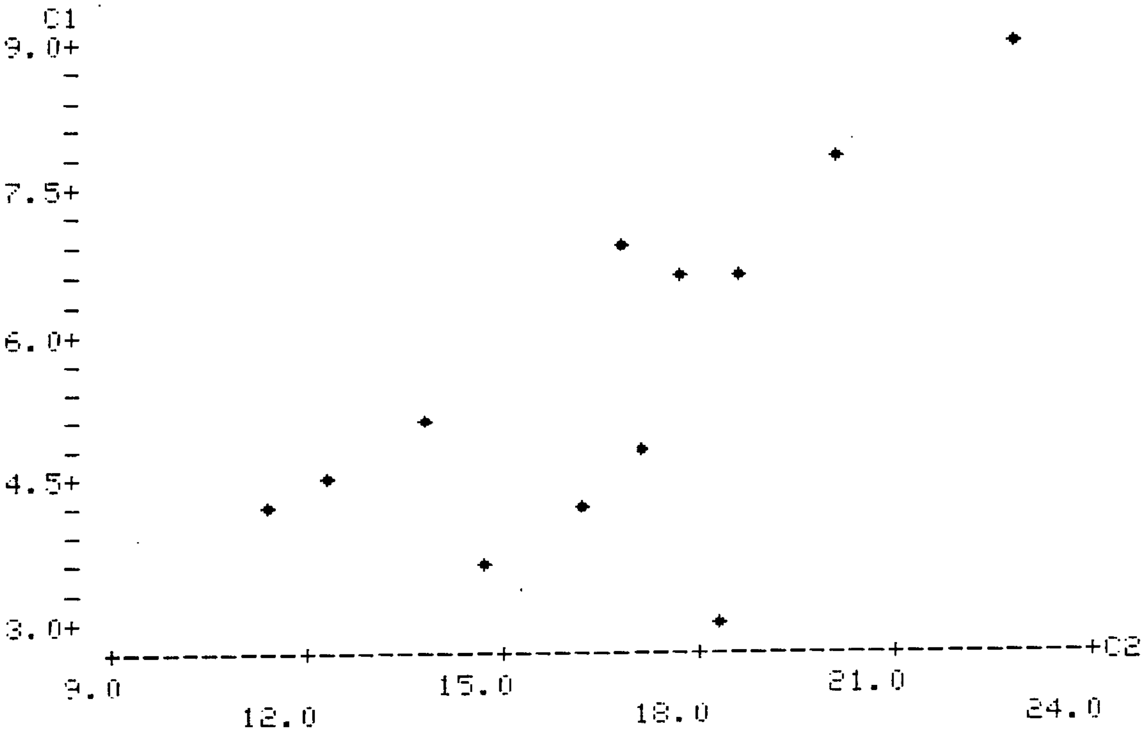


Fig. 4 Correlation of benzene and toluene at site 5 (Beehive)

Correlation factor = 0.685

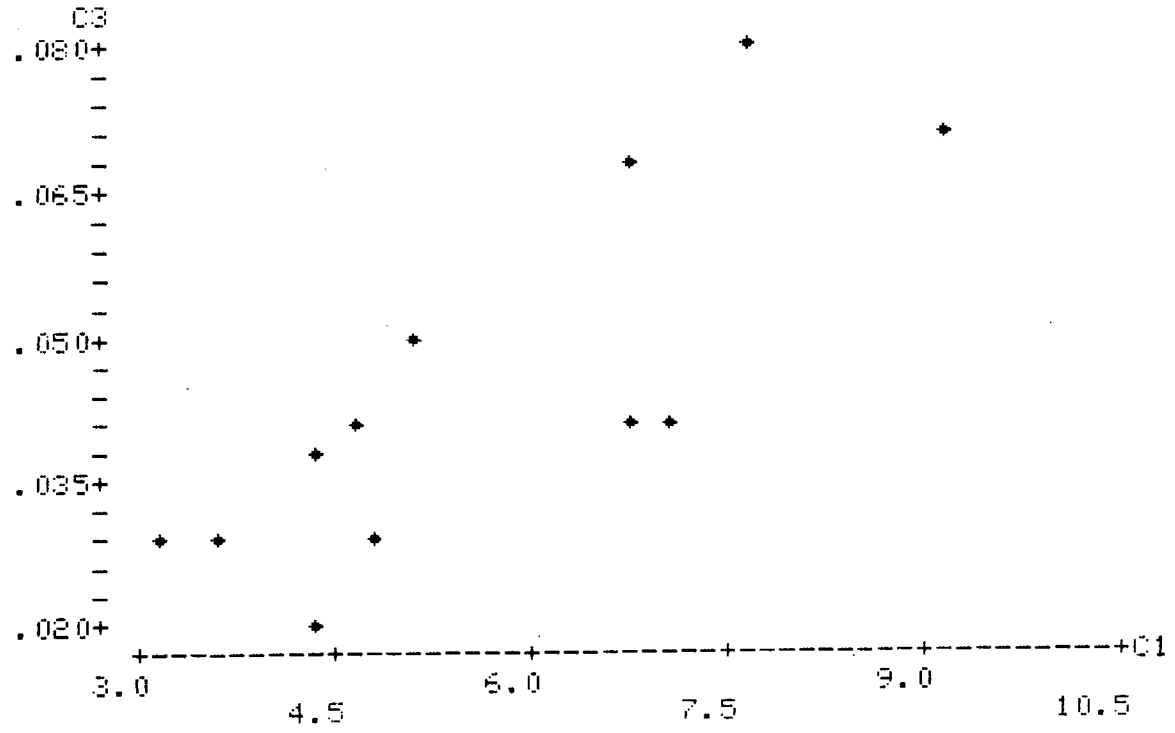


Fig. 5 Correlation of EDB and benzene at site 5 (Beehive)

Correlation factor = 0.803

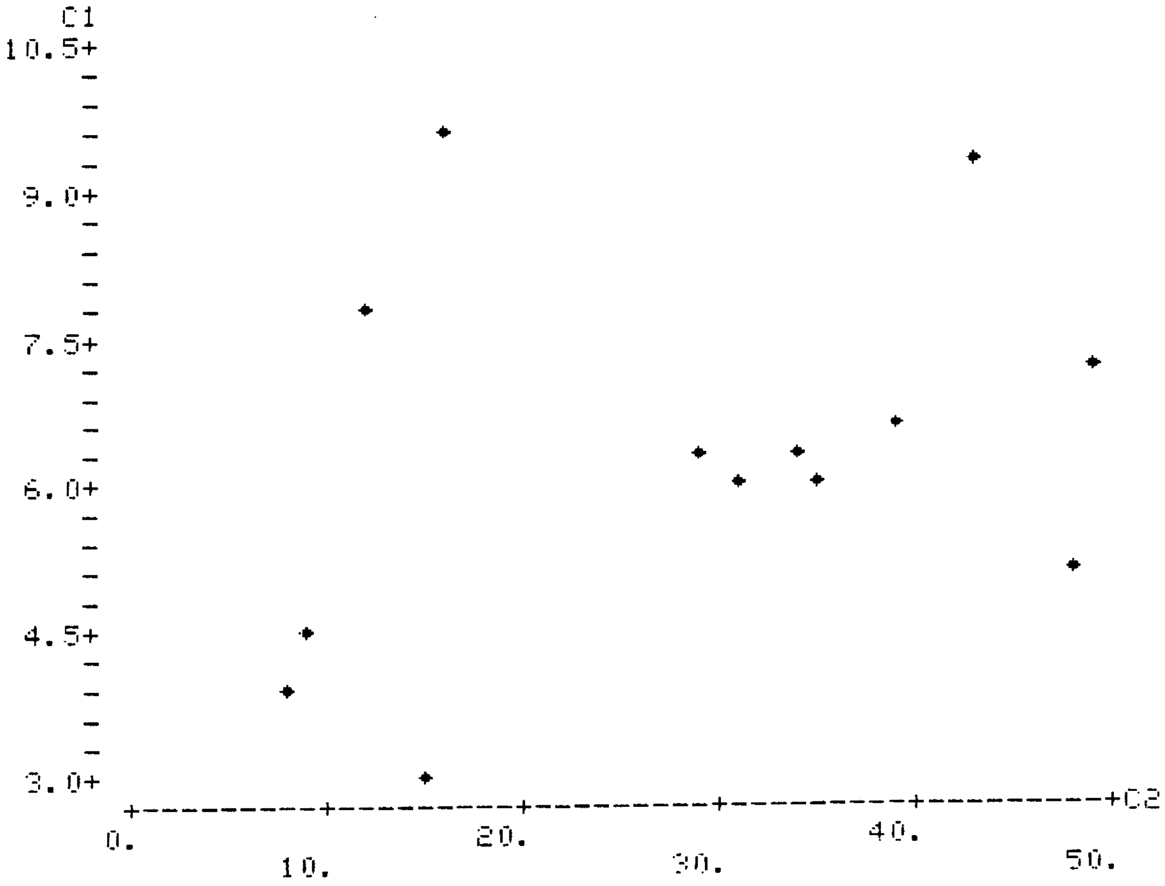


Fig. 6 Correlation of benzene and toluene at site 7 (Brickworks)

Correlation factor = 0.317

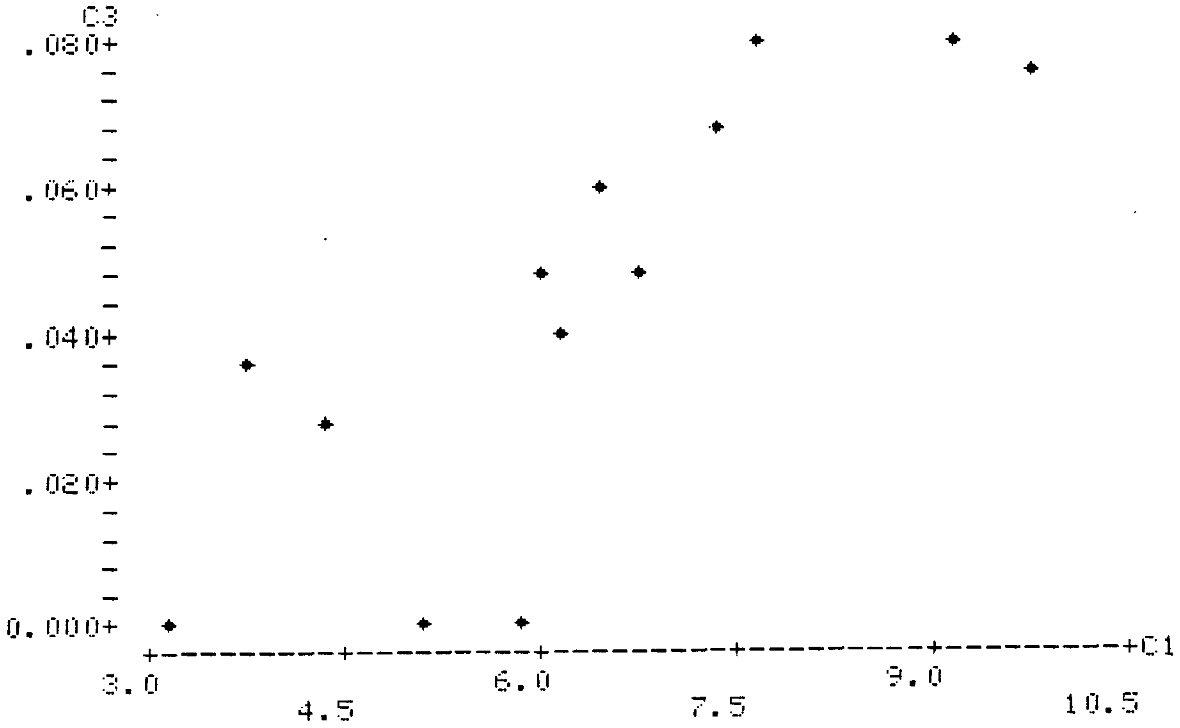


Fig. 7 Correlation of EDB and benzene at site 7 (Brickworks)

Correlation factor = 0.801

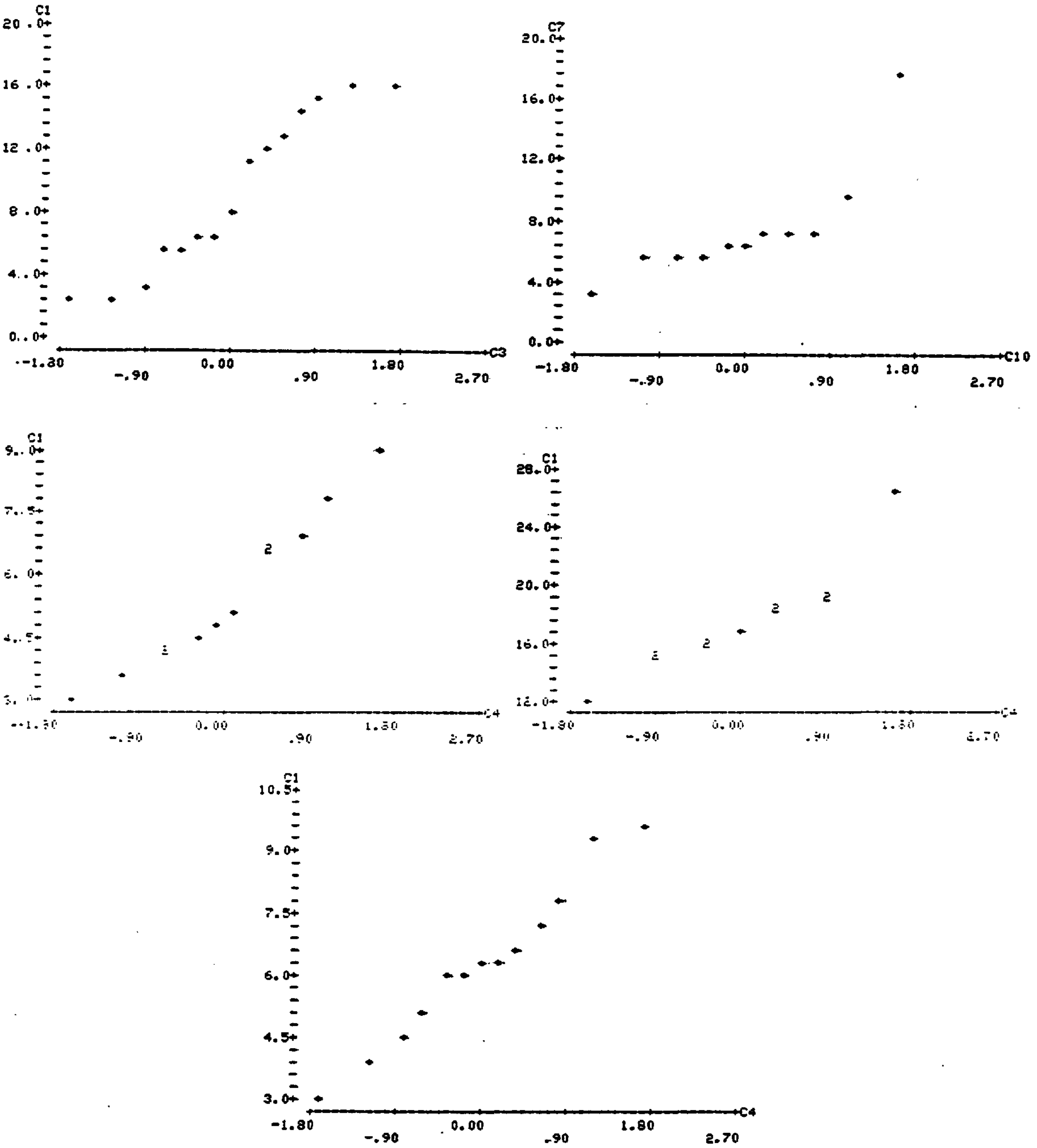


Fig. 8 Frequency distribution of benzene concentrations at Gatwick sites 2,3,5,6 and 7.

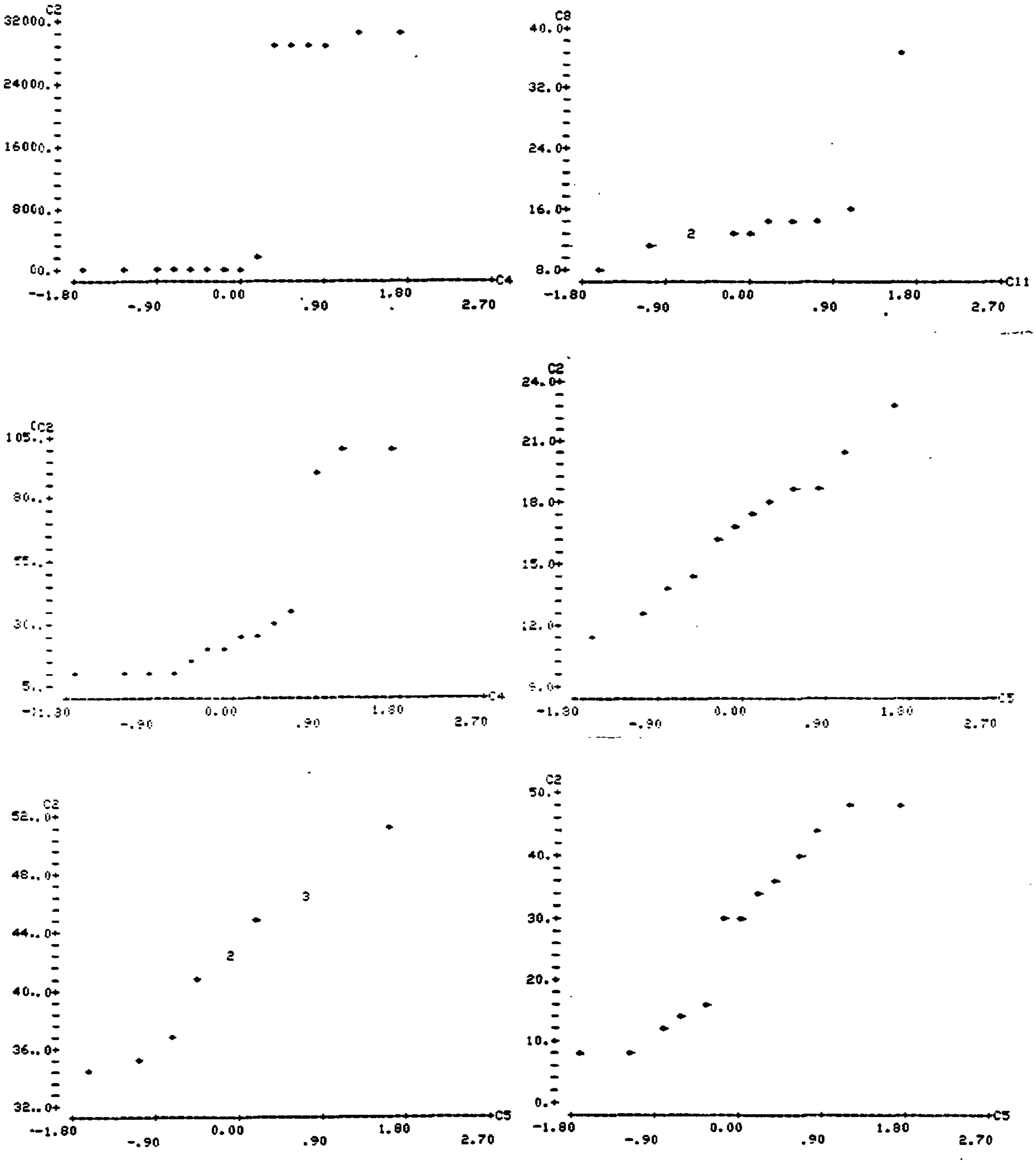


Fig. 9 Frequency distribution of toluene concentrations at Gatwick sites 2, 3, 4, 5, 6 and 7.

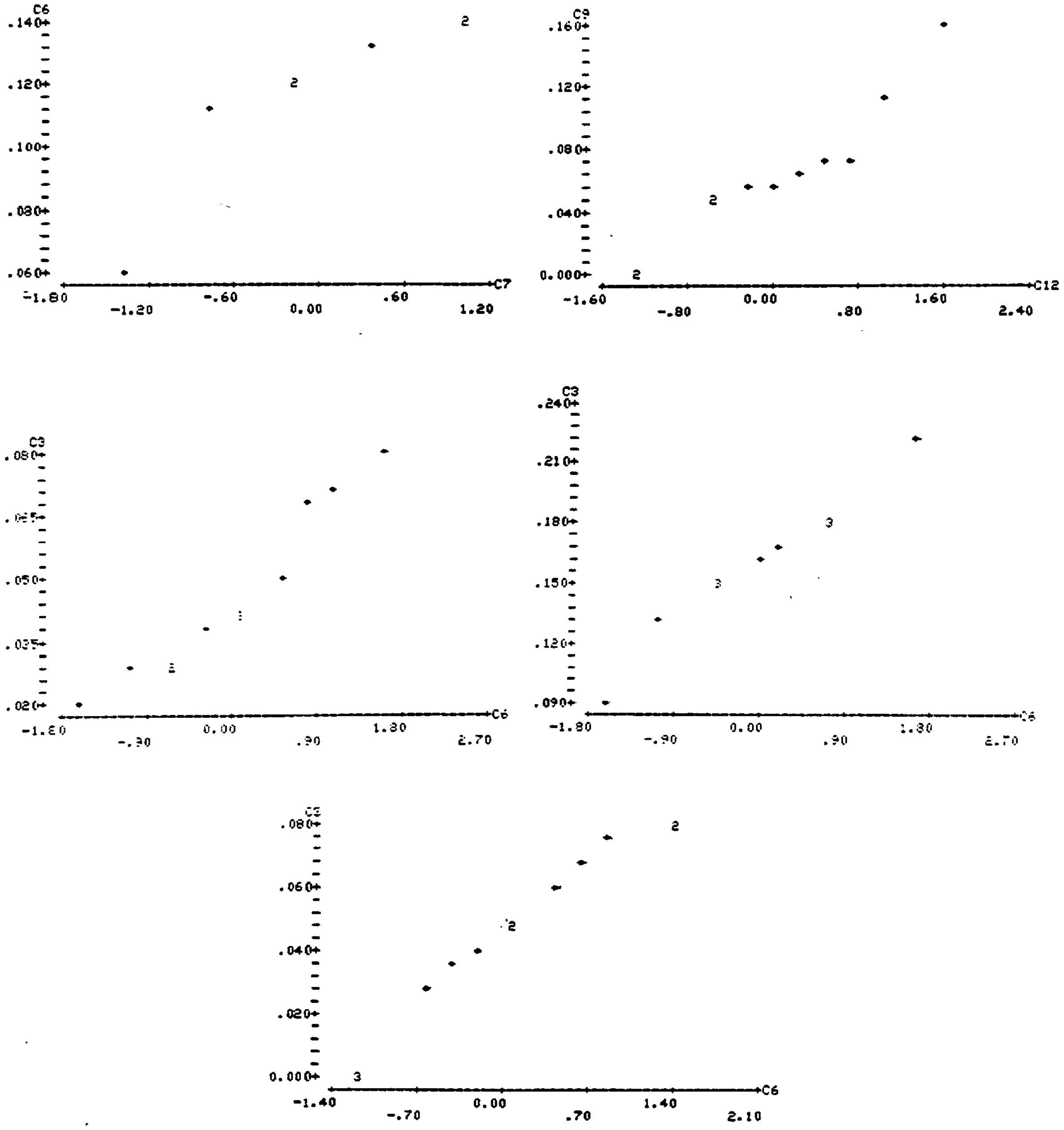


Fig. 10 Frequency distribution of EDB concentrations at Gatwick sites 2, 3, 5, 6 and 7.