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ON-LINE MONITORING OF AMBIENT HYDROCARBON CONCENTRATIONS

A Thesis Submitted to the University of Dublin in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Engineering

by

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February 2001

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Ian Marnane

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SUMMARY

The result of a comprehensive set of hydrocarbon measurements undertaken at an urban roadside, rural and industrial site in Ireland are presented. Very little reported data on ambient hydrocarbon measurements were previously available. There was a notable lack of short-term measurements, which are particularly useful for characterising the sources and behaviour of ambient hydrocarbon concentrations.

Monitoring was carried out at the urban site between March and August 1998. Other measurements taken by the EPA at the same site between July and December 1999 are also reported. Monitoring at the rural site took place in June and July 1999, and between September and December 1999 at the industrial site.

An on-line hydrocarbon monitoring system was employed to provide hourly measurements of 27 hydrocarbons in the C_2 to C_9 range, including the carcinogenic compounds benzene and 1,3-butadiene. Samples were cryogenically trapped, followed by thermal desorption and gas chromatography-flame ionisation detector analysis. Pumped and passive sampling methods were also employed using adsorbent filled tubes to trap compounds of interest. These tube were analysed off-site. At the urban and rural monitoring sites, the on-line system only was employed, while all three monitoring methods were employed during monitoring at the industrial site. Meteorological data (windspeed, wind direction and temperature) were measured at all three sites.

Assessment of the performance of each of the above monitoring methods was an important part of the project. The utility of each method is discussed, and their relative performance is assessed.

Dispersion modelling of emissions was undertaken at the industrial site using two Gaussian based models, ADMS and ISC. The performance of each of the models relative to the on-line measurements was assessed using a range of statistical and graphical methods. The relative performance of each of the models is discussed.

Analysis of the urban roadside results indicated vehicle emissions as the dominant hydrocarbon source at this site, though other sources were also identified. A very strong correlation was observed between most hydrocarbons, indicating vehicle emissions as a common source. Ethane and propane were observed to have a large contribution from natural gas leakage. Meteorological variations were noted to have a measurable effect on ambient hydrocarbon concentrations. Increased evaporative emissions were noted as ambient temperatures increased. Comparison of ambient hydrocarbon measurements with results from detailed hydrocarbon analysis of Irish fuel samples collected during the project revealed good agreement between the relative fuel and ambient hydrocarbon composition. Comparison of hydrocarbon concentrations with exhaust measurement studies revealed the best agreement for non-catalyst tests, indicating that non-catalyst vehicle emissions dominate ambient concentrations in Dublin.

Monitoring results from the industrial site indicated very high concentrations of a number of hydrocarbons which were associated with local point source emissions. The influence of emissions from Mullingar town and from a local petrol station were also noted. Good performance was noted for the pumped sampling method in comparison with the on-line method, however, the passive sampling method tended to underestimate the on-line measurements.

Comparison of measured and modelled hydrocarbon concentrations indicated good performance of both models in predicting long-term average and short-term hourly concentrations. The performance of the models in predicting the highest measured concentrations was better than their prediction of lower concentrations. The ISC model tended to slightly overpredict the measured concentrations while ADMS predictions were closer to the measured values. ADMS performed better than ISC over the range of measured hydrocarbon concentrations. The ADMS model performed significantly better under stable atmospheric conditions compared to ISC. The model performance was improved using local meteorological data compared to regional data.

Monitoring results from the rural site indicated low average concentrations for most compounds. Elevated concentrations of ethane and isoprene were, however, measured at this site.

ACKNOWLEDGEMENTS

Many people have offered advice to me throughout the course of my postgraduate studies. I would, therefore, like to thank all these people, in no particular order, as all contributions were gratefully received and have added tremendously to the outcome of my studies, which is summarised in the following thesis.

Thanks to my parents, Laura and Sean Marnane, who supported me in my decision to continue beyond my primary degree. Many thanks to Andrea Lazenby-Simpson, my best friend, who has put up with me over the last four years, and gained some insider knowledge of the world of hydrocarbon monitoring into the bargain.

My gratitude must also go to many people in the Department of Civil, Structural and Environmental Engineering. Many thanks to my supervisor, Dr. Brian Broderick; to Bruce Misstear; to Anne Desmond; and to all the other postgraduates, including my office-mate, Dawn Keating, who was a constant source of amusement, and all the members of the highly successful Civil Engineering soccer team who made college life immensely more entertaining.

Other people who deserve mention are: Declan Keoghegan of FOSS Electric; Brian Jones, John Abbott and Keith Vincent of AEA Technology in the UK; Michael Barrett of Bord Gais; Paddy Wallace from the Whitegate Refinery in Cork; John McDermott from the Department of the Environment; Billy King from the State Laboratory; Jack Treacy from the Dublin Institute of Technology; John Nugent from Enterprise Ireland; Eunan McCormack from Penn Racquet Sports Company; Christopher Reilly from Taconic International; Paraic Carrigan from Met Eireann; Peter Webster, Eidin Christie, Ciaran O'Donnell, Nick Kenny and Elizabeth Nagel from the EPA; Dan Hogan from the Electricity Supply Board; Kathy Cocker and Joe Norbeck from the University of California; Hilary Main from Sonoma Technology in California; and Dennis Atkinson from the USEPA.

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ABBREVIATIONS

$\mu g/m^3$	Microgrammes per cubic metre
ADMS	Atmospheric dispersion modelling system
AIRS	Aerometric information retrieval system (US database)
ANOVA	Analysis of variance
ATD	Automated thermal desorption
AutoGC	Automated gas chromatograph
BP	Balanced phase (capillary column)
BTEX	Benzene, toluene, ethylbenzene and xylene
BTX	Benzene, toluene and xylene
CEC	Council of the European Communities
CERC	Cambridge Environmental Research Consultants
CFC	Chlorofluorocarbon
CO	Carbon monoxide
C_X	Hydrocarbon with X carbon atoms
DETR	Department of the Environment, Transport and the Regions
DOAS	Differential optical absorption spectroscopy
DOE	Department of the Environment
DSRB TIME	Desorb time
ECD	Electron capture detector
EEA	European Environment Agency
EI	Enterprise Ireland
EIA	Energy Information Administration
ELCD	Electrolytic conductivity detector
EMEP	European monitoring and evaluation programme
EPA	Environmental Protection Agency (Ireland)
EU	European Union
FB	Fractional Bias
FID	Flame ionisation detector
FPD	Flame photometric detector
FS	Fractional Standard Deviation
GC	Gas chromatography
GEMS / AIR	Global Environmental Monitoring System for Air Pollution
HC	Hydrocarbon
HGV	Heavy goods vehicle
HSE	Health and Safety Executive
IPC	Integrated pollution control (licensing)
ISC	Industrial source complex
kPa	Kilopascals (units of pressure)
L	Leaded (petrol)
LCD	Liquid crystal display
LGV	Light goods vehicle
LIDAR	Light detection and ranging
LPG	Liquefied petroleum gas
LRD	Least representative day
MARC	The monitoring and assessment research centre
MRD	Most representative day
MS	Mass spectrometry
MTBE	Methyl tertiary butyl ether
MW	Megawatt

NETCEN	National Environmental Technology Centre
NILU	Norwegian Institute for Air Research
NMHC	Non-methane hydrocarbon
NMSE	Normalised mean square error
NMVOC	Non-methane volatile organic compounds
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
NPD	Nitrogen phosphorous detector
NPL	National Physical Laboratory
°C	Degrees celsius
OECD	Organisation for Economic Co-Operation and Development
PAMS	Photochemical assessment monitoring stations
PAN	Peroxyacetylnitrate
PC	Personal computer
PCA	Principal component analysis
PID	Photoionisation detector
PLOT	Porous layer open tubular (capillary column)
PM_{10}	Particulate matter with a diameter of less than 10 micrometres
PORG	Photochemical Oxidant Review Group
ppb	Parts per billion
ppm	Parts per million
psi	Pounds per square inch
QUARG	Quality of Urban Air Review Group
RIVM	Dutch National Institute of Public Health and Environmental Protection
RON	Research octane number
RVP	Reid vapour pressure
SAE	Society of Automotive Engineers
SL	Super-leaded (petrol)
SO_2	Sulphur dioxide
STD INJ	Standard injection time
SUL	Super-unleaded (petrol)
SVOC	Semi-volatile organic compound
T_{50}	50 percent distillation temperatures (of an automotive fuel)
T_{90}	90 percent distillation temperatures (of an automotive fuel)
TCD	Thermal conductivity detector
TRRL	Transport and road research laboratory
UAT	Unified Air Toxics (USEPA website)
UK	United Kingdom
UL	Unleaded (petrol)
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compound
WHO	World Health Organisation
PTFE	Polytetrafluoroethylene

1. INTRODUCTION

1.1 INTRODUCTION TO AIR POLLUTION

1.1.1 Historical Background

The earliest air pollution occurred in primitive huts where smoke would build up at ceiling level before finding its way out through a hole in the roof. The effect of this pollution may be seen in nearly all bodies which have been preserved through freezing or desiccation, showing quite high levels of blackening of the lung tissue due to smoke inhalation (Brimblecombe, 1987).

As communities began to grow and cities were created, outdoor air pollution became a problem, some of the early sources being ovens (for baking), kilns (for baking bricks), furnaces (in steel mills and blacksmiths) and fires in the home. In England, use of coal became prevalent in the 13th century, and created severe problems due to smog, particularly in large cities such as Manchester and London. In 1285, a commission was set up to investigate the problems associated with air pollution due to coal. In 1306 a proclamation banning the use of coal was announced, but largely ignored, and the coal pollution problem continued. The adverse health effects of this air pollution were recognised by early doctors, who sent patients with weak lungs or breathing problems to stay in the suburbs or the countryside (Brimblecombe, 1987).

Air pollution due to coal combustion also became a problem historically in Dublin city, as noted by Jonathan Swift in the Dublin Weekly Journal of 1729, who paints a grim picture of Dublin air quality in the early 18th century (Swift, 1729):

'Are there any people in this kingdom so free from asthmas as in the county of Kilkenny; not only the inhabitants, but all that resort thither can testify, and much is owing to thier (sic) fire, free from smoke. The constant thick cloud of smoke that hangs over Dublin is so nauseous, the air so corrupted, that the smell of the smoke is perceptible some miles off, in somuch that few or none, ever escape without some disorder. Who is there here that can't see the cause and has not felt the effect. None but those that are inur'd to this fire and smoke that has so intoxicated their brains that they are void of all thier senses, and in such

a lethargy, they will not seek relief. The physicians in Dublin make it thier constant practice to remove thier patients to some purer air near the suburbs, out of the smoke of the city, which in winter is so thick and cloudy, enough to stifle man and beast, so great an influence that it effects even the blossom and bloom of the flowers in the spring. And the chief cause of the bad air about Dublin, proceeds from the great quantity of smoke in the coals used here, the best proof that can be, by your senses, in feeling and smelling.'

In 1990, legislation was introduced which banned the sale of bituminous coal in Dublin. This led to a large reduction in atmospheric smoke and sulphur dioxide concentrations in the Dublin area. Many households now use natural gas or electric storage heaters, rather than coal, for home heating purposes, resulting in further reductions in smoke and sulphur dioxide concentrations.

Though air pollution due to emissions from domestic and industrial combustion of coal is no longer a problem in most major cities, another source of emissions due to fuel combustion was introduced in the early 20th century, and has developed into a major source of air pollution, particularly in major cities, namely, the automobile. In 1907, Asquith, the future Prime Minister of England, called the motor car 'a luxury which is apt to degenerate into a nuisance', a statement which many people would claim has turned out to be true. This new pollutant added to the existing problem, creating serious and prolonged smog episodes, such as the London smog of 1952, which is estimated to have been responsible for several thousand deaths.

In recent decades, road transport emissions have continued to increase and are now regarded as priority atmospheric pollutants. The increased number of cars on the road may well offset the benefits of reductions in unit emissions, although, at present, total emissions from vehicles are dropping slightly each year (PORG, 1997). At the start of 1996 there were 1,262,503 mechanically propelled vehicles on Irish roads, and this number is set to increase in the coming years. A large range of pollutants is emitted from vehicle exhausts, including carbon monoxide, carbon dioxide, oxides of nitrogen, particulate matter and a range of volatile organic compounds, including toxic compounds such as formaldehyde, benzene and 1,3-butadiene, which are known carcinogens.

The fuels which are used in most road vehicles (i.e. petrol and diesel) are composed mainly of a complex mixture of hundreds of hydrocarbon compounds. Hydrocarbons consist only of the elements hydrogen (H) and carbon (C), such as benzene (C_6H_6). It is not surprising, therefore, that a large component of vehicle emissions is composed of products of hydrocarbon reactions (other hydrocarbons) and unburned (vaporised) raw fuel components. Many of the more volatile hydrocarbons, with between two and ten carbon atoms, are included in the definition of volatile organic compounds (VOCs), which are normally defined as any compounds which are involved in the production of photochemical oxidants (Warren Spring Laboratory, 1991), although the USEPA provides a more rigorous definition as: any organic compound with a vapour pressure of greater than 0.13 kPa at 20 °C, and standard pressure (Warren Spring Laboratory, 1991). Photochemical oxidants are secondary products formed by the interaction of VOCs and oxides of nitrogen in the presence of sunlight (ultraviolet radiation). The most important of these photochemical oxidants is ozone (O_3), which is a major pollutant in cities such as Los Angeles, Mexico City and Rio De Janeiro (World Health Organisation (WHO)/United Nations Environment Programme (UNEP) (1992)). Photochemical oxidants such as ozone can cause respiratory problems, particularly in susceptible groups (such as the elderly), and are also associated with damage to building materials and vegetation (Kiely, 1997). Hydrocarbon compounds emitted from vehicles are major precursors of photochemical oxidants. Moreover, many hydrocarbons are toxic pollutants in their own right.

Another important source of hydrocarbons is industrial emissions (see Section 2.4) from processes which use hydrocarbons as raw materials. Hydrocarbon emissions from point sources such as these can result in locally elevated ambient hydrocarbon concentrations, which can be significantly higher than those at roadside sites. Emissions from such facilities are normally of concern because of their impact as a primary pollutant, rather than because of their involvement in the production of photochemical oxidants. A directive has recently been adopted on the limitation of the emissions of volatile organic compounds (VOCs) due to the use of organic solvents in certain activities and installations (Council of the European Communities (CEC), 1999b). The directive covers organic solvent emissions from stationary pollution sources in several sectors including commercial and industrial sources such as the pharmaceutical industry and dry cleaning facilities, and specifies emission limit values for each sector. This directive should result in significant reductions in emissions from activities and installations which use organic solvents (CEC, 1999b).

1.1.2 Introduction to Air Pollution Assessment

It is therefore vital to be able to assess the atmospheric concentrations of these compounds, particularly in areas where elevated concentrations may be expected. These include roadside locations, petrol stations, fuel storage depots, airports, sea ports, sewage treatment works, incinerators and industrial areas where hydrocarbons are used as raw materials. This latter group includes such processes as adhesive and paint production, rubber manufacture, oil refining and many pharmaceutical or chemical production processes. An immense number of possible sources of hydrocarbons can be identified throughout any industrialised country. Because of their health impacts, as both a primary pollutant and in the production of secondary pollutants, ambient hydrocarbon concentrations need to be quantified to assess their compliance with current and future limit values, and hence to decide whether action needs to be taken to reduce emissions of these compounds.

In order to decide on the measures which should be taken to control air pollution problems caused by atmospheric hydrocarbon emissions, it is first necessary to ascertain the extent of the problem and identify the main sources. This is an important aspect of the latest 'ambient air quality framework directive' for the European Union, which requires each member state to make an initial assessment of the air quality over its entire territory (European Commission, 1998). The directive specifies that each member state must be divided into zones, and the ambient air quality must be monitored in each zone.

Although measurements are required under the directive, provision is also made for the use of dispersion modelling to predict ambient air quality in large areas, where it would not be feasible to install monitoring stations (European Commission, 1998). Dispersion models are an important tool in current air quality management, and are specified in the air quality framework directive as a 'key concept' in the characterisation of current ambient pollution levels and in the prediction of the impact of proposed emissions reductions on future air quality - an important task which cannot be carried out using measurements. Moussiopoulos (1997) comments that monitoring can not rely on measurements alone, as observations are made at few locations and may, therefore, not be representative for larger areas. If emissions from a given source are known, dispersion modelling can be used to predict ambient concentrations at a given location at a given time. Results from dispersion modelling are not as accurate as measurements; but they do provide greater spatial coverage. Modelling tools may, therefore, prove extremely useful for EU Member States in

fulfilling their obligation to assess and report on the area(s) where threshold values are approached or exceeded, in accordance with existing EU directives (Moussiopoulos, 1997).

Measurement studies are required to check compliance with ambient air quality limit values, and also to characterise the hydrocarbon concentrations at a given location. The accuracy of current dispersion models is not sufficient to characterise fully the hydrocarbon concentrations at a given location, or the impact of emissions from a particular source. Models are, however, very useful as screening tools, to make initial assessments as to whether or not detailed monitoring is required at a particular location. Larger ambient air quality datasets can help to improve the accuracy of dispersion models by further characterising, spatially and temporally, the expected ambient air quality due to emissions from a given source type. Measurement studies carried out in conjunction with modelling studies can provide accurate results which may be used to evaluate dispersion models. Over the past number of years, such relative assessment of model performance has become an increasing area of research, particularly as dispersion models are now being used in support of laws and regulations (Riswadkar and Kumar, 1994) and must therefore be shown to be reliable. Air quality data can also be used in complex models to predict photochemical oxidant production due to the interaction of VOCs (including many hydrocarbons) and oxides of nitrogen. Detailed knowledge of ambient air hydrocarbon composition is a prerequisite for photochemical modelling (Lanzerstorfer and Puxbaum, 1990).

At present, benzene (a known carcinogen) is the only hydrocarbon which has a proposed limit value specified under EU law. Commission proposal 'COM (1998) 591 final' specifies a limit value for benzene of 5 $\mu g/m^3$ as an annual mean concentration (approximately 1.6 ppb) (CEC, 1998a). In the UK, however, a limit value is also specified for 1,3-butadiene (another carcinogen). The UK limit values for benzene and 1,3-butadiene are 5 ppb and 1 ppb, respectively, as a running annual mean (Department of the Environment and the Scottish Office, 1997). A further impetus to measure hydrocarbon concentrations is contained in the most recent proposed EU ozone directive (CEC, 1999a). This is a daughter directive to the air quality framework directive, providing information on recommended ozone precursors to be measured including NO, CO, and a range of 30 hydrocarbons.

Within this context, the Department of Civil, Structural and Environmental Engineering in Trinity College has established a mobile air monitoring unit, capable of measuring atmospheric concentrations of up to 60 different hydrocarbons. The unit also contains other instrumentation which can measure atmospheric particulate concentrations (diesel emissions, dust particles, etc.), nitrogen dioxide (NO_2) and carbon monoxide (CO). The unit is also fitted with a weather station which measures windspeed, wind direction and temperature, allowing pollutant concentrations to be correlated with meteorological data.

1.2 OBJECTIVES AND SCOPE OF RESEARCH

The scope of this research was to carry out hydrocarbon monitoring at a range of different site types in Ireland. The initial objective of this project was to commission the on-line hydrocarbon monitoring system, including initial set-up, conditioning, calibration and testing of the system. Three studies were carried out, in which hydrocarbon concentrations were monitored at an urban centre (Phase 1), and rural and industrial (Phase 2) monitoring locations. The location of each of these sites is illustrated in the map of eastern Ireland, Figure 1.1, while more detailed maps are included in Chapter 4 (urban site) and Chapter 6 (rural and industrial sites). The main objectives of each study are described below.

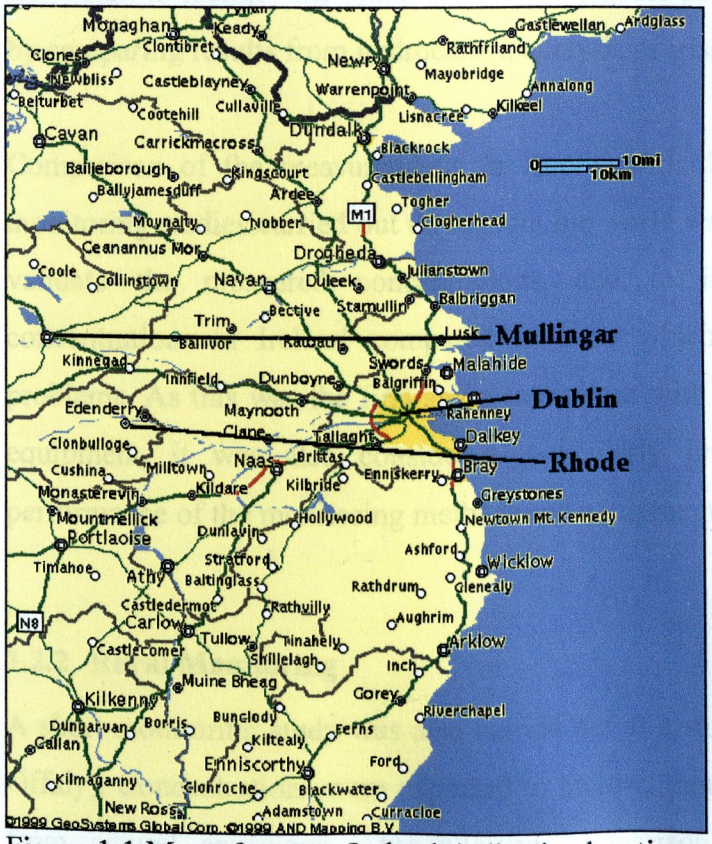


Figure 1.1 Map of eastern Ireland, indicating location of each monitoring site

1.2.1 Urban Monitoring

The first site where monitoring was carried out was at a busy roadside location in Dublin city centre. Measurements at this site were carried out to characterise short-term (hourly) variations in roadside concentrations of a range of hydrocarbons in Dublin. Only long-term averages had been previously reported, and a much smaller range of hydrocarbons (benzene, toluene, ethylbenzene and the xylenes) was measured. Hourly measurements allow detailed analysis of the hydrocarbon data, in terms of source identification and other factors which affect the short-term concentrations. Characterisation of the hydrocarbon composition is also necessary if photochemical modelling is to be carried out, to assess the ozone creation potential due to the pollutants present in the atmosphere (mainly hydrocarbons and NO_X are involved in ozone production).

Assessment of the impact of meteorological factors on measured concentrations was considered a main objective at this site, particularly the effect of temperature on evaporative emissions from vehicles. Identification of the relationship between the measured compounds, and identification of the main sources of these hydrocarbon emissions were also considered important. Emissions from vehicles at this site were expected to be large (dominating the measured concentrations), therefore, the opportunity was taken to identify the relationship between fuel and ambient hydrocarbon components, by comparing results from hydrocarbon analysis of Irish fuels with ambient concentrations.

Comparison of the measurements in Dublin with those from a range of hydrocarbon monitoring studies carried out throughout the world was also considered important, both to validate the measured concentrations, and to indicate the relative hydrocarbon concentrations in Ireland compared to areas which have smaller or larger pollution problems. As this was the first study carried out with the on-line hydrocarbon monitoring equipment, it was also considered particularly important to assess the utility and performance of the monitoring methods and equipment used.

1.2.2 Rural Monitoring

A short monitoring study was also carried out at a rural site in the midlands (Rhode, Co. Offaly). Concentrations were expected to be low, though some contribution was expected from natural emissions. This allowed comparison of rural and urban hydrocarbon

measurements, and identification of the main hydrocarbon sources in rural areas. These measurements were expected to give an indication of background concentrations which could be anticipated at a rural site, and identify any hydrocarbon emissions from local sources, such as the nearby peat-burning power station and emissions from the nearest towns and villages. The impact of the power station on measured hydrocarbon concentrations was expected to be negligible. Rather, monitoring at Rhode was carried out as part of an Environmental Protection Agency (EPA) project, and the priority pollutants measured at this site were sulphur dioxide, particulates and oxides of nitrogen.

1.2.3 Industrial Monitoring

The third monitoring site, at Lynn Industrial Estate, in Mullingar (Co. Westmeath) typified the situation where monitoring may be required at a complex location, with emissions likely from a number of point sources (industrial manufacturing emissions and fugitive emissions from petrol stations), and area sources (vehicle emissions). It was decided to monitor at such a site as very little published work exists on the assessment of hydrocarbon concentrations due to emissions from low level point sources (emissions from low stacks and vents). However, emissions from such sources can be significant, and can lead to hydrocarbon concentrations in the vicinity of the source significantly higher than those experienced near even the most heavily-trafficked roads. The location in Mullingar was selected after a detailed study of known sources of hydrocarbon emissions throughout Ireland, using the Environmental Protection Agency (EPA) database of Integrated Pollution Control (IPC) licensed facilities and their emissions.

Once Lynn Industrial Estate had been selected as the monitoring location, the position of the monitoring site was chosen using dispersion modelling of the known emissions from two IPC licensed facilities in the industrial estate. On-line hydrocarbon analysis and pumped and passive (new radial diffusion method) tube sampling techniques were employed at this site. The utility of each of these methods in point source monitoring and the situations in which each method can be used most effectively were assessed. The advantages and disadvantages of each method are noted. The utility of two dispersion models, ISC (USEPA, 1995) and ADMS (CERC, 1999), in predicting longer term and short-term (hourly) hydrocarbon concentrations is assessed by comparing the results from on-line, pumped tube and passive tube analyses to modelled hydrocarbon concentrations.

This monitoring study was also carried out as part of an EPA project, and it is hoped that the methodology employed during this project will enhance future studies in this area, and also make model users aware of the benefits and shortcomings of Gaussian dispersion models, and the merit of using a combination of monitoring and modelling methods.

1.3 THESIS OUTLINE

Chapter Two provides general background information related to ambient hydrocarbons. Background information on the impacts of hydrocarbon concentrations on human health, and on the formation of secondary pollutants, such as ozone, are detailed. The dominant sources of hydrocarbons are also discussed, and their fates in the atmosphere are described. Commonly used sampling and analysis methods are also discussed and the advantages and disadvantages of each method are detailed. Finally, a review of previous hydrocarbon monitoring studies carried out in Ireland, the UK, other European countries and elsewhere is presented.

Chapter Three describes the monitoring equipment which was used during the study. The on-line monitoring system is described in some detail, including the initial equipment set-up, testing and conditioning. Details of the pumped and passive sampling tubes used during monitoring at Lynn Industrial Estate are also presented.

Chapter Four provides an introduction to the hydrocarbon monitoring which was carried out during Phase 1 monitoring at the Dublin roadside site. The monitoring site is described in Section 4.1, including details of typical traffic flows and a typical composition of the Dublin vehicle fleet. As the first operation of the on-line unit was at this site, detailed assessment of the system performance is presented, including details of the calibration procedure used, and the qualitative and quantitative precision of the equipment. This is presented in Section 4.2. In Section 4.3, summary results for all hydrocarbon monitoring carried out in Dublin are presented. Finally, Section 4.4 compares the meteorological data collected at the monitoring unit with that collected by Met Eireann at their synoptic monitoring station at Dublin airport.

In Chapter Five, analysis of the hourly hydrocarbon concentrations from Phase 1 monitoring is presented. Section 5.1 concentrates on analysis of the hourly data, describing

the typical diurnal patterns described by the hydrocarbons, and the correlation which can be expected between the measured concentrations. The concept of the representative day is also introduced, which identifies the actual day which is closest to the averaged diurnal pattern. In Section 5.2, the impact of meteorological variations on measured hydrocarbon concentrations is assessed, particularly the effect of temperature variations on evaporative emissions from vehicles. The impact of atmospheric stability on night-time hydrocarbon concentrations is also investigated. Pollution roses are used to assess the likely sources of the measured hydrocarbons. In Section 5.3, various methods are used to estimate the contribution of vehicle emissions to the measured hydrocarbon concentrations. Principal component analysis indicates that most of the measured hydrocarbons are associated strongly with vehicle emissions, while comparison of the measured concentrations with tunnel and exhaust measurement studies is carried out to assess the agreement between ambient roadside concentrations and these measurements which are known to be dominated by vehicle emissions. The relationship between typical Irish fuels and ambient hydrocarbon composition is also investigated by comparing results from hydrocarbon analysis of Irish fuels collected during the project with the roadside concentrations.

Chapter Six provides an introduction to the hydrocarbon monitoring which was carried out at the industrial and rural monitoring sites during Phase 2 monitoring. The two monitoring sites are described in Section 6.2. The Monitoring programmes at Mullingar and Rhode are described in Section 6.3 and 6.4, respectively. The qualitative and quantitative precision for the on-line monitoring equipment for the Mullingar monitoring period is also discussed in Section 6.3. Section 6.5 presents summary results for on-line, pumped sampling and passive sampling analyses carried out at Lynn Industrial Estate (Mullingar), and also results for on-line analysis carried out at Rhode. The frequency distribution of the data collected at Mullingar is also investigated. Comparison of the meteorological data collected at the Mullingar site and at the Met Eireann regional monitoring station is presented in Section 6.6. Dispersion modelling is discussed in Section 6.7, including background information on dispersion modelling and the two models which are used in this study. Details of the modelling programme at Lynn Industrial Estate, including the emissions estimates and other model input parameters, are also included.

Chapter Seven concentrates on the analysis of the results from the air quality assessment carried out at Lynn Industrial Estate. Section 7.2 investigates the variation in the hourly

measured concentrations at Lynn Industrial Estate, including correlation analysis and presentation of diurnal patterns. The impact of meteorological variations on measured concentrations, particularly wind direction and atmospheric stability, is presented in Section 7.3. The results from the analysis of pumped and passive tube samples is presented in Section 7.4, including comparison of samples collected at the monitoring unit with the corresponding on-line results. Summary results from dispersion modelling are presented in Section 7.5. Results from dispersion modelling of emissions from the two IPC-licensed facilities are compared to hourly measurements in Section 7.6. Several methods (both graphical and numerical) are employed to compare the measured and modelled results, in terms of overall performance, and in terms of the model ability to predict the highest measured concentrations. Assessment of the reliability of model inputs is also made. Based on these analyses, the performance of the two models is compared. Analysis of the results from rural hydrocarbon monitoring at Rhode are presented in Section 7.7.

Conclusions are drawn in Chapter Eight, based on the hydrocarbon monitoring carried out at each of the three monitoring sites.

2. BACKGROUND TO HYDROCARBON MONITORING THEORY

2.1 INTRODUCTION

This chapter provides background information on hydrocarbons and their measurement in the atmosphere. Section 2.2 describes the hydrocarbon species which are present in the atmosphere, while Section 2.3 summarises the health effects of several toxic hydrocarbons and the general health impacts which are associated with hydrocarbons. Sources of atmospheric hydrocarbons are presented in Section 2.4. Removal mechanisms of hydrocarbons from the atmosphere are outlined in Section 2.5. Commonly used methods for sampling and analysis of ambient hydrocarbons are detailed in Section 2.6. Finally, previous hydrocarbon monitoring studies in Ireland, the UK, Europe and elsewhere are summarised in Section 2.7.

Hydrocarbons are defined as an 'organic compound consisting exclusively of the elements carbon and hydrogen' and as raw materials are derived principally from petroleum, coal tar, and plant sources (Lewis, 1993). Increased interest in hydrocarbons over the last fifty years has resulted from greater awareness of their harmful effects as both primary pollutants and in the formation of secondary pollutants.

The problems associated with hydrocarbons came to prominence in the 1950s and 1960s as the city of Los Angeles in the United States began to experience severe smog episodes which lasted several days and caused sickness in both humans and flora. Haagen-Smit (1952) identified the important interactions between hydrocarbons, oxides of nitrogen and sunlight in the production of photochemical oxidants such as ozone. Other countries had experienced smog episodes, but up until this time these were usually associated with domestic and industrial burning of coal, such as the infamous smog episodes in the city of London (see Chapter 1). The smog in Los Angeles, however, was what is now referred to as 'photochemical smog'; ozone (O_3) usually being the main photochemical oxidant, others being peroxyacetyl nitrate (PAN) and nitrogen dioxide (NO_2).

Photochemical oxidants are formed due to a reaction between volatile organic compounds (VOCs) and oxides of nitrogen (NO_X) in the presence of sunlight (ultraviolet radiation). VOCs are a broader range of compounds than hydrocarbons, and only certain hydrocarbons

are included in the VOCs group. Warren Spring laboratory give the following working definition of a VOC (Warren Spring Laboratory, 1991):

'a volatile organic compound is any organic compound, other than methane, that is capable of producing photochemical oxidants as a result of reaction with oxides of nitrogen in the presence of sunlight.'

The United States Environmental Protection Agency (USEPA) describes VOCs as organic compounds having a vapour pressure of greater than 0.13 kPa at 20°C, 1 atm (Derwent, 1995). Because of their low reactivity, many hydrocarbons may not be classified as VOCs using these definitions, while some could be described as semi-volatile organic compounds (SVOC). Strictly speaking, only light hydrocarbons, in the C_2 - C_{10} range, are classified as VOCs due to their greater reactivity compared to the heavier hydrocarbons (> C_{10}) (Bonsang and Boissard, 1999). However, this strict definition of a VOC is rarely adhered to, and VOCs are usually considered to be any carbon containing compound found in the atmosphere, excluding elemental carbon, carbon monoxide and carbon dioxide (Derwent, 1995).

2.2 HYDROCARBON SPECIES

The two main types of hydrocarbons are aliphatic (straight chain) and cyclic (closed ring).

The principal species of aliphatic hydrocarbons include (Lewis, 1993):

1) *Alkanes* (also known as paraffins, e.g. ethane, propane, pentane) which have the generic formula C_nH_{2n+2}. These are saturated compounds with single bonds. Saturation is the state in which all available valence bonds of an atom (especially carbon) are attached to other atoms. Saturated compounds tend to be relatively unreactive.

2) *Olefins* (e.g. ethylene, propylene, 1-butene) which have the generic formula C_nH_{2n}. This group is further sub-divided into alkenes which are unsaturated compounds with one double bond, and alkadienes which are unsaturated and have two double bonds. As olefins are unsaturated compounds they tend to be highly reactive.

3) *Alkynes* (also known as acetylenes, e.g. acetylene) which have the generic formula C_nH_{2n-2}. These are unsaturated hydrocarbons with triple bonds.

The principal species of cyclic hydrocarbons includes:

1) *Alicyclic* compounds contain three or more carbon atoms in a ring structure with properties similar to those of aliphatic compounds. The alicyclic group consists of cycloparaffins (cycloalkanes or naphthenes), cycloolefins, and cycloacetylenes (cyclynes).

2) *Aromatic* compounds are unsaturated, hexagonal ring compounds with three double bonds. Compounds can have either single ring (benzene group), two rings (naphthalene group) or three rings (anthracene group).

The hydrocarbons measured during this study were from the aromatic, alkene, alkane and alkyne groups. Several of the compounds are isomers (e.g. the xylene isomers, ortho, meta and para-xylene). An isomer indicates one of two or more molecules having the same number and kind of atoms and hence the same molecular weight, but differing in respect to the arrangement or configuration of the atoms (Lewis, 1993).

As mentioned above, the reactivity of different hydrocarbons can vary significantly, and has a major influence on the expected lifetime of each hydrocarbon in the atmosphere. A distinction can be drawn between reactivity and volatility in describing hydrocarbons. Hydrocarbon reactivity is discussed in Section 2.5. Volatility is defined as the tendency of a solid or liquid material to pass into the vapour state at a given temperature (Lewis, 1993). Volatility is an important parameter in assessing evaporative emissions, as volatile compounds such as butane are likely to experience substantial evaporation from vehicle fuel tanks. In fact, the high volatility of the butanes can also account for substantial losses during refining and distribution (QUARG, 1993). However, because the butanes are saturated hydrocarbons, they are not as reactive as some of the unsaturated alkenes and aromatics. While individual alkenes and aromatics generally have a greater ozone creating potential than the alkanes, the more abundant alkanes can have a more significant impact on ozone concentrations due to the larger quantities present in the atmosphere.

2.3 HEALTH EFFECTS OF HYDROCARBONS

Initial concerns relating to the health impacts of hydrocarbons arose due to their role in the production of photochemical oxidants, which were known to be injurious to human health. However, investigation of the health effects of individual hydrocarbons indicated that several hydrocarbons are themselves toxic compounds. Many act as irritants at low level continuous exposure dosages. Hydrocarbons are thought to be linked to the "sick building syndrome", which can arise in new buildings where hydrocarbons are emitted from solvents used in construction, or from new furnishings, carpets and paints in the workplace.

Hydrocarbons are also responsible for many of the odours experienced in everyday life (Warren Spring Laboratory, 1991). In general, when hydrocarbon concentrations are low, their odour will not be detectable, and the odour threshold is usually a good indication of critical hydrocarbon concentrations.

2.3.1 Individual Hydrocarbons

Previously, the technical expertise and costs of gas chromatographic analysis have prevented speciated hydrocarbon measurements from becoming a standard component of air pollution monitoring networks (Sexton and Westberg, 1984). More recent speciated monitoring studies, such as the UK hydrocarbon monitoring network (Dollard *et al.,* 1995; PORG, 1997), and the US ozone and precursor monitoring network (USEPA, 1996b; Evans *et al.,* 1992; Lewis, 1997) have revealed the large number of hydrocarbons present in the atmosphere in varying quantities, in both urban and rural areas. The speciation of ambient hydrocarbons has had two main consequences. The first is the identification of the ambient concentration of those compounds which make the largest contribution to photochemical oxidant formation. The second consequence of speciation is the quantification of the possible impact of individual hydrocarbons on human health.

Indoor and in-vehicle hydrocarbon concentrations can be higher than ambient outdoor concentrations (Seifert and Abraham, 1982; Chan *et al.,* 1994; Kostiainen, 1995; Jo and Park, 1999; Leung and Harrison, 1999) and are important sources in assessing the metabolic uptake of a pollutant.

Individual hydrocarbons can have a range of different health effects and chronic (i.e. long term) exposure is associated with carcinogenic, mutagenic (a mutagen is an agent that causes heritable chromosome change at the cellular level), teratogenic (a teratogen is an agent that causes physical defects in the developing embryo) and neurological health effects (Cohen *et al.,* 1991). The documented health impacts of several individual toxic hydrocarbons are detailed below. There still exists large uncertainty about the health effects of many air pollutants, particularly chronic effects. Acute (short-term) effects are generally associated with irritation of the eyes, nose and throat. Hydrocarbons from C_4 upwards are reported to exhibit somewhat greater irritancy to the upper respiratory tract and increasing depression of the central nervous system (HSE, 1992b).

Exposure of subjects to a mixture of 22 VOCs (including hexane, xylene, ethylbenzene, and trimethylbenzene) at low concentrations for a short period of time (< 3 hours) resulted in a significant increase in irritation of the eyes, nose and throat (Molhave *et al.,* 1986). However, the lowest exposure concentration employed in this study (5 mg/m^3 in total) was higher than would generally be found in the ambient atmosphere. Although many of the hydrocarbons mentioned below have serious health effects at high concentrations, ambient levels generally experienced in urban areas are unlikely to cause serious health effects in the majority of healthy individuals. However, the long term effects of low concentrations of many compounds have yet to be determined, and the general health effects of most individual hydrocarbons are still unclear. Most hydrocarbons are non-toxic or are mildly toxic in the short-term.

Benzene

Benzene is a known carcinogen. Chronic exposure to low concentrations of benzene vapour causes blood disorders and damage to bone marrow, inducing aplastic anemia and leukaemia (USEPA Unified Air Toxics website (*www.epa.gov/ttn/uatw/hapindex.html*); WHO, 1987; Department of Health, 1997; Beim *et al.,* 1998; Rushton and Cameron, 1999). Benzene in the bloodstream is distributed mainly to fat rich tissue in the body (such as bone marrow) due to its high liposolubility (Romieu, 1999). It is estimated that a lifetime exposure to 1 $\mu g/m^3$ of benzene (~ 0.3 ppb) would result in between 0.08 and 10 excess leukaemia deaths per million population (Romieu, 1999). Guerra *et al.* (1995) carried out extensive benzene monitoring in Milan, in attempting to identify the carcinogenic risk

associated with normal exposure to this compound. The vast majority of measured benzene concentrations were associated with vehicle emissions. It was calculated that exposure to benzene results in 4 to 10 percent of the 300 deaths (on average) due to leukaemia recorded annually in Milan. Acute (short-term) health effects in humans include drowsiness, dizziness, headaches, irritation of skin, eyes and throat, and unconsciousness. However, the concentrations generally present in the atmosphere are unlikely to result in the onset of such effects. It has been found that those occupationally exposed to 1 ppm or less of benzene have not shown any observable carcinogenic effects (CONCAWE, 1996). The suggestion by CONCAWE (1996) that there is a safe exposure level for benzene is at odds with most other studies. The WHO (World Health Organisation) recommend that, because of its carcinogenic effects, there can be no safe level of benzene in the ambient air (WHO, 1987). The USEPA has set an inhalation reference concentration of 0.1 ppm (100 ppb). The Reference Concentration (RfC) is the level of continuous exposure that is unlikely to cause an appreciable risk of deleterious non-cancer health effects during a lifetime (Rushton and Cameron, 1999). The average annual concentration measured in UK cities is in the range 1 - 2 ppb (PORG, 1997), well below the RfC value. The UK limit for benzene is 5 ppb as a rolling annual mean (Department of the Environment and the Scottish Office, 1997). Table 2.1 describes the health effects due to inhalation of benzene (Rushton and Cameron, 1999).

Table 2.1 Health effects due to inhalation of benzene (Rushton and Cameron, 1999)

Effect	Description	Length of exposure	Level (ppm)
Death		5 - 10 min	20,000
Central nervous system	Vertigo, drowsiness, headache, nausea	Hours	250 - 500
Haematological	Pancytopenia, aplastic anemia, myelodysplastic syndrome	Years	100
	Cytopenia	Years	35
Mutagenic	Chromosome aberrations	Years	20 - 100
	Adduct formation	Years	13 - 63
Carcinogen	Leukaemia	Years	20 - 50

1,3 - butadiene

1,3-butadiene has also been identified as a likely carcinogen (USEPA Unified Air Toxics website (*www.epa.gov/ttn/uatw/hapindex.html*); WHO, 1987; Department of Health, 1997; Beim *et al.*, 1998; Rushton and Cameron, 1999). The USEPA classify 1,3-butadiene as a

probable human carcinogen of medium carcinogenic hazard (USEPA Unified Air Toxics website (*www.epa.gov/ttn/uatw/hapindex.html*)). As with benzene, short-term exposure can lead to irritation of the eyes, nose and throat, headaches and unconsciousness. The USEPA has not established an RfC value for 1,3-butadiene, however, the UK limit for the annual rolling average 1,3-butadiene concentration is 1 ppb (Department of the Environment and the Scottish Office, 1997). The average annual concentration measured at UK automated monitoring sites is below 0.5 ppb (PORG, 1997). It has been suggested that benzene and 1,3-butadiene exposure may account for around 10 percent of leukaemia incidence across the UK (Colls, 1997).

Ethylbenzene

As with many hydrocarbons, acute exposure to ethylbenzene results in irritation of the eyes, nose and throat, dizziness and chest constriction (UAT website (*www.epa.gov/ttn/uatw/hapindex.html*); Beim *et al.,* 1998). Chronic exposure has been linked to effects on the blood and depression of the central nervous system. The USEPA RfC value for ethylbenzene is 1 mg/m^3 (~ 225 ppb). In contrast, a typical annual mean concentration from the UK hydrocarbon monitoring network is less than 1 ppb (PORG, 1997).

n-Hexane

Acute exposure to high concentrations of hexane causes mild depression of the central nervous system and irritation of the skin and mucous membranes (UAT website (*www.epa.gov/ttn/uatw/hapindex.html*); Beim *et al.,* 1998). Chronic exposure to hexane is associated with polneuropathy, numbness in the extremities, muscular weakness, blurred vision, headache and fatigue (UAT website (*www.epa.gov/ttn/uatw/hapindex.html*); HSE, 1992c; Beim *et al.,* 1998). The USEPA RfC value for hexane is 0.2 mg/m^3 (~ 56 ppb), while a typical annual average concentration from the UK hydrocarbon monitoring network is less than 1 ppb.

Toluene

Acute exposure to high concentrations of toluene results in irritation of the eyes, nose, lungs and throat, headaches and shortness of breath (UAT website

(*www.epa.gov/ttn/uatw/hapindex.html*); WHO, 1987; HSE, 1989; Beim *et al.,* 1998; Rushton and Cameron, 1999). Chronic exposure results in depression of the central nervous system. The USEPA RfC value for toluene is 100 ppb, compared to a typical ambient annual average toluene concentration in the UK of less than 5 ppb (PORG, 1997).

Xylene Isomers

Exposure to the xylene isomers, ortho, meta and para-xylene, results in irritation of the eyes, nose and throat (UAT website (*www.epa.gov/ttn/uatw/hapindex.html*); Beim *et al.,* 1998). Chronic effects include central nervous system effects such as headache and dizziness, and liver and kidney damage.

The compounds detailed above are generally classified as toxic hydrocarbons. Others may be classified as asphyxiants (e.g. butenes, ethane, propylene) while some act as narcotics at high concentrations (e.g. n-pentane), with others acting as irritants (e.g. isoprene).

Many epidemiological experiments have been carried out to assess the impact of air pollutants on human health. However, it has proved very difficult to find a definitive link between levels of pollutants found in the ambient atmosphere and human illnesses. It is generally thought that healthy individuals are unlikely to be affected by normal ambient concentrations of air pollutants (Department of Health, 1997). However, those with existing health problems are more likely to be affected by air pollution. A review of the medical links between air pollution and asthma (Niven and Longhurst, 1995) concluded that those suffering from asthma exhibit reduced lung function after exposure to a mixture of air pollutants, and a greater propensity for asthmatic attack due to this reduction in lung function. However, this study found no convincing evidence linking increased asthma in children with air pollution, in agreement with other studies carried out in the UK (Department of Health, 1997). However, it has been observed that in the past 30 years there has been an increase of 50 percent in the number of cases of childhood asthma in the UK, and also increases in other allergies such as hay fever (Department of Health, 1997). A more recent study (Herbarth *et al.,* 1998) suggests a link between the exposure of new born babies and very young children to indoor and outdoor volatile organic compounds and the development of allergies. Air pollutants pose the greatest risk to susceptible population groups such as the young and the elderly (with developing and deteriorating respiratory and

cardiac systems, respectively) and those with existing respiratory problems (Department of Health, 1997; Romieu, 1999).

Ethylene is the only hydrocarbon to have a known effect on plants. It is associated with sepal withering, leaf abnormalities, flower dropping and abscission (Arya, 1999). Older leaves are generally most affected. Ethylene is released from plants in response to environmental stresses (Mansfield and Lucas, 1996; Fall, 1999). However, very high concentrations of ethylene results in damage to plants.

2.3.2 Ozone Formation and Health Effects

While many hydrocarbons have no known effect on humans, they may be involved in the production of photochemical oxidants which can have quite serious health effects. As mentioned previously, hydrocarbons are an important factor in the production of photochemical oxidant pollution, mainly ozone (O_3) and PAN. The reactions which occur to form ozone are extremely complex. The basic photolytic process is as follows (Harrison, 1996; Kiely, 1997):

i $NO_2 + h\upsilon \rightarrow NO + O$

ii $O + O_2 \rightarrow O_3$

iii $O_3 + NO \rightarrow NO_2 + O_2$ (Ozone scavenged by NO)

$h\upsilon$ = Photon of solar radiation or energy

Hydrocarbons make this cycle unbalanced, otherwise the amount of ozone created and destroyed would be equal. Peroxy radicals (RO_2) are produced by the degradation of hydrocarbons through oxidation of NO to NO_2, which leads to net formation of ozone. The process is as follows (Nurnberg, 1985) :

$RO_2 + NO \rightarrow RO + NO_2$

$NO_2 + h\upsilon \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

NET RESULT = $RO_2 + O_2 + h\upsilon \rightarrow RO + O_3$

M is an unreactive third molecule such as N_2

The health effects of ozone on humans can be quite serious, particularly if the exposure is continuous and if an individual is particularly susceptible (Boubel, 1994). The main effects on humans are a decrease in pulmonary function, coughing, and irritation of the eyes and mucous membranes. Ozone is also known to cause headaches.

Ozone has other environmental effects, forest damage and crop losses have been attributed to ozone (WHO/UNEP, 1992) and particular types of vegetation are very susceptible to ozone damage. According to the WHO, damage to building materials (and other materials such as nylon and rubber) and to works of art are linked to excessive levels of O_3. The effects of ozone are quite varying and costly to the environment. It is estimated that in the Canadian state of Ontario, the damage caused to food production due to ozone damage can be as high as US$70 million per year (Ciccioli, 1993). In Ireland, ozone concentrations are generally low and limit values are rarely exceeded (McGettigan, 1998). However, it has been reported that low concentrations of ozone and sulphur dioxide together have a greater effect on pulmonary function than when either is breathed separately (Ball, 1976).

2.4 SOURCES OF HYDROCARBONS

As mentioned previously, hydrocarbons are derived principally from petroleum, coal tar, and plant sources. Hence, processes involving any of these raw materials are likely to result in hydrocarbon emissions. The principal sources of anthropogenic (resulting from human activities) hydrocarbon emissions in most countries are combustion of fossil fuels and organic solvent use (Derwent, 1995; EEA, 1995; Friedrich and Obermeier, 1999). Evaporation is also a very important source of hydrocarbons in the air, including evaporation of petrol from motor cars, evaporation during distribution and storage of liquid hydrocarbons (including petrol), and evaporation during processes involving organic solvent use. Other sources of hydrocarbon emissions to the atmosphere include oil refining, agriculture and landfill sites. Biogenic (natural) emissions can also be important sources of hydrocarbons, particularly in rural atmospheres.

Different sources of hydrocarbons have markedly different hydrocarbon 'fingerprints' and hence the emissions may be of concern for different reasons. For example, emissions from vehicles may be of concern due to their photochemical oxidant creation potential, while emissions from the solvent industry may be of concern due to their toxic properties.

2.4.1 Hydrocarbons from Combustion of Fossil Fuels

It has been previously estimated that 96 percent of the global consumption of energy occurs in the northern hemisphere, with 86 percent between 30 and 60 degrees (OECD, 1975). Hence, emissions due to combustion of fuels is particularly important in these regions.

Particularly in urban areas, road vehicle emissions are one of the major sources of hydrocarbon emissions. The fuels used in these vehicles are a complex mixture of several hundred hydrocarbons (see Section 5.3.3)). The constituents of the fuel can have a significant influence on exhaust emissions, as a large percentage of these are unburned or partially oxidised fuel components. Under ideal conditions, fuel combustion would be complete as indicated below:

$$\text{Fuel (hydrocarbons)} + \text{air (oxygen and nitrogen)} \rightarrow$$
$$\text{Carbon dioxide} + \text{water} + \text{unaffected nitrogen}$$

However, in reality, the process is better represented as:

$$\text{Fuel} + \text{air} \rightarrow \text{Unburned hydrocarbons}$$
$$+ \text{nitrogen oxides} + \text{carbon monoxide} + \text{carbon dioxide} + \text{water}$$

Emissions from stationary combustion sources such as households and power stations tend to have a greater influence on suburban and rural areas. Again, incomplete combustion of the fuels leads to emissions of compounds other than carbon dioxide, water and nitrogen.

The more incomplete the reaction, the greater the resultant hydrocarbon emissions (Friedrich and Obermeier, 1999). Table 2.2 compares the hydrocarbon emission factors assigned to the combustion of different fossil fuels. In general, combustion of liquid or gaseous fuels leads to a lower emission factor than the combustion of solid fuels. Mopeds (two stroke engines) have the highest emission factor. Even though the emission factors for petrol vehicles with three-way catalysts are comparatively low, the larger number of cars imply that they still represent one of the most important sources of hydrocarbon emissions. Table 2.3 provides estimates of the hydrocarbon emissions from different fossil fuel types in the UK. In 1990, approximately 38 percent of hydrocarbon emissions in the UK were due to fossil fuel combustion, the majority of which were vehicle fuels (PORG, 1993).

Table 2.2 Hydrocarbon emission factors for fossil fuel combustion in Germany, kg per terajoule of fuel (Friedrich and Obermeier, 1999)

Source type	Description	Gas	Petrol	Diesel	Light fuel oil	Heavy fuel oil	Coal	Wood, other solid fuel
Passenger car	Petrol, without catalyst Petrol, with three-way catalyst		473 17					
Passenger car	Diesel, before 1990 Diesel, after 1996			38 33				
Light-duty vehicle	Petrol, without catalyst Petrol, with three-way catalyst		454 17					
Light-duty vehicle	Diesel			49				
Heavy-duty vehicle	Diesel, before 1990 Diesel, after 1996			170 135				
Moped	Two-stroke Two-stroke with uncontrolled catalyst		4859 2168					
Households	Space heating Warm water Cooking	5 8 25			5 5		400	350 1600 2000
Other consumers		5			5		30	210
Industry		5				8	30	210
Power plants		0.6				7	3	65

Table 2.3 Hydrocarbon emissions by type of fuel for the UK (K tonnes), (PORG, 1993)

Fuel type	1980	1985	1990	% of total for 1990
Coal	87	78	47	2
Solid smokeless fuel	5	4	3	-
Petroleum:				
Motor spirit	620	584	652	27
DERV	131	134	175	7
Gas oil	21	21	20	1
Fuel oil	4	3	4	-
Other petroleum	3	3	4	-
Other gas	4	5	5	-
Non-combustion emissions	1421	1435	1485	62
TOTAL	2297	2267	2395	100

Vehicle Emissions

Hydrocarbon emissions from vehicles are highly dependant on the compounds present in the fuel, as much of the exhaust emissions are unburned fuel components. Partial oxidation products will also be present in the exhaust emissions, and some of these may not have been present in the original fuel. These combustion products include acetylene and the suspected carcinogen 1,3-butadiene. Several factors can influence the actual emissions from a given vehicle. These include the fuel used, the state of tune of the vehicle, whether a catalyst is fitted to the vehicle and the situation in which the vehicle is being driven, such as heavy traffic or motorway driving.

As can be seen from Table 2.2, petrol vehicles with three-way catalysts emit substantially smaller quantities of hydrocarbons compared to non-catalyst and diesel vehicles. McGinty and Dent (1995) estimated that 80 percent of vehicles emissions in Europe (in the year 2000) would be from cars not fitted with catalysts. Emissions from both catalyst and non-catalyst equipped vehicles can increase significantly if the vehicle is not properly maintained and serviced. In the US, it has been estimated that nearly 30 percent of all vehicle emissions were due to less than one percent of the vehicle fleet (USEPA, 1993). In Australia, the Federal Office of Road Safety (1996), has shown that for a given fleet of vehicles, up to 80 percent of the total reduction in emissions achievable through proper vehicle maintenance and tuning, were delivered by only 20 percent of the vehicles. This study concluded that achieving acceptable air quality lies as much in ensuring that vehicles are well maintained as it does in introducing tighter new vehicle standards. This is

particularly important as existing catalyst equipped vehicles begin to experience deterioration in the performance of the catalyst. A detailed review of vehicle emissions assessment and control is presented by Field (1995).

Driving conditions can have a significant effect on emissions from vehicles, as indicated in Table 2.4. Emissions from catalyst equipped petrol engines are lower than or equal to diesel engine emissions for all driving modes except traffic jams. This is likely to be due to the fact that the temperature, and hence the efficiency, of the catalyst reduces while the vehicle is stationary or moving at low speed. For alkane compounds, in particular, catalyst efficiency can be reduced from over 90 percent to less than 20 percent when engine load is reduced from 50 percent to idle (Shore and Tonkin, 1991). Emissions from vehicles are also temperature dependant, with cold start emissions being significantly higher than those from a vehicle with a warm engine, especially for catalyst equipped vehicles. Roadway gradients also affect vehicle emissions, with both positive and negative slopes leading to greater emissions (Friedrich and Obermeier, 1999).

Table 2.4 Exhaust hydrocarbon emissions from different vehicle types due to different driving modes, grammes per kilometre (Friedrich and Obermeier, 1999)

Type	Description	Motorway mode	Rural mode	Urban mode	Traffic jam
Passenger car	Petrol without catalyst	0.87	0.86	2.14	4.58
Passenger car	Petrol with three-way catalyst	0.04	0.03	0.06	0.48
Passenger car	Diesel	0.04	0.05	0.12	0.23

Petrol is the most frequently used fuel in Irish vehicles, followed by diesel which is popular for HGVs and buses. The formulation of petrol can alter slightly from country to country but the basic constituents are still very similar. Diesel is a less volatile fuel than petrol, resulting in lower evaporative emissions (Garrett, 1994). Combustion of diesel fuel results in a larger proportion of heavier hydrocarbons (> C_{10}) in the exhaust, compared to petrol vehicles where lighter hydrocarbons are dominant in both fuel and exhaust (Zielinska and Fung, 1994; Sagebiel *et al.,* 1996). The heavier hydrocarbons emitted by diesel fuelled vehicles are often referred to as semi-volatile hydrocarbons. While other fuels such as LPG (liquefied petroleum gas) and electric power (batteries) are used in very few vehicles, the associated hydrocarbon emissions are very low (EIA, 1994).

Evaporative emissions can be expected to exceed exhaust emissions under certain conditions (Field *et al.,* 1992). However, evaporative emissions are generally not thought to be significant at ambient temperatures below 10 °C (Field *et al.,* 1994). Evaporative emissions can result from refuelling emissions due to displacement of vapour in the tank during refuelling, diurnal losses due to an increase in the temperature of the fuel in the tank (due to ambient temperature increase), running losses where the hot engine and exhaust system can vaporise fuel while the car is running, and hot soak losses due to evaporation after the engine is turned off but remains warm (Goldsmith, 1990; USEPA, 1994).

Stationary Combustion

Several studies have been carried out to assess hydrocarbon emissions from power generating stations (Joos *et al.,* 1990; Garcia *et al.,* 1992; USEPA, 1997; Rubin, 1999). An emissions survey carried out at a number of French power stations found that the most abundant hydrocarbons are generally toluene, ethylbenzene, xylenes and tetrachloroethane; however, this report concluded that the impact of power stations on atmospheric hydrocarbon concentrations is always small when compared to petrol and diesel engine emissions (Garcia *et al.,* 1992). Ethane, ethylene and propylene have also been found to be important hydrocarbon constituents from stationary combustion sources (Friedrich and Obermeier, 1999). The Department of the Environment (1993) in the UK has identified the compounds listed in Table 2.5 as the main VOCs emitted due to industrial combustion of fuel, including power generation and other industrial combustion for generation of energy and heat.

Table 2.5 VOCs emitted during industrial combustion (Department of the Environment, 1993)

Compound class	% by weight	Major compounds involved
Alkanes	60	Ethane, propane, butane, pentane
Alkenes	20	Ethylene
Oxygenates	15	Formaldehyde
Aromatics	5	Benzene, toluene

Concentrations of several non methane hydrocarbons obtained at a distance 5 km downwind of the Le Havre coal fired power plant, at an elevation of 500m, are shown in Table 2.6 (Joos et *al.,* 1990). This indicates significant emissions of both alkanes and aromatics, although the range of hydrocarbons measured was quite small.

Ambient concentrations can vary depending on the quality of the fuel being used (for example, different qualities of coal can result in different compounds being emitted) and the operating conditions at the station, including the efficiency and type of furnace. For example, the emissions of toluene at one station were found to vary by up to a factor of 100 (Garcia *et al.,* 1992). Also, during start-ups, temporary upsets, or other conditions preventing complete combustion, unburned combustible emissions may increase dramatically (Davis and Pakrasi, 1992). Table 2.2 indicates that combustion of gas provides the lowest hydrocarbon emissions per terajoule of fuel, for industrial and power generating scenarios. The above findings, although mainly directed towards power generation, would apply to any stationary combustion situation.

Table 2.6 Ambient hydrocarbon concentrations in the vicinity of industrial combustion sources, parts per billion carbon (ppbC)

Hydrocarbon	Le Havre power station *
Ethane	20
Acetylene	38
Propane / Propylene	159
i-Butane	44
Benzene	300
Toluene	320
Ethylbenzene	88
m+p-Xylene	168
o-Xylene	60

*Measured at 500m above ground

2.4.2 Emissions due to Solvent Use

Crume and Portzer (1992) state that the predominant characteristic of the pharmaceutical industry is its diversity and the large variety of chemical compounds used during product manufacture. This applies equally to the large number of industries which use solvents as raw materials or are involved in the production of solvents. The industrial processes which are associated with solvent use include paint application, degreasing, dry cleaning, chemical product manufacture or processing, rubber processing, pharmaceutical product manufacture, glue / ink / paint manufacture, preservation of wood, printing, and textile and leather finishing (Ritter, 1998). This variety results in a wide range of compounds being emitted, as different facilities, even in the same industry, can employ different processes and raw materials. Monitoring ambient air quality in the vicinity of industrial locations is

rarely carried out, and comprehensive data on air pollution concentrations and exposure near industrial plants and areas in Europe do not exist (EEA, 1995).

Some ambient measurements have shown that emissions from industrial solvent use can lead to ambient concentrations of toxic compounds at higher levels than would generally be experienced due to vehicle emissions (Ends, 1996a; PORG, 1997). In some areas close to industrial emission sources, vehicle emissions can be a minor source of pollution compared to emissions from industrial solvent usage or manufacturing plants (Zainal, 1990; Mohan Rao *et al.*, 1997; Roemer *et al.*, 1999).

In an Irish context, any facility which has significant emissions of harmful substances must apply for a Integrated Pollution Control (IPC) licence, and as part of the licensing process, regular measurements of these emissions must be made. Each IPC licensed facility has a public file held by the Environmental Protection Agency (EPA) where the results of any emissions sample analysis can be viewed. IPC Licensing is applied to 13 industrial sectors (including intensive agriculture), as detailed in Table 2.7. These 13 sectors are further subdivided into 61 classes of activity. Licensing of established activities has been phased in over an extended period since May 1994 and was originally expected to be completed by the summer of 1999 (EPA, 1997). IPC licensing is scheduled to apply to coal/oil fuelled generating stations from March 2000, to gas fuelled generating stations from September 2000, and to peat-fuelled stations from January 2001.

Table 2.7 Industrial sectors covered by IPC licensing (EPA, 1997).

1. Minerals and other activities	8. Wood, paper, textiles and leather
2. Energy (production)	9. Fossil fuels
3. Metals	10. Cement
4. Mineral fibres and glass	11. Waste
5. Chemical	12. Surface coatings
6. Intensive agriculture	13. Other activities
7. Food and drink	

In Table 2.7, sectors 5 and 12 are of most relevance for solvent use. Table 2.8 presents the number of IPC facilities in each county by activity class. The data provided in Table 2.8 have been collated from the EPA database which contains details of all the IPC facilities. Some facilities have two activity classifications assigned by the EPA. In these cases the facility has been included in each of the activity classifications. The majority of Class 5

facilities are located in either Dublin or Cork. There is a slightly greater spread of Class 12 facilities, with the majority located in the Leinster region. It is interesting to note that Classes 5 and 12 have a greater number of licensed facilities than any other class.

Table 2.8 Facilities with licensed air emissions (as of December 1998)

	EPA ACTIVITY CLASS													
COUNTY	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**COUNTY TOTAL**
Carlow						1							1	2
Cavan					2	4	3					1		10
Clare			1		6			2			1	6	1	17
Cork		2	2		22	5	4	9	2		3	3	3	55
Donegal							1	3				1	1	6
Dublin	1		5	1	26		1	6			3	20	1	64
Galway			2		2		2	3				4		13
Kerry					1			1				1	1	4
Kildare			2		3			2				7	1	15
Kilkenny			1		1	1	1	1			1	1		7
Laois					2		1	2				2		7
Leitrim								2				1		3
Limerick	1	1	3		1	1	3	2		1		6	1	20
Longford						1		5						6
Louth						1	1			1		1	1	5
Mayo						1	1	3		1		1		7
Meath	1		2			2	3	3				3		14
Monaghan			1		2	2	2	2				4		13
Offaly			1			2		1						4
Roscommon					1							1		2
Sligo					1			1				1		3
Tipperary	1			1	2	3	6	2				1		16
Waterford			2	2	2	3	4	3				4		20
Westmeath						1						4		5
Wexford			2		1	1	2	1				1		8
Wicklow					4		1					6		11
Class Total	4	3	24	4	79	29	36	54	2	3	8	80	11	337

2.4.3 Natural Sources of Hydrocarbons

Natural, or biogenic, sources of hydrocarbons includes only emissions from completely natural sources. Emissions from managed forests, farm animals, burning of stubble, etc. are not included in this category. Examples of sources which can be included are forest fires, wetlands, rivers and volcanoes (Ritter, 1998). In most countries, emissions from natural sources are significantly lower than anthropogenic emissions. However, in rural areas, natural emissions can be important. Indeed, on a global scale, the magnitude of biogenic

non-methane hydrocarbons emissions exceeds that from anthropogenic sources (Isidorov *et al.,* 1999; Simeonidis *et al.,* 1999).

Emissions from the leaves of trees are the most important source of natural hydrocarbons. As mentioned earlier (Section 2.3.1), plants and trees emit ethylene in response to environmental stresses. Ethane, propane, butanes, pentanes and higher molecular weight alkanes are emitted in seepage of natural gas from bacterial fermentation processes (Altshuller, 1983); however, the quantity of these emissions are low. Many hydrocarbons are emitted from plants and trees, including isoprene which is emitted primarily by deciduous trees, and monoterpenes, which are emitted primarily from conifers (Altshuller, 1983; Lamb *et al.,* 1987; Hewitt *et al.,* 1995; PORG, 1997). Isoprene emissions are dependant on light intensity and temperature (Hewitt *et al.,* 1995). As isoprene is emitted mostly from deciduous trees, emissions are highest during the summer, and insignificant during the winter (Lamb *et al.,* 1987). Isoprene was originally believed to be emitted almost exclusively from natural sources. However, more recently isoprene has also been linked to vehicle emissions (Dollard *et al.,* 1995; PORG, 1997).

Many of the compounds emitted from trees and plants (including isoprene) are highly reactive compounds and are involved in the production of photochemical oxidants. Early suggestions that hazes formed over heavily wooded areas were due to photochemical oxidants associated with natural hydrocarbon emissions have been borne out. Recent studies indicate that the forests surrounding population centres, such as Atlanta in the south-east United states, are the primary source of reactive organic compounds responsible for photochemical oxidant formation (Fall, 1999).

2.4.4 Hydrocarbon Emission Estimates

Inventories of hydrocarbon emissions are available for most European countries. While the accuracy of these inventories has improved, emissions estimates for some source types are relatively crude, and may be based on only a small number of measurements. In the UK emissions inventory for example, emissions of certain hydrocarbon groups may have been underestimated by 40 percent (PORG, 1997). As part of the EU CORINAIR programme, emission inventories for several pollutants, including NMVOC, are compiled for all European countries every five years. The Organisation for Economic Co-operation and

Development (OECD) also regularly publishes emissions inventories of priority pollutants (including VOCs) for many countries world-wide (OECD, 1997).

As these inventories are updated, revisions have been made to the emission factors employed. However, emission estimates for VOCs in Ireland remain highly uncertain in absolute terms (McGettigan and O'Donnell, 1995; EPA, 1996), hence VOC estimates from the CORINAIR programme for Ireland should not be relied on for quantitative purposes. Also, emissions are given only in terms of total NMVOC. However, speciated emission estimates for different source types are available for the UK (Department of the Environment, Transport and the Regions, 1998c) and are presented in Table 2.9 for a selection of hydrocarbons measured during this study. Although the quantity of each compound emitted from each source type is much larger than would be expected in Ireland, it can be assumed that the ratios of the hydrocarbons from each source type would be similar, particularly for transport related emissions.

Emission inventories are generally produced by the EPA in Ireland on an annual basis (EPA, 1996) based on the CORINAIR methodology. Table 2.10 indicates the NMVOC emission estimates for Ireland from the 1990 and 1994 revisions of the CORINAIR programme (Ritter, 1998). There are generally only small differences between the 1990 and 1994 emissions. Importantly, emissions from road transport have decreased, although emissions from the agricultural sector have increased. Compared to other EU countries, Ireland has one of the highest percentage contributions from the agriculture sector to total NMVOC emissions. Sweden and Greece also have large contributions from the agricultural sector. Emissions from natural sources are quoted as zero in the 1994 inventory; this is likely to be due to a change in the methodology.

Table 2.9 Estimated UK emissions of speciated hydrocarbons by source category, K tonnes C per year (DETR, 1998c)

	Road transport (diesel)	Road transport (petrol)	Petrol evaporation	Off-road	Other transport	Stationary combustion	Extraction and distribution of fossil fuels	Processes	Solvent use	Waste treatment	Total (thousand tonnes)
1,2,3-trimethylbenzene	0.45	2.79	0.28	0.24	0.09				2.98		6.83
1,3,5-trimethylbenzene	0.45	3.69	0.35	0.30	0.11				3.00		7.90
2-methylpentane	1.87	8.55	2.75	0.80	0.36		1.65		0.34		16.32
3-methylpentane	0.98	5.94	1.83	0.52	0.22		0.70		0.31		10.49
Acetylene	2.85	21.20		2.90	0.61	0.40		1.43		0.19	29.58
Benzene	1.81	22.69	1.82	2.88	0.74	1.76	0.59	6.32		2.72	41.33
Butane	3.56	15.89	18.17	1.50	0.90	4.18	99.57	18.61	23.23	5.90	191.51
Ethane	0.45	4.19		0.90	0.11	4.31	16.59	4.57		0.22	31.33
Ethylbenzene	0.71	17.60	1.20	1.28	0.36	0.40	0.07	0.19	0.25	0.55	22.62
Ethylene	9.79	35.20		5.23	2.42	1.68	0.20	11.01			65.53
Heptane		3.06	0.64	0.21	0.06	0.74	18.05	1.62	0.37	1.46	26.21
Hexane	0.89	7.07	1.84	0.59	0.23	1.49	15.02	4.19	11.13	0.99	43.43
m-Xylene	0.71	26.87	1.71	1.91	0.51	0.94	0.00		6.54		39.21
o-Xylene	0.71	21.11	1.45	1.52	0.42	0.27	0.00	0.16	6.95	0.03	32.62
Pentane	2.49	7.38	6.56	0.80	0.48	5.50	34.04	9.31	17.97	3.79	88.32
Pentane other isomers					0.01	0.75	0.08	9.23		5.66	15.72
Propane		0.95		0.62	0.02	2.67	30.51	15.71	23.23	2.58	76.29
Propylene	3.03	17.51		2.11	0.84	1.24	0.12	5.49		0.01	30.35
Toluene	0.71	60.77	5.14	5.90	1.08	1.44	0.61	4.17	54.51	2.01	136.36
Xylenes (mixture)					0.10	0.03		4.67	29.78	0.70	35.29
Total NMVOCs	90	453	91	97	22	48	294	285	604	46	2,031

Table 2.10 Estimated NMVOC emissions for Ireland, 1990 and 1994 (Ritter, 1998)

Source	1990 tonnes/yr	1990 % of total	1994 tonnes/yr	1994 % of total
Public power, cogeneration, heating	244	0.12	305	0.17
Commercial and residential combustion	7,957	4.04	5,688	3.24
Industrial combustion	334	0.17	152	0.09
Production processes	707	0.36	917	0.52
Extraction / distribution of fossil fuels	3,117	1.58	3,448	1.97
Solvent use	21,369	10.84	21,994	0.13
Road transport	62,289	31.62	58,283	33.24
Other mobile sources and machinery	1,198	0.61	1,872	1.07
Waste treatment and disposal	4,740	2.41	450	0.26
Agriculture	78,461	39.82	82,165	46.86
Nature	16,600	8.43	0.00	0.00
Total in tonnes	197,016		175,274	

NMVOC emissions from several European countries are illustrated in Figure 2.1. Ireland has the lowest total NMVOC emissions of all these countries. On a per capita basis, only the Netherlands and Portugal have lower emissions than Ireland (Ritter, 1998).

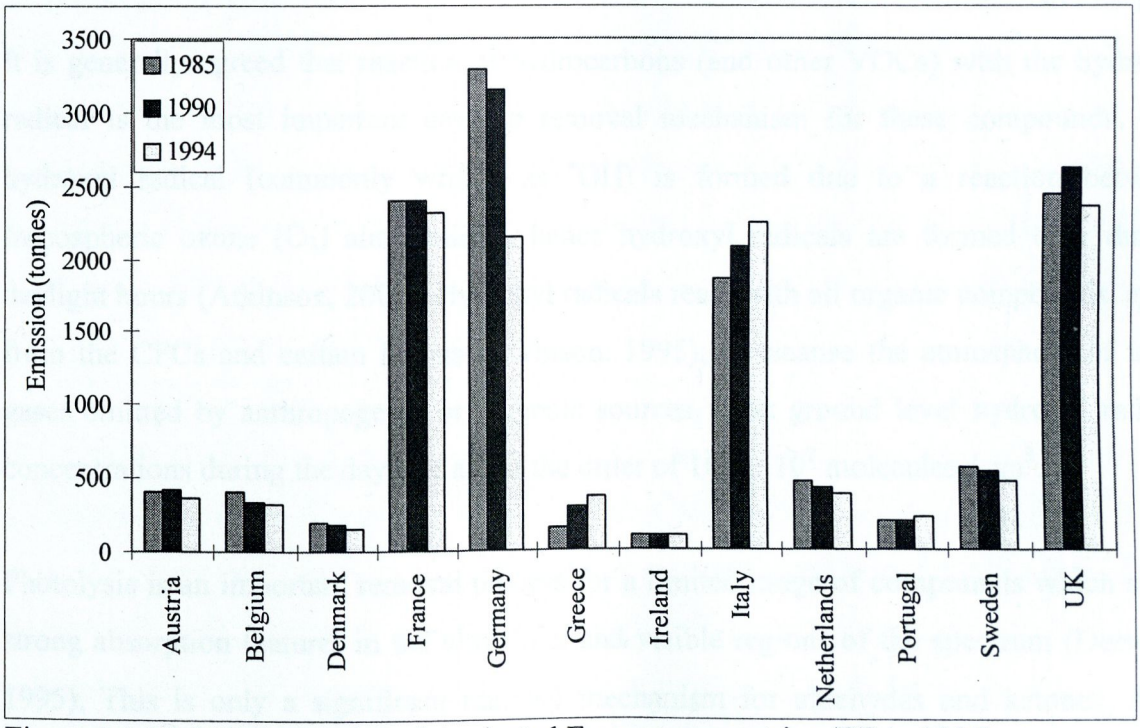


Figure 2.1 NMVOC emissions for selected European countries (EEA, 1997)

2.5 FATES OF HYDROCARBONS

As a hydrocarbon emission travels further from it's source, concentrations tend to reduce, initially due to dispersion and dilution effects. However, over time other mechanisms also become important, removing hydrocarbons from the atmosphere through reaction. As a

consequence, the dominant hydrocarbons in rural areas can often be saturated hydrocarbons (i.e. least reactive), due to removal of unsaturated compounds from the atmosphere by reaction during transportation from the original source (Sexton and Westberg, 1984). Removal of hydrocarbons from the atmosphere can take place in a number of ways and the expected lifetime of different compounds can range from a few hours (for compounds such as isoprene) to a few weeks (ethane), to the extreme case of methane which has a lifetime of years.

The main removal mechanisms for hydrocarbons in the atmosphere are (Derwent, 1995):

- photochemical oxidation by the hydroxyl radical;
- photolysis in the troposphere and stratosphere;
- deposition and uptake at the earth's surface;
- reaction with other reactive species such as chlorine atoms, nitrate radicals at night, and ozone.

It is generally agreed that reaction of hydrocarbons (and other VOCs) with the hydroxyl radical is the most important daytime removal mechanism for these compounds. The hydroxyl radical (commonly written as $^{\bullet}OH$) is formed due to a reaction between tropospheric ozone (O_3) and sunlight, hence hydroxyl radicals are formed only during daylight hours (Atkinson, 2000). Hydroxyl radicals react with all organic compounds, apart from the CFCs and certain halons (Atkinson, 1995), to cleanse the atmosphere of trace gases emitted by anthropogenic or biogenic sources. Peak ground level hydroxyl radical concentrations during the daytime are of the order of 10^6 to 10^7 molecules / cm^3.

Photolysis is an important removal process for a limited range of compounds which show strong absorption features in the ultraviolet and visible regions of the spectrum (Derwent, 1995). This is only a significant removal mechanism for aldehydes and ketones. After absorbing radiation, the compound undergoes chemical transformation by dissociation or isomerisation (Atkinson, 1995).

Deposition and uptake of compounds at the earth's surface includes two mechanisms, dry deposition and wet deposition. Dry deposition involves the reaction or uptake of a compound at the surface or on surface elements, which can include water surfaces, plants

and soil surfaces (Derwent, 1995). Little work has been carried out in estimating the dry deposition rates for hydrocarbons, although the general consensus is that dry deposition of hydrocarbons is not an important removal mechanism (Field *et al.,* 1992; Derwent, 1995; PORG, 1997). Wet deposition results from the incorporation of a pollutant into falling precipitation (known as wash-out), or the incorporation of the pollutant into cloud droplets (rain-out) (Derwent, 1995). This mechanism is generally only important for compounds which are easily soluble, and this does not include light hydrocarbons. It has also been suggested that the carrying liquid may evaporate during descent resulting in the re-entry into the atmosphere of the pollutant, and that hydrocarbons may be removed by volatilisation after deposition (Field *et al.,* 1992). Dry and wet deposition are generally only important removal mechanism for semi-volatile organic compounds (i.e. > C_{10}).

Hydroxyl radicals are not the only reactive species in the atmosphere which react with organic trace gases. Fluorine and chlorine atoms also react with a wide range of organic compounds but the atmospheric concentrations of these atoms is limited, and this removal mechanism can generally be ignored (Derwent, 1995). Hydroxyl reactions become less important at night as production of the hydroxyl radical ceases. However, at night, build-up of the nitrate radical ($NO_3^{\bullet}$) occurs and can dominate night-time removal processes. The nitrate radical tends to react only with the more reactive hydrocarbons, compared to the wide range of compounds which react with the hydroxyl radical. Removal of organics due to reactions with ozone (O_3), appears, like the nitrate radical, to be more effective for the more reactive hydrocarbons (Derwent, 1995).

In summary, reaction with the hydroxyl radical is the most important removal mechanism for hydrocarbons. For the majority of hydrocarbons the rate of removal by reaction with O_3, or due to photolysis, has been estimated to be less than 1 percent of the OH removal rate (Field *et al.,* 1992). Different hydrocarbon groups exhibit varying removal efficiencies for each mechanism. For example, the potential loss processes for alkanes and aromatics are reaction with the hydroxyl and nitrate radical; while for alkenes, reaction with the hydroxyl and nitrate radicals, as well as with ozone, are important loss processes (Atkinson, 1990). Derwent *et al.,* (1996) provide details of the dominant degradation routes for a number of individual hydrocarbons, as well as their respective ozone creating potentials. The overall lifetime of any organic compound can be expressed as (Atkinson, 1995):

$$1/\tau_{overall} = 1/\tau_{wet_dep.} + 1/\tau_{dry_dep.} + 1/\tau_{phot.} + 1/\tau_{OH} + 1/\tau_{NO3} + 1/\tau_{O3} + 1/\tau_{Cl} \quad 2.1$$

$\tau_{overall}$ = the overall lifetime of the compound

$\tau_{wet_dep.}$ = lifetime due to wet deposition

$\tau_{dry_dep.}$ = lifetime due to dry deposition

$\tau_{phot.}$ = lifetime due to photolytic reaction

τ_{OH} = lifetime due to reaction with the hydroxyl radical

τ_{NO3} = lifetime due to reaction with the nitrate radical

τ_{O3} = reaction with reaction with ozone

τ_{Cl} = lifetime due to reaction with the chlorine atom

Examples of the expected atmospheric lifetime of several hydrocarbons are given in Table 2.11 (Atkinson, 1995). For most of these compounds, hydroxyl reaction is by far the dominant removal mechanism. Photolytic removal is insignificant for all of these compounds.

Table 2.11 Atmospheric lifetimes for sample hydrocarbons (Atkinson, 1995)

	Lifetime due to		
Compound	Hydroxyl Radical[b]	Nitrate radical[c]	Ozone[d]
Propane	13 days	a	> 4500 years
Ethylene	1.7 days	225 days	10 days
Propylene	7 hours	4.9 days	1.6 days
Isoprene	2 hours	50 minutes	1.3 days
Benzene	12 days	> 4 years	> 4.5 years
Toluene	2.4 days	1.9 years	> 4.5 years
m-Xylene	7 hours	200 days	> 4.5 years

[a]Data are not available for calculation of this lifetime, though the influence of this process is expected to be insignificant
[b]Calculated using a 12 hour daytime average hydroxyl radical concentration of 1.6×10^6 molecules / cm^3
[c]Calculated using a 12 hour night-time average nitrate radical concentration of 5×10^8 molecules / cm^3
[d]Calculated using a 24 hour average ozone concentration of 7×10^{11} molecules / cm^3

2.6 SAMPLING AND ANALYSIS METHODS

In order to measure the ambient concentration of hydrocarbons two distinct procedures are required. Firstly, an air sample must be collected, secondly the air sample must be analysed. The sample may also be pre-concentrated prior to analysis. Popular sampling and analysis methods are described below.

2.6.1 Sampling Methods

The two commonly used methods for sampling hydrocarbons in air are whole air sampling and adsorbent sampling (Cao and Hewitt, 1999). Whole air sampling involves, as the name suggests, collecting a complete sample of the atmosphere under examination. This is normally carried out using either a rigid canister or a bag sampling method. Adsorbent or sorbent sampling involves removing the compounds of interest from the atmosphere under examination, normally by passing an air sample through an adsorbent filled tube. The air may be forced through the tube using a pump (pumped or active sampling), or allowed to permeate naturally through the tube (passive or diffusive sampling). A summary of the most common hydrocarbon sampling methods are given below.

Stainless Steel Canisters

An air sample is drawn from the atmosphere into a stainless steel canister whose internal walls have been treated with an inert coating. The sample can either be pumped into the canister or air can be drawn into an initially evacuated canister. Polar compounds tend to be adsorbed onto the internal walls of the canister, particularly in a very dry air sample (Cao and Hewitt, 1999). Canister sampling methods are generally not useful for sampling hydrocarbons with more than 10 carbon atoms.

Bag Sampling

Bags made of materials such as Tedlar, Mylar, Scotchpak and Teflon are used to collect environmental samples. Many of these bags are fitted with a valve and filled using a pump, while some (particularly the smaller bags) are fitted with a septum to facilitate sample injection using a syringe. Although this is one of the cheaper sampling methods, it has a number of associated disadvantages. There can be problems with samples leaking out through the pores in the bag, chemical reactions between the sample and the bag wall, and sample adsorbtion onto the bag wall. The bags can also be difficult to clean for re-use. Wang *et al.* (1996) found significant hydrocarbon losses from Tedlar bags, even over a 24-hour period.

Solid Adsorbent Sampling

Adsorbent sampling is now the most popular sampling method. This method involves drawing an air sample through a tube (usually glass or metal) filled with a solid adsorbent material. Sampling periods of at least 24 hours are normally required for passive samplers, while much shorter sampling periods (1 to 4 hours, or less depending on the pump flow rate) can be used for pumped sampling. A typical sampling tube is shown in Figure 2.2.

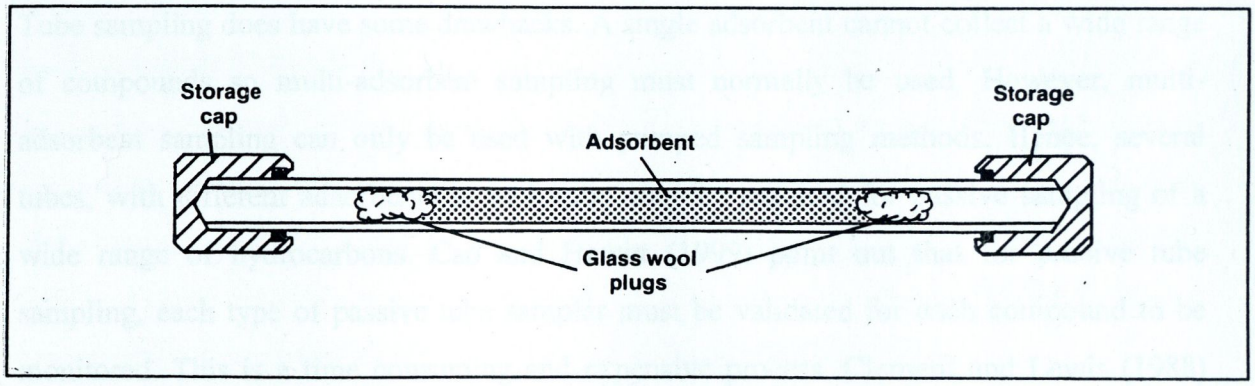


Figure 2.2 Typical adsorbent filled sampling tube

Many different adsorbent materials can be used, depending on the compounds which are to be collected. Adsorbent selection is probably the most important factor in ensuring effective tube sampling results. Some adsorbents have low capacities for certain hydrocarbons and this must be taken into account during selection. Different adsorbents can also be arranged in series (for pumped sampling only) to trap a wider range of compounds. The adsorbents must be kept in separate layers, using glass wool or stainless steel gauzes. The adsorbents must also be packed in order of strength, with the weakest adsorbent being placed at the front of the tube (i.e. so that the air sample passes this adsorbent first) and the strongest at the back. Two of the more popular adsorbents for hydrocarbon sampling are Tenax and Chromosorb 106. Tenax has a very low safe sampling volume for hexane, hence another adsorbent may need to be used (perhaps in series with Tenax) to prevent hexane breakthrough, i.e. the elution of hexane through the non-sampling end of the tube (Perkin-Elmer, 1994). A more suitable adsorbent for the above example would be Chromosorb 106, which has an SSV of 30 litres (on 300 mg of Chromosorb) for hexane (Perkin-Elmer, 1994). Detailed guidelines on the selection and use of adsorbents are given by the USEPA (USEPA, 1999).

Sampling tubes are small and considerably less bulky than canisters and bags, and can be re-used at least 100 times. They can be cleaned and prepared for reuse by the thermal desorption process used for analysis (Woolfenden, 1997). Passive sampling tubes can be located discretely on site with no other equipment required for sampling, while pumped sampling only requires a small pump. Another advantage of adsorbent sampling is that there is no requirement for highly skilled operators, particularly with passive sampling equipment (Nugent, 1999).

Tube sampling does have some drawbacks. A single adsorbent cannot collect a wide range of compounds so multi-adsorbent sampling must normally be used. However, multi-adsorbent sampling can only be used with pumped sampling methods. Hence, several tubes, with different adsorbents in each tube, may be required for passive sampling of a wide range of hydrocarbons. Cao and Hewitt (1999) point out that for passive tube sampling, each type of passive tube sampler must be validated for each compound to be monitored. This is a time consuming and expensive process. Clement and Lewis (1988) also suggest that unknown reactions occur during tube sampling. This can lead to the detection of compounds not originally present in the sample, and reduce the accuracy with which the concentration of compounds originally present in the atmosphere are measured.

Because adsorbent filled tubes collect only the components of interest and not a complete air sample (as with the canisters and bags), the sample can be passed directly from the tube to the analyser. In contrast, whole air sampling methods require the sample to be passed through a focusing trap before transfer to the analytical system. However, single stage thermal desorption of adsorbent filled tubes is only compatible with packed column chromatography. In order to utilise high-resolution capillary chromatography, trapped components must be re-focused between the tube and the column (Woolfenden, 1997).

Impingers

This basic process involves pumping an air sample through an absorber liquid contained in a glass bottle. The absorber liquid can dissolve the gas and/or convert it to another form. Impingers are usually used for the collection of non-reactive gases and vapors which are highly soluble in the absorbing liquid. Condensation of materials in the sampling line can cause problems.

Before a sample collected using any of the above methods can be analysed they may need to be concentrated or focused. Cryogenic techniques are commonly used for this purpose. The method involves passing the sample through an adsorbent filled trap held at sub-ambient temperatures, which can be anything from - 30 °C to - 190 °C depending on the cooling method used. Normally, liquid coolants such as liquid oxygen or nitrogen have been used, however (as employed in this project) electrical 'peltier' cooling methods are now available.

2.6.2 Analysis Methods

The analysis of hydrocarbons normally involves gas chromatography (GC). GC methods are used to separate mixtures of compounds, and are employed with a method of detection. The two most popular detection methods are FID (Flame Ionisation Detector) and MS (Mass Spectrometry). A comprehensive review of gas chromatography theory, instrumentation, and applications can be found in Baugh (1993).

Chromatographic methods are used to separate a number of compounds from a mixture, and involves the flow of a mobile phase over a stationary phase. In capillary chromatography, the sample is passed through a narrow bore capillary column in a stream of inert gas such as helium. As the stationary phase in the column has different affinities for each compound in the mixture, each compound passes through at a different rate and the compounds are eluted from the column individually. The columns are normally installed in a temperature controlled oven to aid the eluting process. Without temperature programming, the more volatile compounds will be well resolved, however compounds with higher boiling points will have very long retention times and broad peaks (Bartle, 1993). Increasing the oven temperature during the chromatographic process allows faster elution and better resolution of these less volatile compounds.

Upon elution, compounds must be quantitatively identified. The Flame Ionisation Detector (FID) is one of the most common detectors used in hydrocarbon analysis of ambient air samples. The sample stream from the column is burned in a very hot hydrogen / air flame to ionise the organic compounds. Particles produced in the flame are collected at two terminals, producing a small current which is amplified by an electrometer. This current is proportional to the carbon content of the solute. Therefore, if the compounds are

sufficiently separated and identified after leaving the column, each compound can be individually quantified. A trace of the current at the FID electrodes over time is represented as a chromatogram. The area under each peak in a chromatogram is proportional to the quantity of that compound present in the original ambient sample. Normally, a calibration standard with a known mixture of gases is passed through the system periodically. The response of the FID to the known concentrations of each compound in the calibration mixture is compared with that observed with each ambient air sample, and the ambient concentration determined. The combustion gases normally used in FIDs are hydrogen and zero air. Zero air has a very low hydrocarbon content and should not interfere in the quantitative measurement of hydrocarbons eluting from the column.

Mass spectrometry is a common method used for the identification of organic compounds. In mass spectrometry the substance to be analysed is heated and placed in a vacuum. The resulting vapour is exposed to a beam of electrons, which causes ionisation to occur. The ions are separated according to their mass by passing through a magnetic field. These separated ions are then passed on to the detector. In contrast to FID, MS can be used to definitively identify, as well as quantify, the compounds in the sampling stream. In GC-FID systems, peak identification is achieved by comparing the retention times of standard solutions with those from sample analyses, therefore, misidentification of compounds can occur (Cao and Hewitt, 1999). While GC-FID systems cannot separately quantify compounds which co-elute (i.e. compounds which are not sufficiently separated by the chromatography and hence reach the FID together), GC-MS systems are capable of performing this operation. Results from GC-FID systems will, for example, normally present m-xylene and p-xylene as a composite concentration. GC-MS systems are, however, more expensive than GC-FID systems.

Other detectors which are used in the analysis of hydrocarbons include the photoionisation detector (PID) and the electron capture detector (ECD). While FID is a highly non-selective detector and can respond to most organic compounds, the PID is very selective, especially for alkenes, aromatics and other reactive hydrocarbons (Cao and Hewitt, 1999). The PID is therefore useful in studies concerned only with the reactive hydrocarbons involved in photochemical oxidant production. The PID also has significantly lower detection limits than the FID. Electron capture detection is an extremely sensitive detection method with a sensitivity up to 10,000 times lower than an FID (Cao and Hewitt, 1999). However, ECDs

are highly selective and are generally used only for the detection of CFC compounds as ECD response to hydrocarbons is very low.

All of the above detection methods are used in conjunction with gas chromatography. However, Differential Optical Absorption Spectroscopy (DOAS) may also be used to identify concentrations of individual compounds in ambient air. DOAS is based on the absorption of light at specific wavelengths for different compounds. Only a small range of hydrocarbons can currently be measured using DOAS systems and it has previously been more successfully used for monitoring inorganic compounds (Cao and Hewitt, 1999). The correlation between DOAS results and GC-FID data is reported as being very poor by Cao and Hewitt (1999), however Brocco *et al.* (1997) found good agreement between the two methods.

As more hydrocarbon analysis is performed in response to legislative requirements, greater use has been made of automated monitoring systems, particularly in monitoring networks. Such automated systems can be defined as, 'systems that are beginning to be used in air monitoring network stations to provide frequent, usually hourly, analysis of ambient air for VOCs, over monitoring periods of days to months' (McClenny, 1993). AutoGCs should be capable of operating unattended virtually continuously. Such a system is employed in this project. These automated systems carry out all aspects of sampling, focusing, analysis, data collection and data storage. Data collection, and system monitoring can also be carried out remotely.

2.7 SUMMARY OF SELECTED PREVIOUS MONITORING STUDIES

Due to the capital cost, and the expertise required to sample and analyse atmospheric concentrations of speciated hydrocarbons, only recently have major studies been initiated in this area. This is particularly true for continuous on-site sampling and analysis, as many previous studies have involved collecting discrete samples on site for later analysis at a laboratory. Indeed, Sexton and Westberg (1984) point to this very reason for the scarcity of hydrocarbon measurement studies in pollution monitoring networks. However, since then the situation has improved slightly, and a large amount of data from different site types is now available in many countries.

2.7.1 Previous Hydrocarbon Monitoring in Ireland

Few hydrocarbon monitoring studies have been carried out in Ireland, with previous monitoring tending to focus on the more traditional pollutants such as SO_2 and smoke, with more recent monitoring of NO_X and ozone. Further details of these measurements are provided in: Nolan, 1979; Bailey *et al.*, 1986; Bailey, 1988; Wall, 1991; McGettigan *et al.*, 1993; McGettigan and O'Donnell, 1995; Dublin Corporation, 1997 and McGettigan, 1998.

Recently the Environmental Protection Agency (EPA) established three mobile air monitoring units, which include benzene, toluene and xylene monitoring equipment (Department of the Environment and Local Government, 1999b). The first measurements of one of the units were taken at the same roadside location as this project, and results are presented in Section 4.3.

As part of the preparation of the Dublin Air Quality Management Plan, some monitoring of benzene, toluene, ethylbenzene and o, m and p-xylene was carried out (Envirocon, 1997). The concentrations were measured using a passive sampling method which collects the sample over a period of 14 days. Measurements were taken at thirteen city centre and sixteen urban and suburban sites during five distinct two week sampling periods between September 1995 and March 1996. Two week sampling periods were required due to the low uptake rate of passive samplers. No information is given on analysis techniques. The report identified benzene as an air pollutant warranting reduction strategies over the following five years. Selected results from this report are presented in Table 2.12. Urban measurements are higher than at the suburban sites, as would be expected.

Table 2.12 Selected average BTEX concentrations at urban and suburban sites in Dublin

Location	Benzene	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene
Average concentrations in urban areas of Dublin (18/2 - 3/3/96), ppb					
College Green	8.9	35.6	3.5	8.3	3.0
Donnybrook	7.9	41.9	3.6	7.2	2.3
Dorset Street	7.1	31.6	3.3	5.9	2.0
East Wall Road	7.1	45.1	3.6	7.2	5.3
Average concentrations in suburban areas of Dublin (15/10 - 29/10/96), ppb					
Swords	6.8	21.6	2.5	4.4	1.1
Stillorgan	4.6	10.6	1.7	2.8	2.2
Sandyford	3.4	13.5	2.6	3.1	1.2
Clondalkin	2.6	7.4	1.0	1.6	1.7

A more recent study was commissioned by the EPA to measured hydrocarbon concentrations in the most heavily-trafficked areas of Dublin (Henderson *et al.*, 1997). Benzene, toluene and xylene concentrations were measured. The majority of the 20 sampling points were located adjacent to busy roads, while some background sites were also chosen. Again, passive tube sampling was employed during this study, with exposure time ranging from two to three weeks. Sampling was carried out between March and December 1996. Analysis was carried out using a GC-MS system. Results from this study indicated BTX concentrations which were lower by at least a factor of two than those presented in Table 2.12. Selected results from the EPA study are presented in Table 2.13. Again, higher concentrations are measured at the urban monitoring sites, though the site at Collins Avenue also exhibits high BTX concentrations.

Table 2.13 Selected average BTX concentrations at urban and suburban sites in Dublin

	Benzene	Toluene	p-Xylene	o+m-Xylene
Average concentrations in urban areas of Dublin (27/3 - 18/12/96), ppb				
College Street	2.55	4.11	3.69	4.43
Dorset Street	1.12	3.02	3.58	3.06
Merchants Quay	4.62	2.42	2.88	2.30
Pearse Street	1.12	2.45	1.04	3.00
Average concentrations in suburban areas of Dublin (27/3 - 18/12/96), ppb				
Kylemore Road	1.06	0.40	0.86	0.42
Ashtown Grove	1.81	1.78	0.29	0.30
Collins Ave., Whitehall	1.27	2.69	2.70	3.19
Jamestown Rd., Finglas	0.26	0.60	0.76	0.46

Nugent (1999) recently carried out a diffusion tube sampling survey to assess the impact of emissions from petrol stations on BTX concentrations in the surrounding area. A small number of pumped tube samples were also collected. Samples were collected over two week periods at different locations around, and within the forecourt of three petrol stations in the area of Naas, Co. Kildare. Typical concentrations measured using diffusion tubes and pumped samples are presented in Table 2.14. The pumped samples were collected over four hour sampling periods in the afternoon, when the petrol stations were busy. Hence the concentrations measured from pumped analyses would be expected to be greater than from diffusion tube samples.

Table 2.14 Average diffusion and pumped tube BTX concentrations, over 12 day and four hour sampling periods, respectively (Nugent, 1999).

Sampling location	Benzene (ppb)	Toluene (ppb)	Xylene (ppb)
Diffusion tube sampling results			
Background	0.31	0.31	0.20
Forecourt (at pumps)	2.72	4.16	2.64
Forecourt boundary	2.00	2.95	2.00
Roadside	1.03	1.78	1.32
Pumped tube sampling results			
Background	< 0.3	< 0.3	< 0.3
Forecourt (at pumps)	7.05	9.62	6.24
Forecourt boundary	2.13	2.69	2.00
Roadside	1.74	2.59	2.25

As expected, the highest concentrations were measured at the pumps. Average concentrations at the forecourt boundary are slightly higher than the average roadside concentrations measured in this study (see Table 4.6 and Table 4.7). The performance of two different adsorbent materials, Tenax and Chromosorb 106, were compared over the course of the study. No significant difference was noted between the performance of the two materials.

Research is currently being carried out at the Dublin Institute of Technology (Kevin Street) into the application of Differential Optical Absorption Spectroscopy (DOAS) to organic compound monitoring (Treacy, 2000). Benzene and toluene concentrations are measured by the system, though the sensitivity of the instrument is low, resulting in difficulties in measuring benzene concentrations. As ambient toluene concentrations are generally higher, some success has been had in measurement of ambient toluene concentrations. Some hydrocarbon monitoring was also carried out using a portable GC to measure roadside concentrations of benzene, toluene and m+p-xylene in Dublin city centre over a two day period, giving average concentrations of 0.7, 1.55 and 0.42 ppb, for benzene, toluene and xylene, respectively. These concentrations are lower than measured in this study (though the short duration of the study does not allow detailed comparison). Concentrations measured at rooftop level over the course of a two day period indicated remarkably similar concentrations to those above. This portable equipment was also run beside the DOAS equipment, however, agreement between the two methods was found to be poor, due to the low sensitivity of the DOAS method. Sample plots of 15 minute average BTX

concentration data collected during the short study using the portable monitoring equipment are given in Figure 2.3 and Figure 2.4. Ambient measurements collected at a roadside location are presented in Figure 2.3. Although only a small amount of data are available for analysis, the evening peak between 16:00 and 19:00, and the early morning rise in concentration suggests that vehicle emissions are a significant source of BTX at this location.

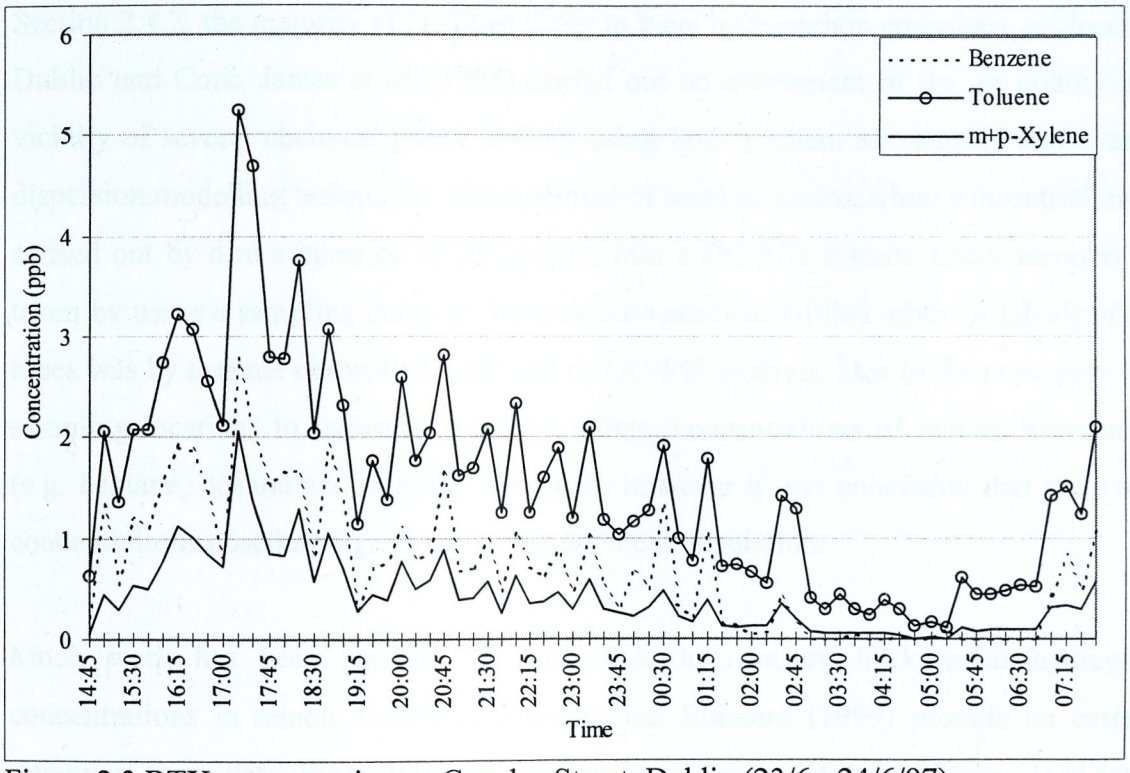


Figure 2.3 BTX concentration on Camden Street, Dublin (23/6 - 24/6/97)

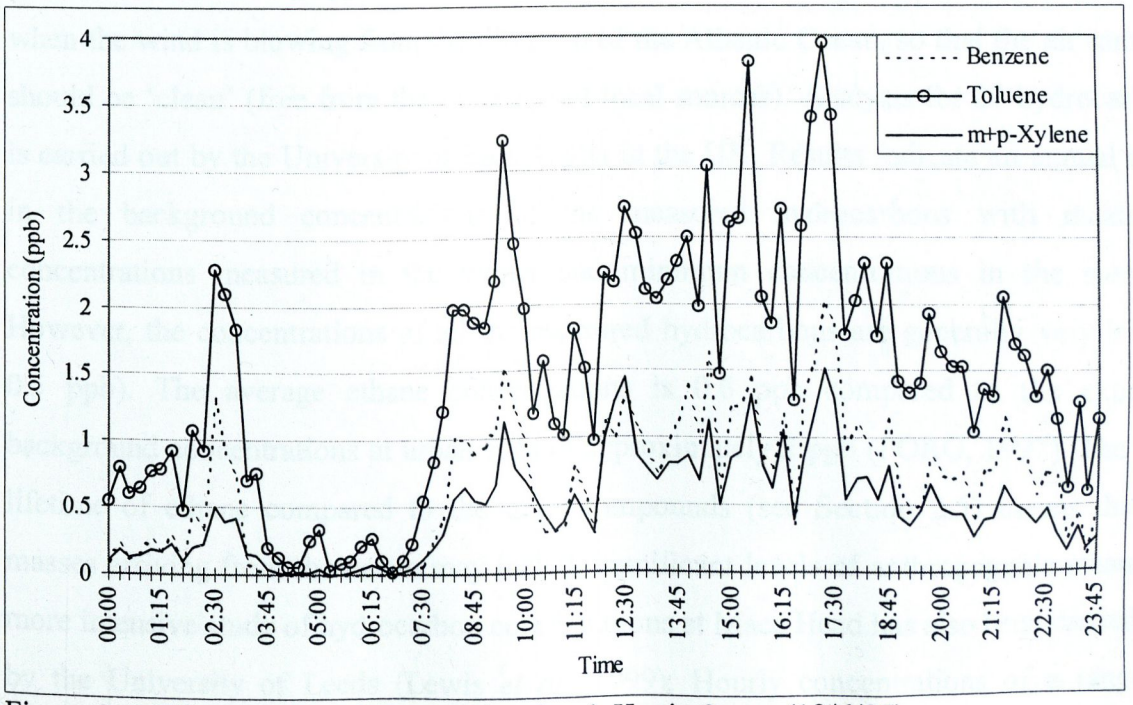


Figure 2.4 BTX concentration at rooftop level, Kevin Street (18/6/97)

The data presented in Figure 2.4 were collected on the top of a five storey building. The impact of vehicle emissions on the measured concentrations is, however, still evident with peaks in concentration corresponding to peak traffic times in the morning and evening.

Little data can be found with regard to hydrocarbon monitoring in the vicinity of industrial sites in Ireland. At present the EPA monitor licensed emissions from many facilities (see Section 2.4.2), but no ambient monitoring is carried out in their vicinity. As mentioned in Section 2.4.2, the majority of facilities likely to have hydrocarbon emissions are located in Dublin and Cork. James *et al.* (1995) carried out an assessment of the air quality in the vicinity of several chemical plants in Cork using both ambient air samples and Gaussian dispersion modelling techniques. Measurement of ambient hydrocarbon concentrations was carried out by direct injection of air samples into a GC-PID system. Other samples were taken by using a sampling pump to draw air onto adsorbent-filled tubes. Analysis of these tubes was by thermal desorption, followed by GC-MS analysis. Due to the proximity of the sampling locations to industrial emission points, concentrations of certain hydrocarbons (e.g. heptane, hexane and toluene) were high, however it was concluded that the average concentrations posed no significant risk to the local population.

Much work has been carried out world-wide to measure background hydrocarbon concentrations in remote locations. Bonsang and Boissard (1999) provide an extensive review of these data. Since 1993, air samples have been collected at Mace Head (on the West coast of Ireland) approximately every two weeks (PORG, 1997). Samples are taken when the wind is blowing from the direction of the Atlantic Ocean, so that the air samples should be 'clean' (free from the influence of local sources). Analysis for 27 hydrocarbons is carried out by the University of East Anglia in the UK. Results indicate an annual cycle in the background concentrations of the measured hydrocarbons with maximum concentrations measured in the winter and minimum concentrations in the summer. However, the concentrations of all the measured hydrocarbons are generally very low (< 0.5 ppb). The average ethane concentrations is 0.6 ppb compared to the expected background concentrations at urban sites of approximately 2 ppb (PORG, 1997). The long lifetime of ethane compared to the other compounds (see Section 2.5) means that air masses arriving from the ocean may include significant levels of anthropogenic ethane. A more intensive study of hydrocarbon concentrations at Mace Head has also been carried out by the University of Leeds (Lewis *et al.*, 1999). Hourly concentrations of a range of

reactive alkenes were collected over a four week period. These measurements indicated that emissions from local coastal waters were responsible for a significant proportion of the measured hydrocarbons.

2.7.2 Hydrocarbon Monitoring Studies in the United Kingdom

The UK hydrocarbon monitoring network consists of thirteen continuous monitoring locations. The first automatic monitoring site was set up in 1991 at Exhibition Road in London. Details of all current sites are given below. Hourly data are provided by each site and can be accessed through the UK Department of the Environment, Transport and the Regions (DETR) website, along with archive data for each site. Details of the equipment used at the sites are given by Dollard *et al.* (1995). The hydrocarbon compounds measured at each monitoring site are the same as those measured in this project, as the calibration standards are all sourced from the National Physical Laboratory (NPL).

Table 2.15 Automatic hydrocarbon monitoring stations (NETCEN, 1998)

Site name	Site type	Start date
Bristol east	Urban background	01/04/94
Belfast south	Urban background	23/08/93
Middlesborough	Urban industrial	01/01/93
London Bloomsbury	Roadside	11/02/93
London Eltham	Suburban	04/03/93
London Marylebone road	Roadside	28/08/97
Southampton centre	Urban centre	01/07/95
Edinburgh centre	Urban background	27/08/93
Liverpool Speke	Urban industrial	01/12/95
Harwell	Rural	01/01/95
Cardiff east	Urban background	01/11/93
Birmingham east	Urban background	23/08/93
Leeds centre	Urban background	13/01/95

As far back as 1973, hydrocarbon concentrations were measured at the rural Harwell site, which is now part of the automatic monitoring network. Other early monitoring work was carried out by the University of East Anglia at two other rural sites (QUARG, 1993). A short-term study was carried out in the early 1970s at a number of roadside sites in Coventry, using a continuous sampling and analysis system fitted in a mobile monitoring unit (Hickman *et al.*, 1973). The compounds measured during this study were methane, ethylene and acetylene, as well as total hydrocarbons. Peak hourly ethylene and acetylene

concentrations of approximately 200 ppb were reported during this study. One of the first continuous urban hydrocarbon monitoring sites was the urban background site in Middlesborough while the first long term continuous roadside site was located on Exhibition road in London. Analysis of initial results from the Middlesborough site are presented by Derwent *et al.* (1994). A range of C_2 to C_9 hydrocarbons, similar to those detailed in Table 3.1, were reported in this study. Average measured concentrations were low. For example, average benzene and toluene concentrations in 1993 were 1.0 and 1.7 ppb, respectively. Detailed analysis of results from the Exhibition Road monitoring site are presented by Field *et al.* (1994), Derwent *et al.* (1995) and Field (1995). Again, significant concentrations of hydrocarbons in the C_2 to C_9 range were reported. For example, from July 1991 to September 1992 the average isopentane and benzene concentrations were 10.2 and 4.5 ppb, respectively. In-depth analysis of data from 12 of the UK automatic hydrocarbon monitoring sites is presented by Derwent *et al.* (2000). Results from a number of sites in the UK automatic network are presented in Section 4.3 and compared to the measurements made during this project.

Monitoring was also carried out in the 1980s by the University of Lancaster, at an urban and rural site (Colbeck and Harrison, 1985a & 1985b). Samples were collected in Teflon bags with, 22 samples being collected over a two month period. Concentrations of a range of C_2 to C_6 hydrocarbon were reported. Average urban concentrations of acetylene and isobutane were reported at 5.15 and 10.18 ppb, respectively. Several samples were collected during a photochemical pollution episode, associated with polluted air masses arriving from continental Europe. Hydrocarbon concentrations up to six times greater than would normally be expected were measured during this episode.

Results from the UK hydrocarbon monitoring network and other hydrocarbon monitoring sites are presented in the Reports of the Photochemical Oxidant Review Group (PORG) on 'ozone in the United Kingdom', which also details ozone precursors (PORG, 1993 and 1997). The Quality of Urban Air Review Group (QUARG) also publish reviews of urban air pollution data (QUARG, 1993).

Recent concerns over evaporative emissions has also prompted a study on measurements of hydrocarbon concentrations in the vicinity of filling stations using diffusion tube sampling methods, and some continuous monitoring (Uren, 2000). Benzene concentrations on the

station forecourt are reported in the range 2.6 to 20.1 ppb, compared to 1.1 to 5.3 ppb at off-site monitoring locations near the petrol station. Many studies are also carried out by local authorities in response to public complaints. However, results from such studies are not usually published, but copies can normally be obtained from the relevant local authority. For example, reference is made in QUARG (1993) to benzene and toluene concentration measurements made by the Environmental Health Department of Halton Borough Council using a long path absorption (DOAS) technique.

Leach *et al.* (1999) measured hydrocarbon concentrations in the vicinity of a municipal incinerator, waste collection centre and a sewage treatment plant using a diffusive tube sampling method. Significant concentrations of a range of C_2 to C_{20} hydrocarbons were identified with, for example, average benzene concentrations in the range 18.5 to 37.6 ppb. Samples collected after the shutdown of the incinerator indicated significantly lower hydrocarbon concentrations, with average benzene concentrations in the range 9.4 to 14.5 ppb.

2.7.3 Hydrocarbon Monitoring in Other Countries

Europe

Much of the monitoring data collected in EU countries can be accessed through the European Environment Agency's air pollution database, 'AIRBASE'. Monitoring networks in most countries concentrate on pollutants such as sulphur dioxide, oxides of nitrogen, carbon monoxide and particulate matter. However, information on hydrocarbon concentrations is available for several countries.

Rappengluck and Fabian (1999) have recently carried out the first comprehensive hydrocarbon monitoring study in the greater Munich area in Germany using a quasi-continuous hydrocarbon monitoring system to monitor hydrocarbons in the C_6 to C_9 range. The study concentrated on traffic-related hydrocarbon emissions, although impacts of industrial solvent emissions were noted. Benzene and toluene average concentrations around 3.6 and 7.0 ppb, respectively, were reported for urban monitoring sites.

Seifert and Abraham (1982) have reported results of hydrocarbon monitoring at an intersection in Berlin carried out in 1978. Only benzene, toluene and m+p-xylene concentrations are reported, with hourly concentrations in the range 4 to 60 ppb, 5 to 110 ppb and 3 - 61 ppb, respectively. More recent monitoring in Berlin is reported by Thijsse *et al.* (1999a). Measurements were made at a rural background site, a city residential site and a street site in Berlin. Samples for measurements of compounds in the C_1 to C_5 range were collected using aluminium sampling bags, while compounds in the range C_4 to C_{14} were collected using pumped tube sampling. Background concentrations were very low, with most compounds exhibiting average concentrations less than 0.5 ppb, with the exception of ethane, which was reported to have a contribution from natural gas leakage. The roadside concentrations were significantly higher with, for example, isobutane, benzene and toluene average concentrations of 1.8, 1.5 and 4.4 ppb. Further results from this study are included in Appendix B. Assessment of the relative hydrocarbon content of German vehicles was carried out by Becker *et al.* (1999), by employing measurements in the Wuppertal Kiesbergtunnel.

Extensive monitoring has also been carried out in the Netherlands. Roemer *et al.* (1999) describe results from extensive monitoring near two industrial areas. Continuous monitoring equipment was used and results were provided on an hourly basis. Two years of data were available for one of the sites, and ten years of data for the other. However, only compounds in the C_2 to C_5 range were measured. Measured concentrations were highly dependent on wind direction, as emissions from the nearby industrial areas had the largest impact on measured concentrations. Thijsse *et al.* (1999b) present more recent hydrocarbon monitoring at three sites in the southern part of the Netherlands. Hydrocarbon concentrations in the range C_6 to C_{12} are reported. Sampling was carried out using an automated pumped tube sampling system which sampled each adsorbent filled tube for 24 hours, with analysis being carried out off-site. Six years of data are presented for each site. Two of the sites are part of the national air quality monitoring network of the Dutch National Institute of Public Health and Environmental Protection (RIVM). Data from a city centre monitoring site from the national air quality monitoring network are also presented. City centre roadside average benzene and toluene concentrations are reported as 1.4 and 4.2 ppb, respectively. RIVM measure weekly average hydrocarbon concentration at a number of regional, urban and roadside sites throughout the Netherlands. Approximately twenty samples per year are collected at each site. Roorda-Knape *et al.* (1998) measured benzene

concentrations in residential areas close to major motorways using a pumped tube sampling method to assess the decrease in concentration with distance from the motorway. A pumped sampling method was employed, with reported average benzene concentrations 15 metres from the motorways of approximately 0.6 ppb. No clear decrease in benzene concentrations with distance from the roadway was observed.

Much hydrocarbon monitoring work has also been carried out in Italy, as photochemical smog episodes are commonplace in several cities due to meteorological conditions. Brocco *et al.* (1997) carried out an extensive study of a wide range of hydrocarbons (C_2 - C_9) in Rome using a Differential Optical Absorption Spectrometer (DOAS) and an automatic GC-FID monitoring system. Agreement between the two monitoring systems was found to be good. Average measured concentrations reported in this study are high with average isobutane and benzene concentrations of 12.8 and 11.1 ppb, respectively. Ciccioli *et al.* (1999) describe the occurrence of a photochemical smog episode in Rome due to stable atmospheric conditions.

Another city which experiences severe air pollution episodes is Athens. Klemm and Ziomas (1997) measured hydrocarbons above the city of Athens using a monitoring system fitted in a light aircraft. In conjunction with ground based measurements, the relative emissions ratios of several pollutants (including 34 individual VOCs) were determined. As part of an intensive international monitoring project: the Mediterranean Campaign of Photochemical Tracers - Transport and Evolution (MEDCAPHOT - TRACE), a range of C_5 - C_{12} hydrocarbons were monitored on an hourly basis at a roadside location in Athens (Rappengluck *et al.*, 1998; Kourtidis *et al.*, 1999). City centre measurements indicated elevated hydrocarbon concentrations with, for example, average benzene and toluene concentrations of 9.5 and 16.8 ppb, respectively. Assessment of the contribution from evaporative traffic emissions revealed a change in the compounds which were emitted with increase in temperature.

Little information is available on hydrocarbon monitoring in France. Locoge *et al.* (1999) used the same automated monitoring system employed in this study to measure traffic and industrial related hydrocarbons in the town of Douai in northern France. Also, one of the rural monitoring sites of the EMEP programme mentioned below is located in France. Monitoring at a coastal site in the south of France has been carried out by Boudries *et al.*

(1994). Touaty and Bonsang (2000) recently carried out hydrocarbon measurements (C_2 to C_6 compounds) in the Thiais tunnel near Paris to characterise traffic related hydrocarbons in France. Samples were collected using a pumped sampling method.

Extensive details of the Swedish urban air quality network are given by Svanberg *et al.* (1998). Diffusive tube sampling methods are used to determine weekly mean VOC concentrations. More traditional pollutants such as SO_2 and smoke are also measured. Hydrocarbons are also measured in Finland as part of the EMEP (European Monitoring and Evaluation Programme) co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (Solberg *et al.,* 1997). Results from this monitoring station are included Appendix B.

The Norwegian Institute for Air Research (NILU) is the co-ordinator of the above EMEP programme, which reports measurements from twelve monitoring sites around Europe (Solberg *et al.,* 1997 and 1998). Data are available from monitoring sites in Finland, Norway, Latvia, Poland, France, Germany, Slovakia, Czech Republic and Switzerland. Results from several of these EMEP sites are presented in Appendix B. The monitoring sites in Latvia and Poland are no longer operational. Monitoring is also carried out at Mace Head (in Galway), however only carbonyl compounds are measured at this site. All of the sites are rural sites. Most of the samples collected are grab samples, with two samples per week collected at most sites, although the monitoring site at Tanikon in Switzerland, measures hydrocarbon concentrations on a two hourly basis. A number of hydrocarbons are measured at each site including alkenes, alkanes and aromatics.

Another co-operative air pollution monitoring programme is the Global Environmental Monitoring System for Air Pollution (GEMS/AIR) which is an urban monitoring and assessment programme operated jointly by the United Nations Environment Programme and the World Health Organisation (Monitoring and Assessment Research Centre, 1996). There are approximately 86 cities in 45 countries involved in the programme. The monitoring stations are normally part of national networks, with information being supplied to the GEMS/AIR database.

United States

The US Photochemical Assessment Monitoring Network (PAMS) is an extensive network of monitoring stations which are located in ozone non-attainment areas classified as serious, severe or extreme. There are approximately 21 areas in these categories, and each may have up to five monitoring stations (depending on the population) located in several different location types such as upwind, downwind and maximum emissions sites. Compounds measured at the PAMS site include 56 individual hydrocarbon species, ozone, oxides of nitrogen and meteorological data. All are measured on an hourly basis (USEPA, 1996a and b). Details of the PAMS, and other current networks in the United States are presented by Demerjian (2000).

Many hydrocarbon monitoring studies carried out in the United States have been reported. California is probably the most affected state as regards ambient hydrocarbon concentrations and consequent photochemical oxidant episodes. An extensive review of six years of VOC monitoring in the California area is presented by Main *et al.* (1999). The spatial, temporal and statistical behaviour of the hydrocarbons is examined.

Detailed analysis of results from four sites in the Sacramento area are presented by Hammond and Cook (1993). This study focuses only on winter data, as little photochemical reaction would takes place at this time. This aided in the characterisation of the hydrocarbon emissions in the area under study. Most samples were collected automatically in 6 litre stainless steel canisters between 06:00 and 09:00, and 13:00 and 16:00, on a on-in-three-day schedule. One continuous sampling and analysis system was employed at city centre junction, which reported a range of C_2 to C_9 hydrocarbons. Reported average concentrations of benzene and toluene at this site were 1.77 and 3.1 ppb, respectively, which are remarkably similar to the average concentrations measured at the Dublin city centre monitoring site (see Table 4.6). Further results from monitoring in Sacramento are presented in Appendix B.

Cohen *et al.* (1991) carried out a study in the vicinity of a highly industrialised area in Virginia. Hydrocarbons were sampled using a pumped sampling technique, with subsequent analysis by GC-MS. The impact of forest fires on hydrocarbon concentrations was also assessed. Continuous measurements were made by Goldstein *et al.* (1995) using an automated monitoring system fabricated by the project team. The system is capable of

collecting and analysing two samples simultaneously and was used for analysing air samples at two different heights in a forest, to determine biogenic hydrocarbon emission rates. A range of alkanes and alkenes were measured, with typical concentrations being very low, with the exception of ethane, which has a significant ambient background concentration.

Shreffler (1993) employed two different monitoring methods in monitoring hydrocarbons in Atlanta. An automated gas chromatography system provided hourly concentration values, while stainless steel canister samples of ambient air were also collected and analysed by a laboratory GC system. The average total non-methane hydrocarbon concentrations measured from the canister samples were 50 percent higher than from the automated system, due mainly to a large number of unidentified peaks observed during laboratory analysis of canister samples.

Ambient hydrocarbon concentrations at seven urban and six rural US sites are presented by Sexton and Westberg (1984). Hydrocarbon samples were collected in Teflon bags or stainless steel canisters for later analysis. Sampling was carried out on a daily basis between 06:00 and 09:00 in seven urban centres, and concentrations of hydrocarbons in the C_2 to C_{10} range are reported. Average acetylene concentrations ranged from 2.5 ppb in Milwaukee to 7.5 ppb in Houston, with average benzene concentrations from 0.66 to 3 ppb, in the same two cities, respectively.

Results from a hydrocarbon monitoring campaign carried out between 1979 and 1984 in twelve US cities (two weeks sampling at each location) are reported by Singh *et al.* (1985). In this instance, an automated monitoring system (installed in a mobile monitoring unit) was employed, which allowed one sample to be analysed every two hours. Concentrations for a range of aromatic hydrocarbons are reported. Average benzene concentrations ranged from 1.4 ppb in Missouri to 8.7 ppb in California. Toluene concentrations ranged from 1.5 to 16.9 ppb at the same two locations, respectively.

Other Countries

A review of benzene concentrations measured at over 30 sites in Canada over a four year period is presented by Dann and Wang (1995). Samples were collected in stainless steel canisters. Influence of both transportation and industrial emissions on ambient benzene

concentrations were observed during this study. Average benzene concentrations over all 30 sites ranged from 0.4 to 9.1 ppb. In response to summer photochemical smog episodes, an intensive hydrocarbon study was carried out in the Lower Fraser Valley (Canada). Automated sampling and analysis, and grab sampling at both ground level and in a light aircraft were performed. Rogak *et al.* (1998) collected whole air samples in the Cassiar tunnel in Vancouver using Tedlar bags, followed by cryogenic preconcentration and gas chromatographic analysis. The Vancouver vehicle fleet is characterised by a significant number of propane-fuelled cars and trucks, which resulted in higher propane concentrations compared to US tunnel studies. It was also observed that a significant proportion of the measured hydrocarbon concentrations resulted from emissions from poorly maintained vehicles.

Grosjean *et al.* (1998a & 1998b) measured a range of C_2 - C_{10} hydrocarbons at a urban and background locations in the large city of Porto Alegre (Brazil) over a one year period. Samples were collected in stainless steel canisters for later analysis by GC-FID and GC-MS. In Brazil, ethanol is used as a vehicle fuel, resulting in compounds being identified which would generally not be as abundant in other cities. Average urban concentrations for benzene, toluene and acetylene were 3.7, 5.4 and 37.2 ppb, respectively.

Another large city which suffers due to transport related emissions is Mexico City, where Riveros *et al.* (1995) collected a large number of samples in stainless steel canisters at several locations. Total non-methane organic compounds were measured for each sample. It was estimated that up to 70 percent of hydrocarbon emissions from vehicles in Mexico City were due to evaporative emissions. Mugica *et al.* (1998) monitored a range of C_2 to C_{12} hydrocarbons in road tunnels and multi-storey car parks. The most abundant measured species were acetylene, isopentane and toluene.

Hydrocarbon measurements in Bombay (India) identified industrial sources, emissions from crude oil refining and traffic as major contributors to the elevated hydrocarbon concentrations measured in the Bombay area (Pandit and Mohan Rao, 1990; Mohan Rao *et al.*, 1997). Canister sampling was used during the first study while on-line sampling and analysis was employed in the latter (1997) study. Elevated concentrations of many hydrocarbons were observed due to emissions from nearby oil refineries, for example, average propane and n-butane concentrations of 35.3 and 24.3 ppb, respectively, were

measured between January and June 1986 (Pandit and Mohan Rao, 1990), while concentrations measured between March 1993 and May 1994 were reported as 15.4 and 32.2 ppb, respectively (Mohan Rao *et al.*, 1997). Other hydrocarbons with high ambient concentrations include isopentane and n-pentane. A similar study carried out in Bahrain, also identified industrial emissions and oil refining as major sources of ambient hydrocarbons (Zainal, 1990). Although hydrocarbon concentrations were very high at certain locations, the species of hydrocarbon identified were different to those expected from vehicle exhausts, with a significantly lower ozone creating potential.

Road-tunnel measurements have been employed to identify the 'fingerprint' of automobile emissions, as measured concentrations are composed entirely of vehicle emissions. One particularly interesting study was carried out by Zielinska *et al.* (1996) in the Fort McHenry Tunnel in the USA. As heavy duty vehicles and light duty vehicles are directed through different bores of the tunnel, characteristic hydrocarbon emissions from each of these vehicle types were separately assessed. Heavy duty diesel vehicles tend to emit a high proportion of 'semi-volatile' hydrocarbons (in the range C_{10} - C_{20}) compared to petrol fuelled vehicles. Staehelin *et al.* (1997, 1998) carried out a similar study in the Gubrist tunnel in Switzerland, using the results to formulate emission factors for typical Swiss vehicles. Long term aromatic hydrocarbon measurements using a DOAS system were carried out in the Wuppertal Kiesbergtunnel by Becker *et al.* (1999). Touaty and Bonsang (2000) recently carried out a similar study in the Thiais tunnel near Paris. The results from these studies may be applicable to the Irish traffic situation as many of the vehicles would be the same models as those used on Irish roads.

3. MONITORING EQUIPMENT

3.1 INTRODUCTION

Various methods were used for sampling and analysing hydrocarbons during this project. During the first and second monitoring studies (in Dublin city centre and near Rhode generating station, respectively), an on-line sampling and analysis system was used for all hydrocarbon monitoring. During the third monitoring study (at the industrial estate in Mullingar), passive and pumped sampling apparatus were used in addition to the on-line hydrocarbon monitoring system. These pumped and passive sampling tubes were analysed at the EPA laboratory in Cork, and at the Enterprise Ireland laboratory in Dublin. The on-line monitoring system is discussed in detail in Section 3.2, while the pumped and passive sampling apparatus are described in Sections 3.3 and 3.4.

3.2 ON-LINE HYDROCARBON MONITORING SYSTEM

The hydrocarbon monitoring unit used during this study is a Perkin-Elmer 'Ozone Precursor Monitoring System'. The system comprises a number of individual components which are described in the following section. The operation of the system is also described in some detail.

3.2.1 System Components

The monitoring system is composed of several components, each of which required proper installation and continued competent maintenance. In order to ensure the accuracy of the results obtained from an analysis, each component needs to be extremely competent in performing its dedicated task in the sampling process. If each component in the series introduced an error outside the range of expected aberrations, then the final result would be significantly in error. This is especially true given that hydrocarbon concentrations will be measured in the low parts per billion (ppb) range, with most measured ambient concentrations being less than 5 ppb, particularly in rural areas. Expert care of each component is vital, as all results must be reliable. The whole system is housed in a mobile laboratory which also has an in-built meteorological station. The principal components of the on-line hydrocarbon monitoring system are the air sampler, ATD400, Autosystem Gas

Chromatograph, 900 series interface and the Turbochrom analytical software. These components are illustrated in Figure 3.1, and are described in the following sections.

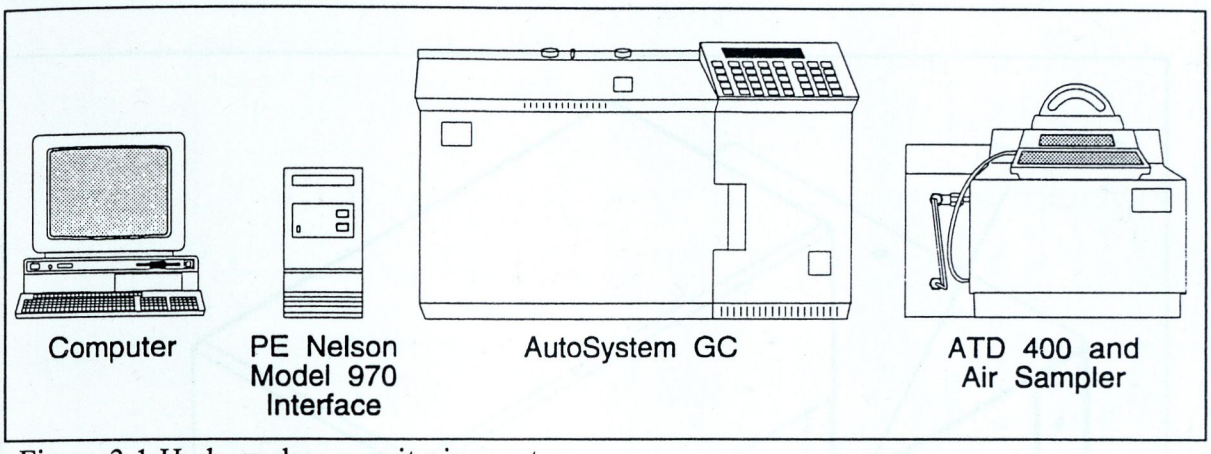


Figure 3.1 Hydrocarbon monitoring system

The Air Sampler and Accessories

Figure 3.2 and Figure 3.3 show front and rear views of the air sampler, respectively. The air sampler is attached to the back of the ATD 400 which is described below. Valve C controls whether sample gas or calibration gas is drawn through the system. Valve B is used to connect and disconnect the sample flow to the ATD 400. Dry air, from the air generator, is circulated through the Nafion drier to dry the ambient air sample prior to analysis. This prevents the cold trap (which remains at -30 °C during sample collection) from icing. The flow of dry air can be adjusted using the needle and toggle valves.

A mass flow controller is used to control the flow of the sample through the system. This flow controller is an integrated part of the sampler, but can be adjusted by the operator. An external readout display is used to alter the flow rate and to turn the flow off via a connection to a solenoid valve in the air sampler. The sampling rate is normally set to 15 ml / minute.

The air-sampling pump is an external device. The inlet port of the air-sampling pump is connected to the pump port on the air sampler using nylon tubing. The pump is used to draw the sample, or the calibration gas (depending on the position of valve C) through the cold trap in the ATD400.

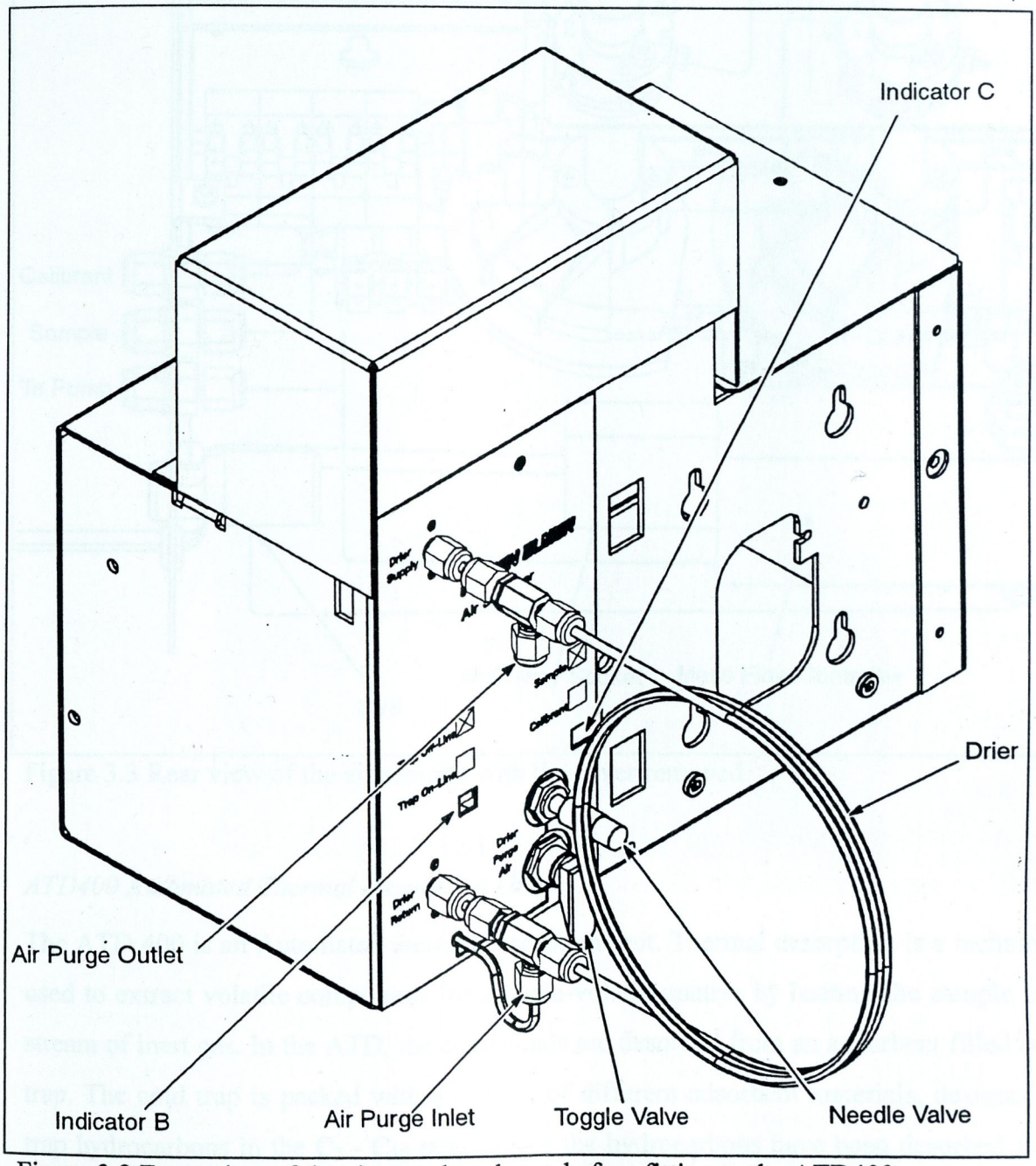


Figure 3.2 Front view of the air sampler, shown before fitting to the ATD400

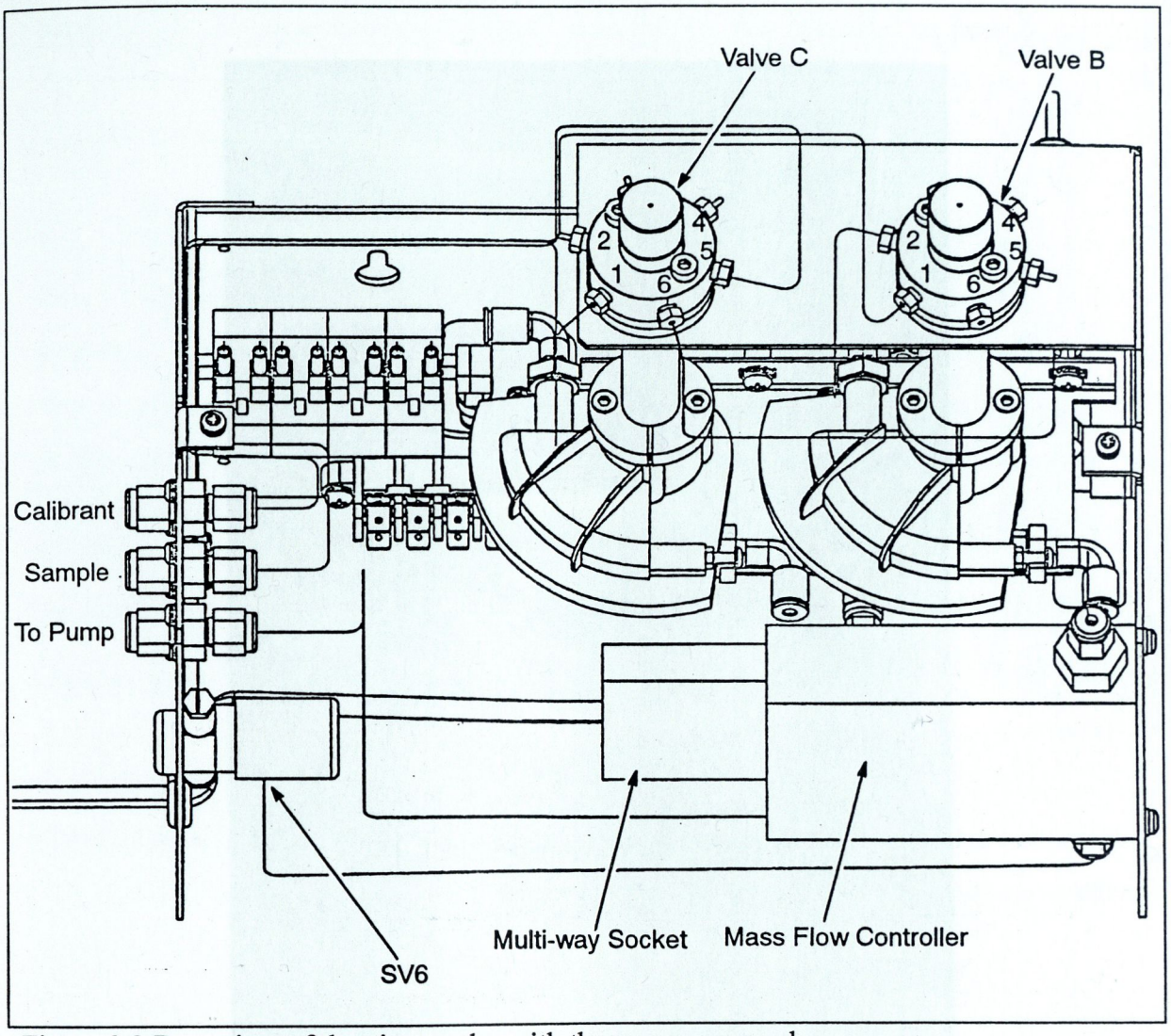


Figure 3.3 Rear view of the air sampler with the cover removed

ATD400 Automated Thermal Desorption Unit

The ATD 400 is an Automated thermal desorption unit. Thermal desorption is a technique used to extract volatile compounds from a non-volatile matrix by heating the sample in a stream of inert gas. In the ATD, the compounds are desorbed from an adsorbent filled cold trap. The cold trap is packed with a number of different adsorbent materials, designed to trap hydrocarbons in the C_2 - C_{10} range. Once the hydrocarbons have been desorbed from the cold trap, they are transferred through a heated transfer line to the gas chromatograph.

A picture of the ATD 400 is provided in Figure 3.4. The ATD 400 can be controlled either directly from the gas chromatograph to which it is attached or through a separate keyboard with LCD display as shown in Figure 3.4. The latter option was employed in this project.



Figure 3.4 ATD400 Thermal desorption unit with external keyboard

The ATD is fitted with a carousel (shown on the top of the ATD in Figure 3.4), which can be used if samples are collected in adsorbent filled tubes (such as the pumped or passive sampling tubes detailed in Section 3.3 and 3.4). Up to 50 sample tubes can be placed in the carousel at one time. However, in the on-line system, the air sampling accessory described in the previous section is used to deliver ambient air directly to the cold trap in the ATD, negating the need for a separate sampling phase before analysis is carried out. A blank sampling tube is placed in the carousel, which is then inserted into the sampling path during analysis, simply to complete the sample path circuit. However, at no point during the sampling process does the carousel rotate.

An oven is installed in the ATD to heat the sample during the thermal desorption stage. The oven temperature can be set between 50 and 400 °C. The actual temperature used

depends on the experimental 'method' selected by the operator to provide optimal performance (see Section 3.2.6). For this study, the upper temperature limit was set at 325 °C while the minimum temperature was set at -30 °C.

The ATD heated valve is a six-port rotating valve which is used to direct the carrier gas flow to the cold trap during the desorption process, or to isolate the cold trap in other situations. The heated valve may be heated to between 50 and 225 °C depending on the experimental method being used. The valve must be heated to allow a constant temperature to be maintained during the desorption process while the trapped components are transferred through the heated transfer line, to the GC.

The cold trap concentrates the hydrocarbons before they are injected into the capillary columns in the GC. The cold trap consists of a straight quartz tube approximately 165mm long by 3mm internal diameter and can be cooled electrically to temperatures between -30 and +30 °C. The trap is packed with Perkin-Elmer proprietary adsorbent materials which allows hydrocarbons with boiling points as low as -90 degrees centigrade to be trapped. The sampling method used during this study holds the cold trap at - 30 °C during sampling, while the desorb temperature is 325 °C.

A heated transfer line connects the ATD400 to the gas chromatograph and consists of a heated stainless steel tube containing a silica sample transfer line. The transfer line may be heated to between 50 and 225 °C.

Autosystem GC Gas Chromatograph

The Autosystem GC (illustrated in Figure 3.5) is a dual-channel, temperature-programmable, gas chromatograph. The GC can work alone, but for on-line hydrocarbon monitoring, the sample is supplied to the GC through the heated transfer line running between the ATD400 and the GC. The GC, which is controlled by a built-in microprocessor, can be installed with up to two detectors. The types of detector which can be installed include Flame Ionisation Detectors (FID), Electron Capture Detectors (ECD), Thermal Conductivity Detectors (TCD), Photoionisation Detectors (PID), Electrolytic Conductivity (ELCD), Nitrogen Phosphorus Detectors (NPD), and Flame Photometric Detectors (FPD). The flame ionisation detector responds in proportion to the carbon

content of the sample, and hence almost any organic sample can be detected. For the type of monitoring carried out during this study, the FID is the most widely used detector type as it is non-selective (see Section 2.6.2). The FID has been reported to have the best record for reliable performance among the ionisation type detectors, and it is highly sensitive and relatively rugged compared to some of the other types of detectors. For these reasons, two flame ionisation detectors have been fitted to the GC used in the on-line system.

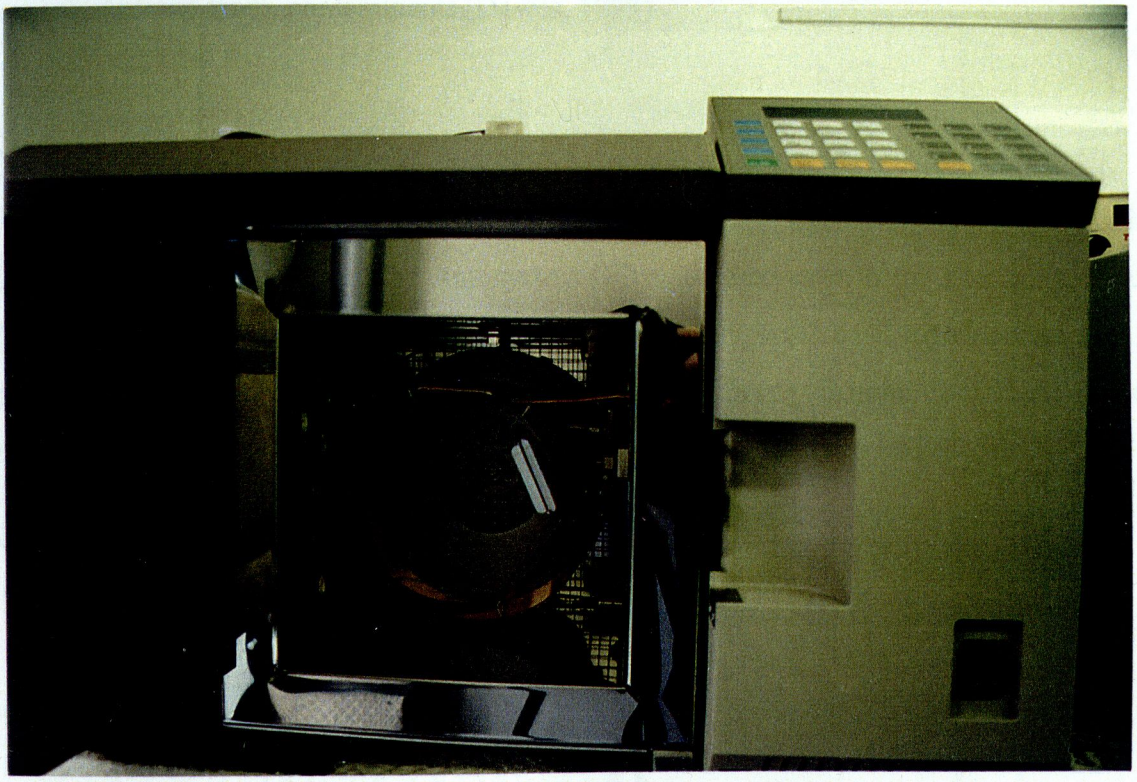


Figure 3.5 Autosystem GC used in this study, with oven door open

The GC also contains an oven in which the capillary columns are installed (see Figure 3.5). The oven temperature is regulated either through the keyboard on the GC or through the Turbochrom software installed on the PC. Up to two columns can be installed in the oven at one time.

Capillary and Packed Columns

The various constituents of the sample can be separated in either a capillary column or a packed column. In this study, capillary columns were be used for all analyses. Capillary columns are usually between 10 and 100 metres in length, whereas packed columns are between 2 and 4 metres in length. Obviously the efficiency and time of analysis must be taken into account when deciding on the type and length of the column. Each column can

only separate a certain range of compounds so, depending on the study objectives, more than one column may be required. In the system described here, two columns are fitted in the GC. Each column is connected to one of the flame ionisation detectors, allowing a wider range of compounds to be detected compared to single column chromatography. The two columns used in this study are a 50 metre PLOT (Porous Layer Open Tubular) column and a 50 metre BP1 (Bonded Phase) column. Compared with conventional packed columns, capillary columns tend to give greater sensitivity, increased speed of analysis and less interference from contaminants (Dawes, 1993).

900 Series Interface

The 900 series interface is an analogue-to-digital interface which acquires the analytical data (the FID response) from the Autosystem GC and transfers it to the host computer. A diagram of the back panel of the interface is shown in Figure 3.6. The two connectors on the top left hand side are the detector connections, one being channel A (CH A) and the other channel B (CH B) allowing data from the two FID detectors to be processed.

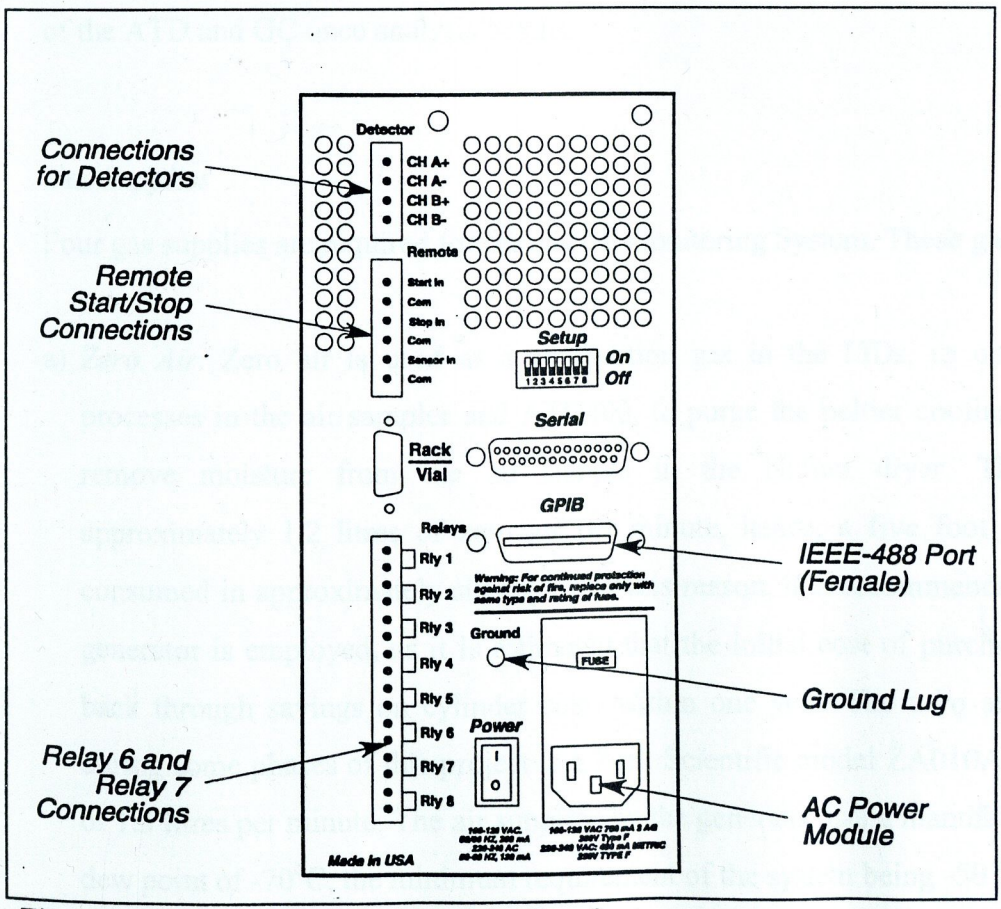


Figure 3.6 Rear panel of the 900 series interface

The relays, which are the bottom left set of connections in Figure 3.6 are used to control external devices such as the air sampler valves, i.e. valves B and C described earlier in this section.

Turbochrom Analytical Software

The Turbochrom analytical software is a windows based application which can be installed on any PC with more than 8 MB of RAM. It is necessary to install a new board (supplied by Perkin-Elmer) into any of the free expansion slots of the computer. The connector on this board is used to connect the 900 series interface to the PC.

The Turbochrom software processes the raw data transferred to the PC from the GC detectors via the 900 series interface. This software is also used to write analysis 'sequences' which provide instructions to the ATD400, the air sampler, and the GC on forthcoming sampling and analysis runs, which allows the system to then operate unattended. Sequences are discussed in more detail in Section 3.2.7. Once the sequence has been written, it is then downloaded to the 900 series interface, which control the operation of the ATD and GC once analysis begins.

Gas Supplies

Four gas supplies are required for the on-line monitoring System. These gases are:

a) *Zero Air*. Zero air is used as a combustion gas in the FIDs, to operate pneumatic processes in the air sampler and ATD400, to purge the peltier cooling system, and to remove moisture from the air sample in the Nafion dryer. The system uses approximately 1.2 litres of zero air per minute, hence, a five foot cylinder will be consumed in approximately six days. For this reason, it is recommended that a zero air generator is employed, as it is estimated that the initial cost of purchase will be made back through savings on cylinder costs within one year. The zero air generator used during some phases of this project is a Peak Scientific model ZA010A with a flow rate of 1.5 litres per minute. The air supplied by the generator has a manufacturer's specified dew point of -70°C, the minimum requirement of the system being -50 °C.

b) *Helium.* This is used as the carrier gas, and as approximately only 5 millilitres per minute is used, a cylinder will last 3 months. The helium must be 99.999 percent pure. Hydrogen cannot be used as a carrier gas during this study, as hydrogen reacts with acetylene, and eliminates it from the air sample.

c) *Hydrogen.* This is used as the fuel for the Flame Ionisation Detectors (FIDs), along with zero air. Approximately 80 millilitres per minute are used so a cylinder will last about 5 weeks.

d) *Calibration Gas.* The calibration gas is the most expensive gas used in the operation of the system. The calibration gases used during this study were supplied by the UK National Physical Laboratory. The components contained in the mixtures are presented in Table 3.1. The compounds are divided according to the capillary column on which they are separated. Cylinder 2 was used during monitoring at Mullingar only.

Table 3.1 Components of the calibration gas mixtures, by capillary column

PLOT column	Cylinder 1 (ppb)	Cylinder 2 (ppb)	BP1 column	Cylinder 1 (ppb)	Cylinder 2 (ppb)
Ethane	21.00	6.74	n-Hexane	19.80	1.75
Ethylene	14.60	10.55	cyclo-Hexane		3.31
Propane	16.20	2.55	Benzene	13.00	3.40
Propylene	25.50	6.65	n-Heptane	32.00	2.75
Isobutane	13.20	2.98	Toluene	30.60	3.20
n-Butane	6.08	2.57	Ethylbenzene	21.70	1.76
Acetylene	23.00	8.79	m+p-Xylene	16.70	1.39
Trans-2-butene	10.80	2.20	o-Xylene	7.49	0.99
1-Butene	22.30	3.30	1,3,5-trimethylbenzene	3.6	0.92
Cis-2-butene	19.20	2.36	1,2,4-trimethylbenzene	6.0	1.12
Isopentane	48.70	1.17			
n-Pentane	17.10	2.63			
1,3-butadiene	17.00	5.28			
Trans-2-pentene	46.30	4.01			
Cis-2-pentene	25.30	1.53			
2-methylpentane	9.95	3.15			
3-methylpentane	24.40	3.61			
Isoprene	40.00	1.83			

Notes 1: cyclo-hexane only contained in cylinder for Mullingar study
2: base gas used in the mixture is nitrogen

3.2.2 The Mobile Monitoring Unit

The on-line monitoring system is fitted into a mobile unit (Figure 3.7). There are two compartments in the monitoring unit: the main section, where the monitoring equipment is fitted, and a smaller compartment where the gases are stored. Other air quality monitoring equipment is also fitted in the unit including particulate and sulphur dioxide measurement apparatus. Photographs of each of these compartments are given in Figure 3.8 and Figure 3.9, respectively. The exterior of the unit can be seen in Figure 6.3.

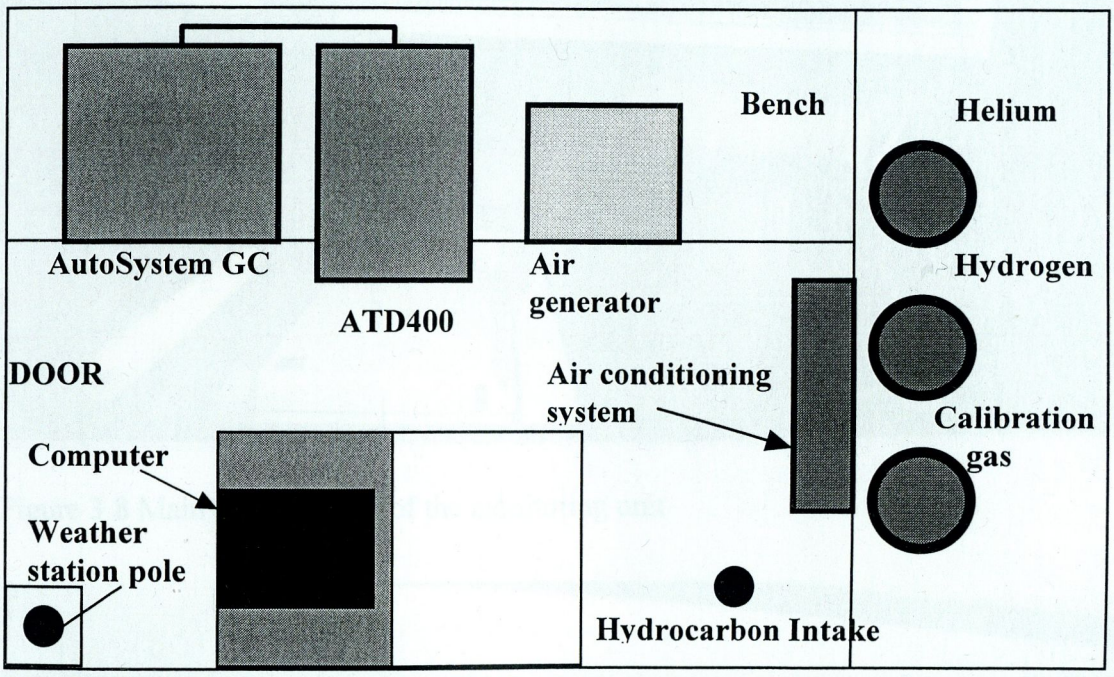


Figure 3.7 Schematic of mobile monitoring unit

Situated on a bench on one side of the unit is the GC and the ATD400, with the zero air generator underneath the bench. On the other side of the unit is a rack which contains the particulate measurement unit and the computer which processes the data from the weather station and the gas chromatograph. The hydrocarbon intake manifold and the weather station telescopic pole are also located on this side of the monitoring unit. The weather station monitors windspeed, wind direction and temperature. The detectors are located on a telescopic pole which can be elevated to approximately 10 metres above ground level.

The unit is fitted with an air conditioning system, which is necessary to keep the temperature inside the unit at a suitable temperature, as the ATD400 and GC oven cooling processes result in warm air being expelled into the main compartment. The power requirement of the unit is very high with an internal fuse board fitted to regulate the supply.

Obviously, wherever the monitoring unit is situated there must be a suitable electricity supply.

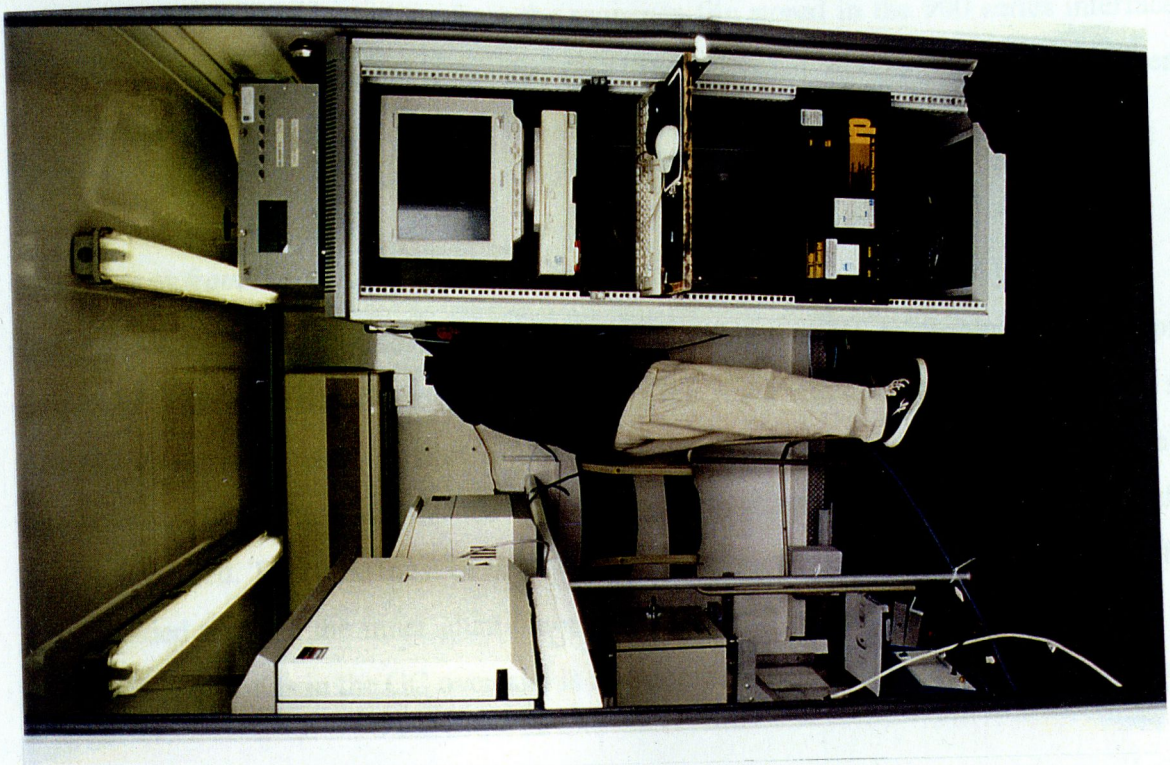


Figure 3.8 Main compartment of the monitoring unit

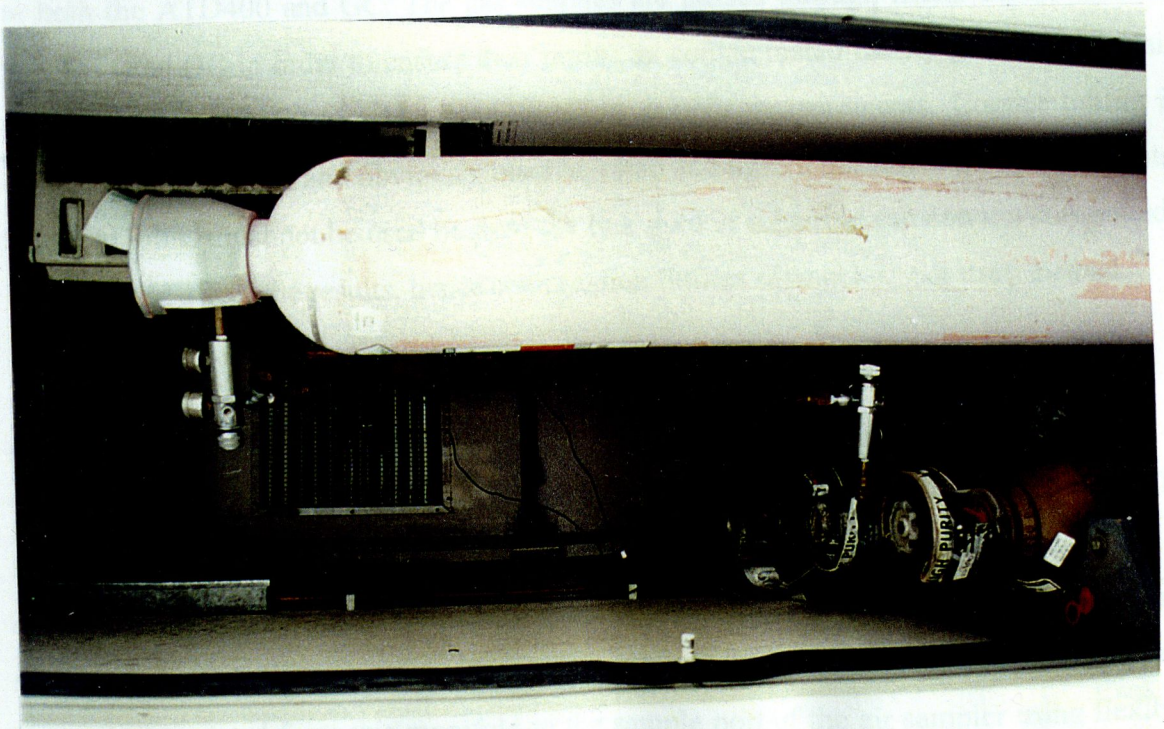


Figure 3.9 Gas storage compartment of the monitoring unit

3.2.3 Physical Connection of the Components

The connection of the system should be based around the ATD400, as it is the ATD which is used to start and stop a sampling sequence. The ATD is the first link in the sampling process and, through instructions from the sequence file stored in the 900 series interface, controls the time of operation of the GC. The physical connection of the system components took approximately three full days to complete.

Connections from the ATD400 to Other Components

The ATD400 is connected to the Autosystem GC using a cable assembly with a 25-pin connector. This connection allows the timing of the ATD and GC to be synchronised so that GC analysis is ready to start as soon as desorption begins in the ATD. The main connection between the GC and the ATD is the heated transfer line through which the sample is passed. This tube must be bent into shape before fitting and a fused silica transfer line threaded through the inner aluminium transfer line. The transfer line is connected to the capillary columns in the GC oven and is connected to the outlet splitter at the ATD end.

The carrier gas (helium) and the air supply (from the zero air generator) must be connected to both the ATD400 and GC. The gas supplies are passed through filters before entering the ATD and GC in order to ensure their purity, as contaminated carrier gases can contain volatile organics which would adversely affect sample measurements. Copper tubing is used to carry the gases and obviously must be clean and have a minimum number of joints. Soldered joints must not be used because the flux used in soldering can contain compounds which would affect the results, hence compression fittings (Swagelok) are used instead.

Air Sampler and Interface Connections

The air sampler must be connected to the ATD. This may be done prior to delivery. The flow controller and the pump must also be connected to the air sampler. Ambient air is drawn through a glass intake manifold located towards the back of the monitoring unit, and samples can be extracted at six different points along the manifold. The air sampling stream is connected from this manifold to the sample port of the air sampler using flexible nylon tubing. The sampling pump, connected to the air sampler, draws a sample through

this nylon tube on a continuous basis, with valve B controlling whether the sample is passed through the ATD cold trap.

The calibration gas is connected to the calibrant port on the sampler (see Figure 3.3). A special regulator is required for the calibration gas cylinder. This regulator is not fitted with a gauge, as this could lead to possible losses of trace hydrocarbons. Hence the calibration supply is set up as shown in Figure 3.10. The delivery pressure of the gas can then be adjusted at the regulator and read at the gauge, but the gas which passes to the gauge is not passed on to the air sampler due to the inclusion of the T-piece. The required pressure of the gas is approximately 2 psig.

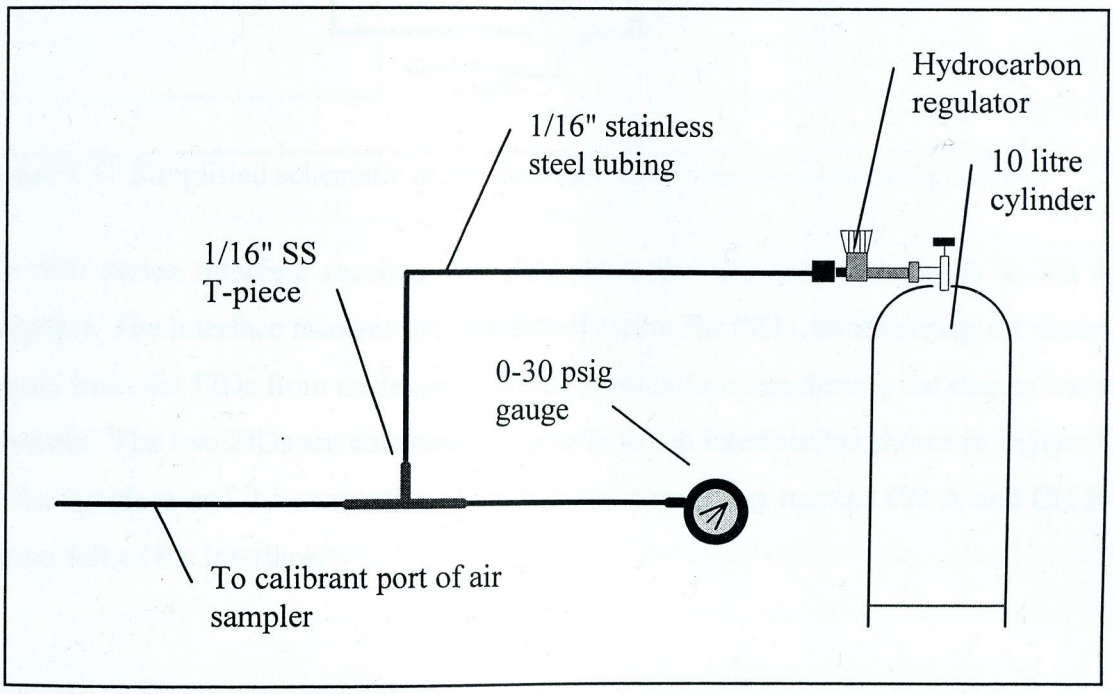


Figure 3.10 Calibration gas supply and pressure measurement set-up

The sample / calibrant valve (valve C) in the air sampler is controlled by the 900 series interface. The position of this valve is controlled by relays 6 and 7 on the interface. Relay 6 is the calibrant relay and when this relay is turned on, the valve will be positioned so that the calibrant gas is being drawn through the system. Figure 3.11 is a simplified schematic of the flow path of a sample through the complete system. Valve C is shown in the upper left hand corner of the diagram. The diagram shows that, as the valve is rotated, the input gas switches between the calibrant and the sample. The status of relays 6 and 7 is controlled by the 'sequence' written by the user using the Turbochrom software (see Section 3.2.7). Section 3.2.4 gives a detailed description of the sample flow through the system.

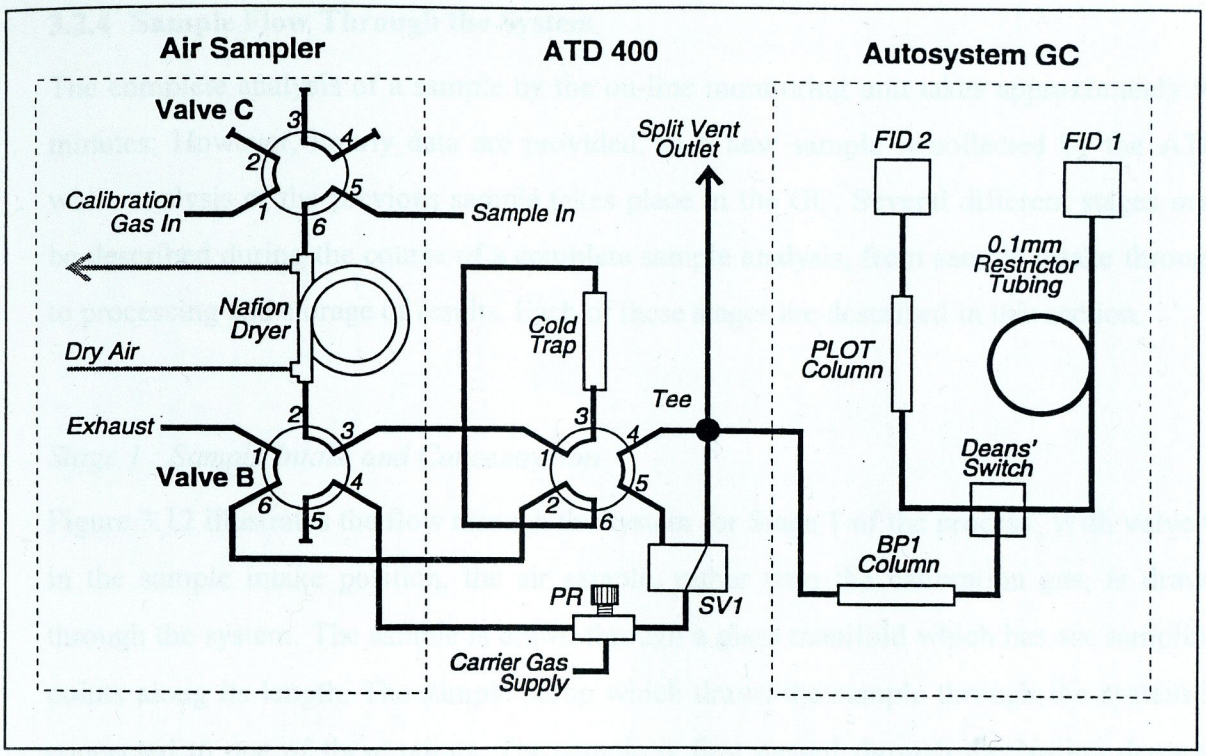


Figure 3.11 Simplified schematic of the flow path in the on-line monitoring system

The 900 series interface receives raw data from the GC and transfers it to the host computer. The interface receives the data directly from the FIDs, transforming the electrical signals from the FIDs from analogue to digital form before transferring the data to the host computer. The two FIDs are connected separately to the interface (as shown in Figure 3.6). At the interface end the connection is made at the connectors marked CH A and CH B on the top left of the interface.

Turbochrom Software Installation

The installation of the Turbochrom software is a relatively simple process. The heart of the system is the Ziatech Card which is installed in one of the expansion slots in the computer. The connection on the Ziatech card is then used to connect the 900 Interface with the host computer using an IEEE-488 cable.

Connection of the Nafion Air Dryer

The Nafion air dryer is connected between dryer return and dryer supply on the front of the air sampler (see Figure 3.2). The dryer uses zero air from the gas supply to dry the ambient sample. The flow rate should be set to approximately 250ml/min using the needle valve.

3.2.4 Sample Flow Through the System

The complete analysis of a sample by the on-line monitoring unit takes approximately 95 minutes. However, hourly data are provided, as a new sample is collected by the ATD while analysis of the previous sample takes place in the GC. Several different stages may be described during the course of a complete sample analysis, from sample intake through to processing and storage of results. Each of these stages are described in this section.

Stage 1 : Sample Intake and Concentration

Figure 3.12 illustrates the flow through the system for Stage 1 of the process. With valve C in the sample intake position, the air sample, rather than the calibration gas, is drawn through the system. The sample is drawn through a glass manifold which has six sampling points along its length. The sample pump which draws the sample through the system is connected to one of these points. The sample is first passed through the Nafion dryer to remove any moisture in the sample. The sample then passes through an empty tube which is permanently situated in the carousel of the ATD400. This empty tube serves no purpose other than to close the path of the sample through the system.

The sample is then passed through the cold trap where volatiles are trapped on the adsorbent material. The compounds retained depend on the type of adsorbent material employed. After prolonged use, the adsorbent material may begin to decompose or become contaminated. This usually manifests itself as a decreased output when a standard test sample (e.g. a calibration standard) is analysed. The adsorbent material in the cold trap should then be replaced or, more usually, the complete cold trap is replaced.

When the sample has passed through the cold trap and the volatiles are adsorbed, the rest of the sample continues on and passes through a filter, before being released through the exhaust of the pump which draws the air sample through the system. The time during which the sample is being drawn through the cold trap is known as the standard injection time (STD INJ) and lasts for exactly 40 minutes. During this stage of the process, the carrier gas flows only through the columns in the GC, with the excess flowing through the outlet split vent.

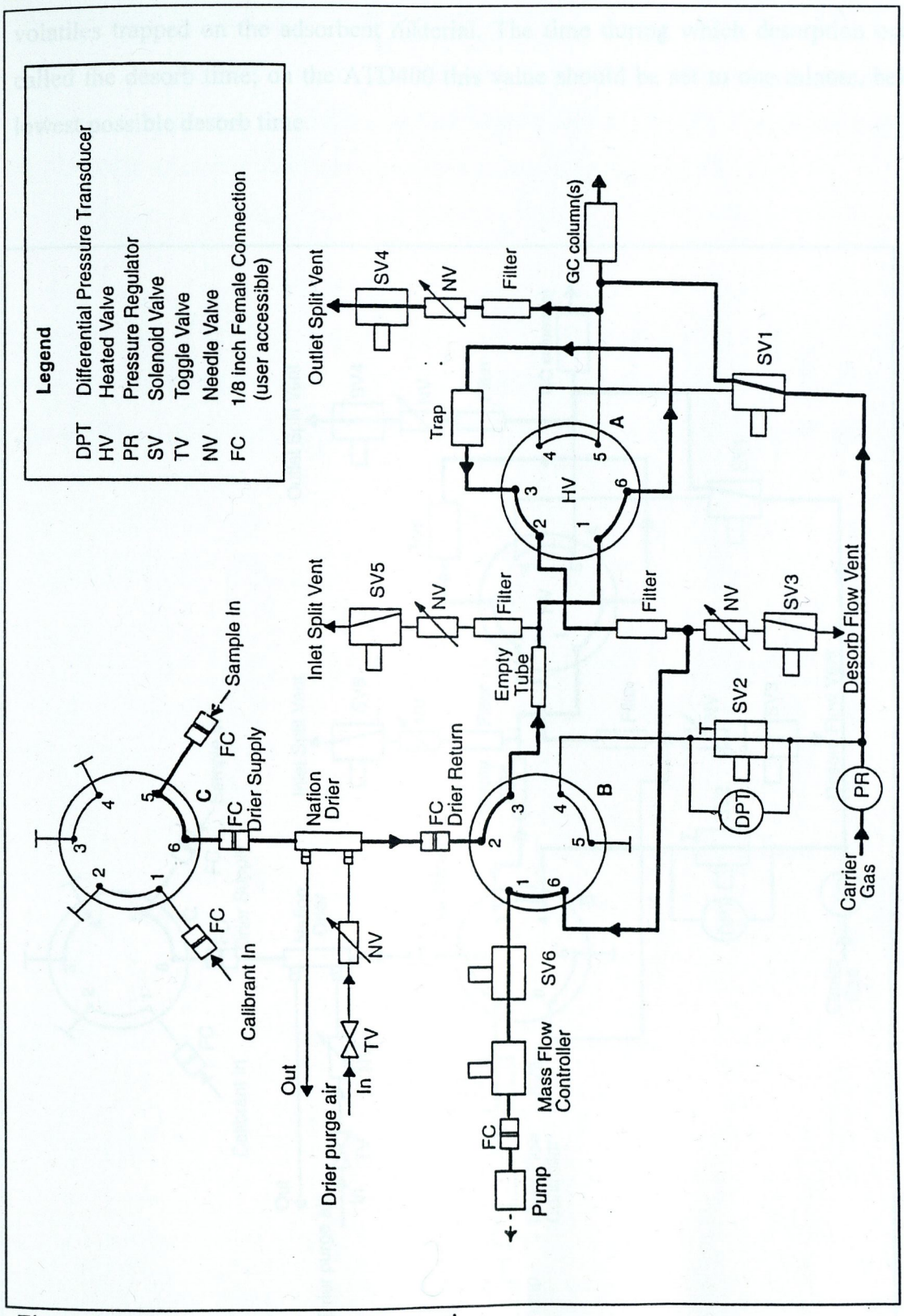


Figure 3.12 Sample intake and concentration

Stage 2 : Desorption

During the desorption stage, Figure 3.13, valve B is rotated and the air sample is no longer drawn through the system (see Figure 3.12 for legend). Air is removed from the cold trap by passing an inert gas (helium, i.e. the carrier gas) through the cold trap, leaving only the

volatiles trapped on the adsorbent material. The time during which desorption occurs is called the desorb time; on the ATD400 this value should be set to one minute, being the lowest possible desorb time.

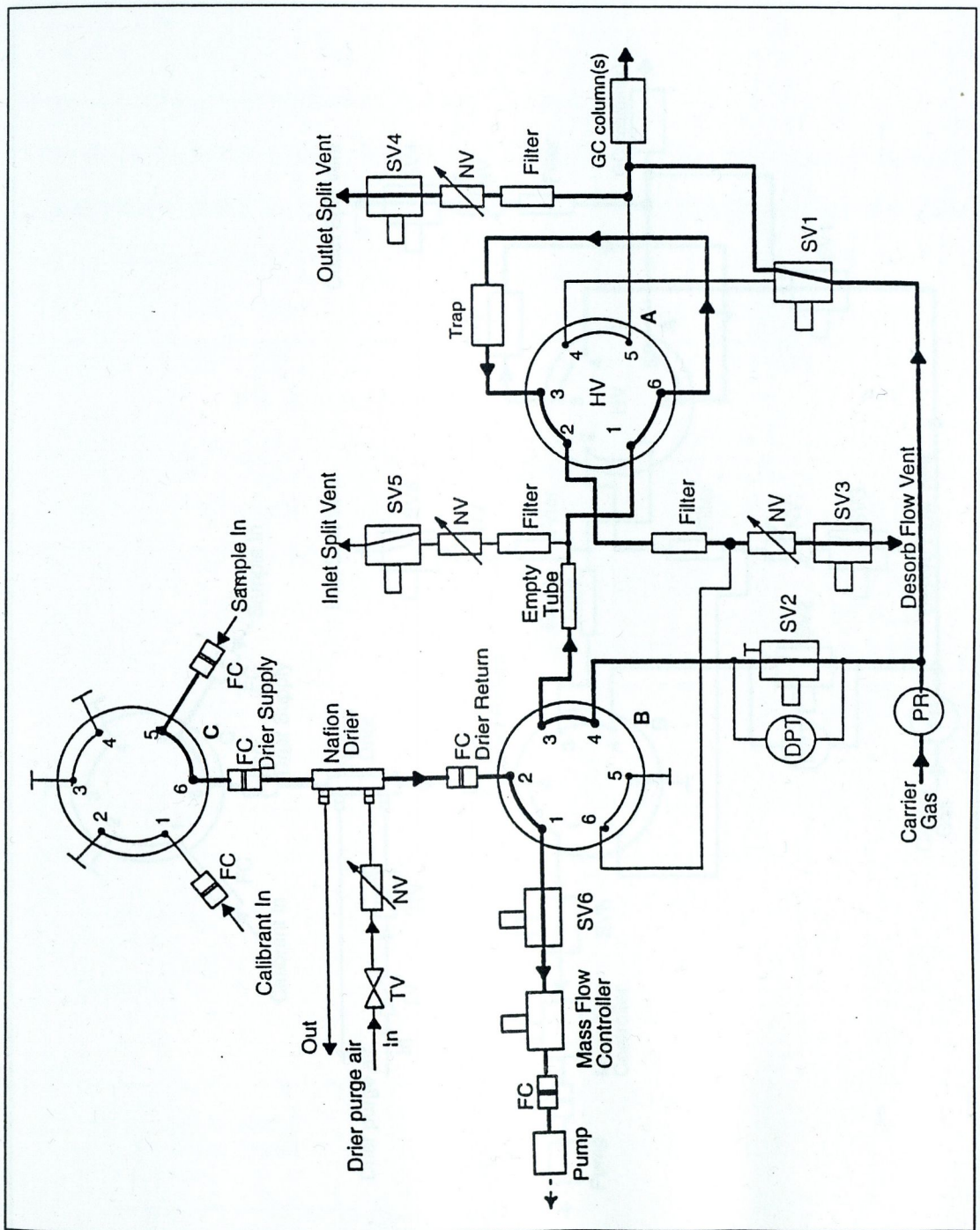


Figure 3.13 System schematic for sample desorption stage

Stage 3: Trap Heating and Sample Transfer

When the desorb time is over, the cold trap is heated and the trapped compounds are flushed from the trap through the heated transfer line to the GC. Firstly, valve A (in the ATD400) is rotated so that the flow path is as shown in Figure 3.14.

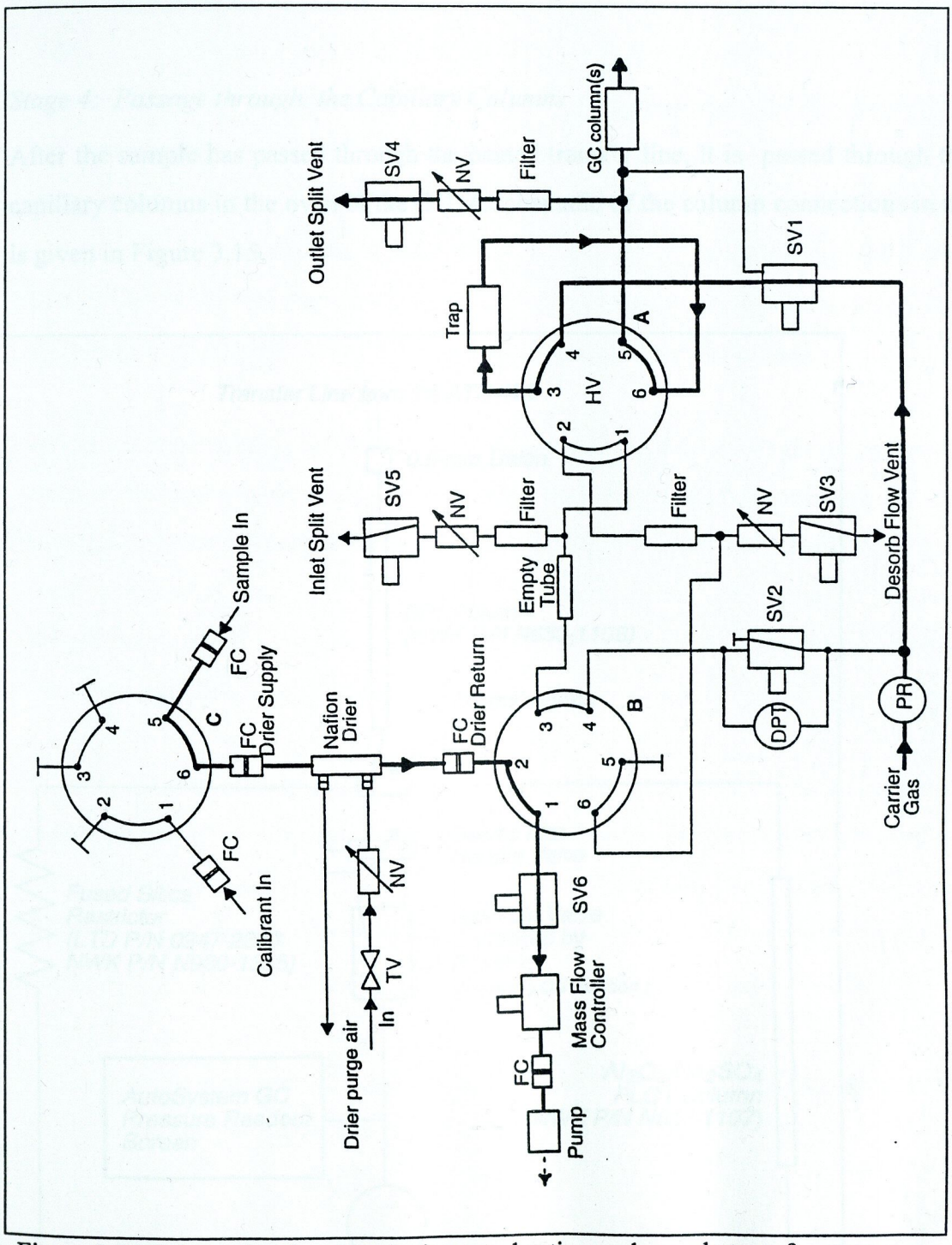


Figure 3.14 Schematic of system during trap heating and sample transfer stage

Solenoid valve 2 (SV2) and solenoid valve 1 (SV1) are switched, setting the system into backflush mode where the carrier gas is passing through the cold trap in the opposite

direction to the sample flow during sample collection. At the same time, the cold trap is heated at a rate of 40 °C/second (up to 325 °C) to ensure that all retained components are removed. The narrow band of vapour created by backflushing of the cold trap is sent through the heated transfer line to the capillary columns in the Autosystem GC. When trap heating begins, an electrical contact is closed to initiate the GC analysis sequence.

Stage 4: Passage through the Capillary Columns

After the sample has passed through the heated transfer line, it is passed through the two capillary columns in the oven of the GC. A schematic of the column connections in the GC is given in Figure 3.15.

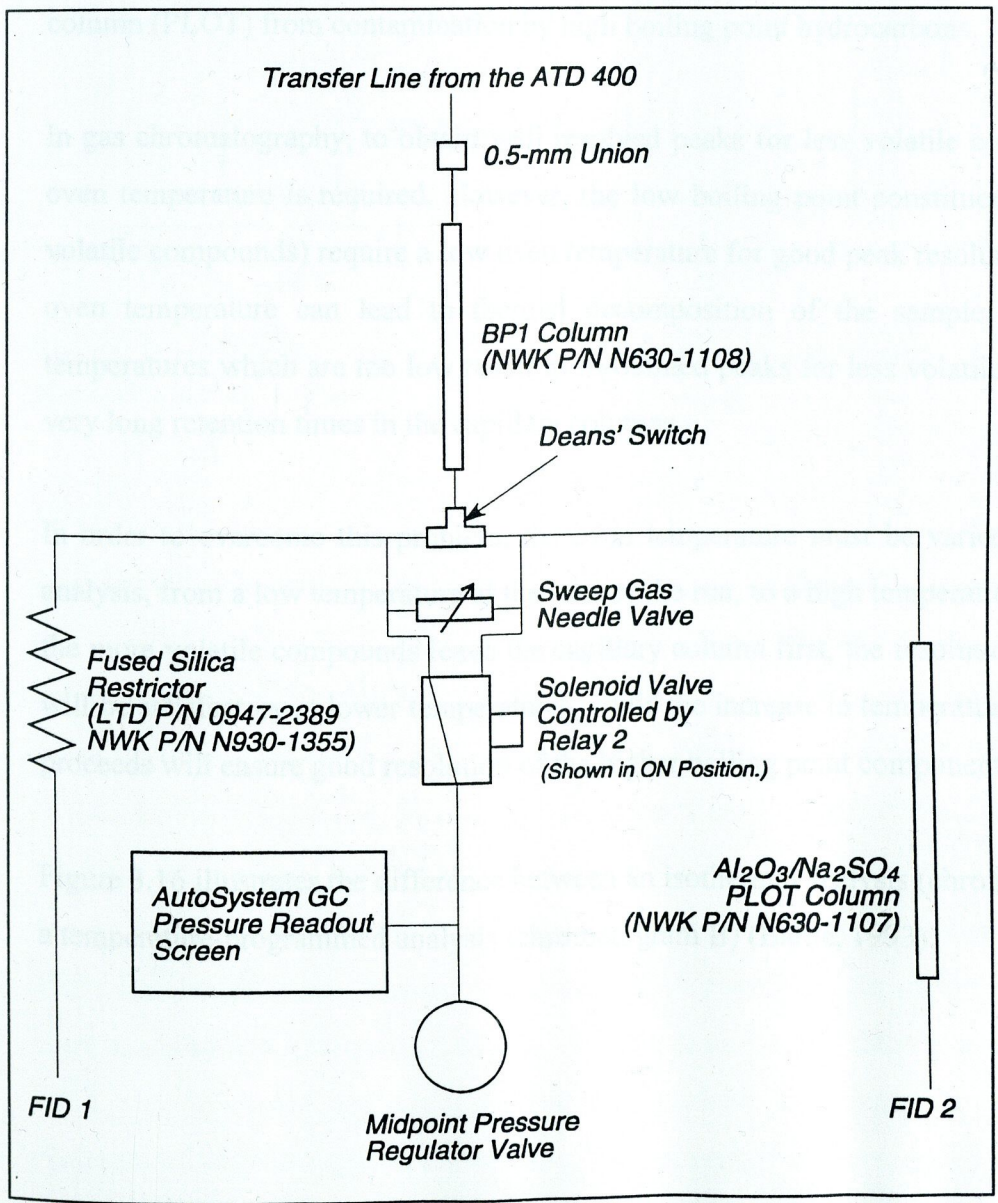


Figure 3.15 Schematic of column connections in the GC

The entire sample is first passed through the BP1 column. However, the lower boiling point components are not well resolved on this column and are therefore passed on to the PLOT column, via the Deans' Switch. At a certain time during the analysis, known as the heart-cut time, the Deans' Switch is activated and the higher boiling point compounds, which are well resolved by the BP1 column, are passed directly to FID 1. The lower boiling point compounds are resolved on the PLOT column and passed on to FID 2 for detection.

The heart-cut time is determined during the initial commissioning of the system by passing a sample through the system, and inspecting the position of the hexene and hexane peaks to determine the time at which these two compounds are eluted. The switching time should be set between these two times, a value of approximately 11 minutes being used during this study. The use of two capillary columns reduces the analysis time and protects the second column (PLOT) from contamination by high boiling point hydrocarbons.

In gas chromatography, to obtain well resolved peaks for less volatile compounds, a high oven temperature is required. However, the low boiling point constituents (i.e. the more volatile compounds) require a low oven temperature for good peak resolution. Too high an oven temperature can lead to thermal decomposition of the sample. However, oven temperatures which are too low result in ill-defined peaks for less volatile compounds and very long retention times in the capillary columns.

In order to overcome this problem, the oven temperature must be varied throughout the analysis, from a low temperature at the start of the run, to a high temperature at the end. As the more volatile compounds leave the capillary column first, the resolution of their peaks will be satisfactory at lower temperatures, while the increase in temperature as the analysis proceeds will ensure good resolution of the higher boiling point components.

Figure 3.16 illustrates the difference between an isothermal analysis (chromatogram A) and a temperature-programmed analysis (chromatogram B) (Bartle, 1993).

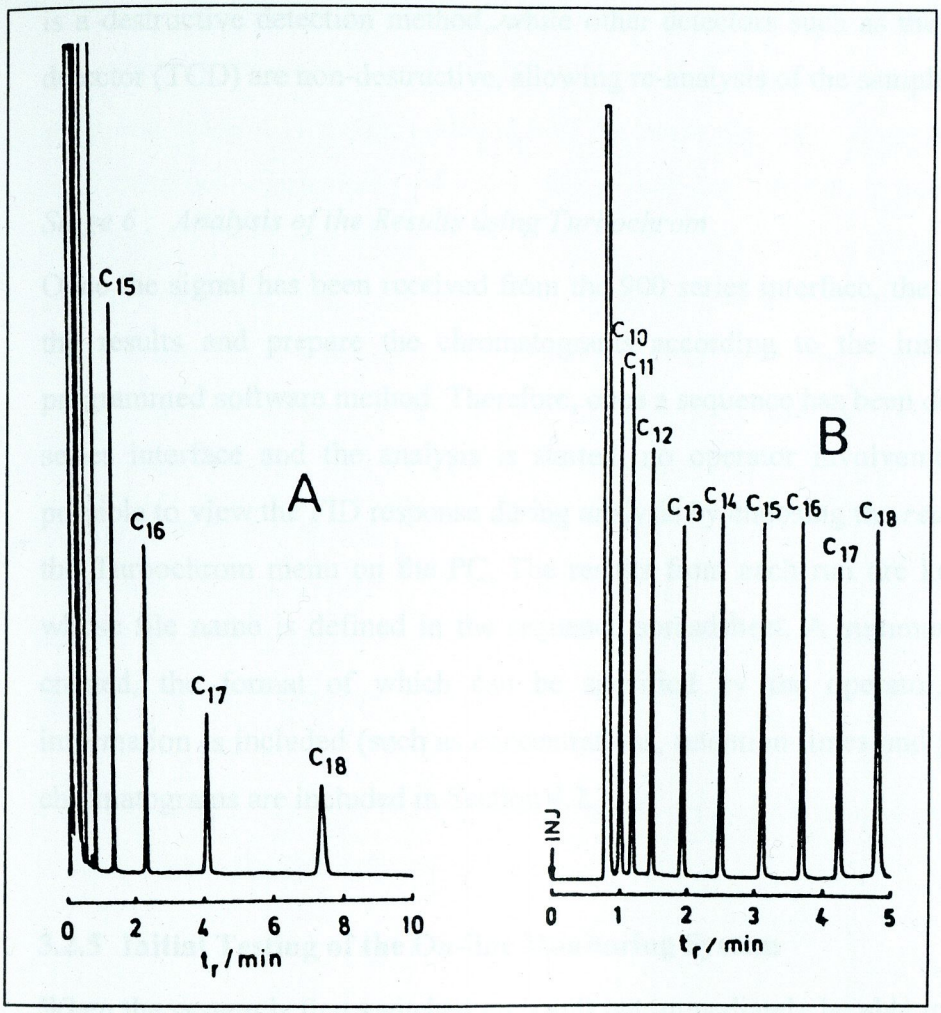


Figure 3.16 Comparison of isothermal (A) and temperature programmed (B) chromatographic analysis

Stage 5: FID

Compounds which exit the PLOT column pass to FID 2, while compounds which exit the BP1 column pass to FID 1. The response of the FID is proportional to the carbon content of the solute (Willett, 1987). The FID operates on the principle that very few ions are present in the flame produced by burning pure hydrogen. However, the thermal energy in the flame is sufficient to ionise the molecules of a compounds passed through the flame. The effluent gas from the capillary column is burned in the FID flame in an excess of air, resulting in approximately 0.001 percent of the carbon atoms undergoing ionisation (Tipler, 1993). These ions result in an increase in conductivity between the tip of the FID and another electrode (Day and Underwood, 1991). The current created by these ions can be as low as 10^{-13} amps (Cowper and DeRose, 1983). However, the current is amplified by an electrometer and the signal is presented as a chromatogram. The output signal is passed to the 900 series interface where it is converted from an analogue to a digital signal. The FID

is a destructive detection method, while other detectors such as the thermal conductivity detector (TCD) are non-destructive, allowing re-analysis of the sample (Flanagan, 1993).

Stage 6 : Analysis of the Results using Turbochrom

Once the signal has been received from the 900 series interface, the software will process the results and prepare the chromatograms according to the instructions in the pre-programmed software method. Therefore, once a sequence has been downloaded to the 900 series interface and the analysis is started, no operator involvement is required. It is possible to view the FID response during analysis by choosing the *real-time plot* icon from the Turbochrom menu on the PC. The results from each run are kept in a separate file whose file name is defined in the sequence spreadsheet. A summary results file can be created, the format of which can be specified by the operator, who defines what information is included (such as concentrations, retention times and peak height). Sample chromatograms are included in Section 4.2.1.

3.2.5 Initial Testing of the On-line Monitoring System

When the system is first switched on it will not immediately be able to perform an accurate analysis of a sample. The system first needs to be conditioned and calibrated. During conditioning of the capillary columns, the carrier gas (helium) is allowed to pass through the columns with a multi-cycle temperature programme starting at 50 °C and increasing by 5 °C / minute up to the maximum column temperature. During this process, an analysis can be performed on the gas which is eluted from the column. Initially, the chromatographic peaks will be very large due to the impurities being flushed through the system. As the conditioning continues, the size of these peaks will reduce, but it will be a matter of days before they reach an acceptable level. The columns must also be leak-tested before any sample analysis is carried out. Several calibration analyses must also be carried out to clear any contaminants from the calibration gas supply. The ATD400 coldtrap is also conditioned using a similar temperature cycling programme.

3.2.6 Analytical Method

The system under discussion is primarily established as an automated hydrocarbon monitoring system. However, analysis of passive and pumped tubes can also be carried out

with some minor modifications. Different instrument 'methods' can be employed depending on the type of analysis which is required. For ambient hydrocarbon monitoring only one method is required for each of the system's major components (ATD, GC and analytical software). Each of these three methods control a number of instrumental parameters which will affect the end result. The GC method, for example, controls such parameters as the oven temperature, the detector temperature and the rate of increase of oven temperature. The ATD400 method controls parameters such as the heated valve temperature, the cycle time (overall analysis time from the start of one sampling time to the start of the following sampling time), the minimum and maximum trap temperature and the heated transfer line temperature. The Turbochrom method controls such events as, how the data analyses are performed, calibrations, the total run time, the number of data channels, and the switching of the relays on the 900 Series Interface in order to rotate the valves in the air sampler. Therefore, the method parameters of each component are specific to that component, but the individual methods act in unison during a sampling run, due to the communications between the three components. This data analysis and collection method is set up using the Turbochrom software.

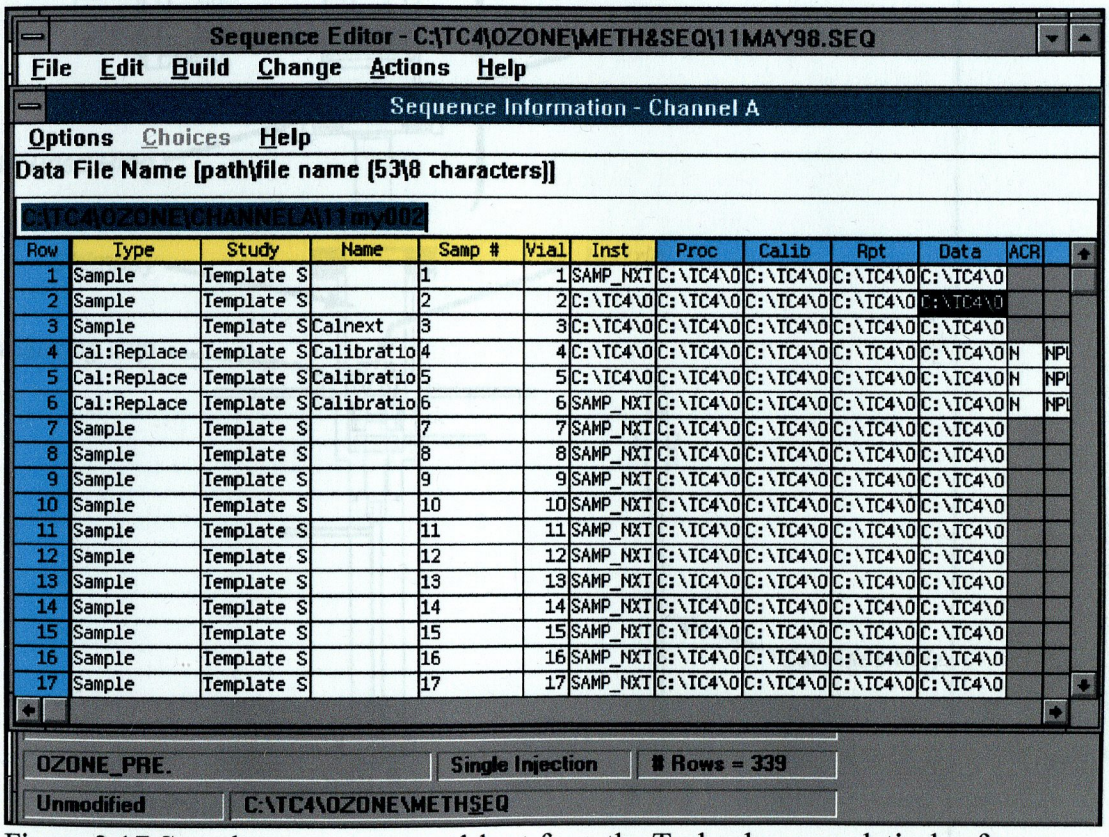
3.2.7 Writing a Sequence to Control an Analysis

A sampling sequence is built up using the Turbochrom software. A sequence is simply a list of 'methods' which the computer passes to the 900 Series Interface which then instructs the ATD400 and the GC. Each line in a sequence controls one sampling and analysis series, defining variables such as:

- The sample type, e.g. calibration or ambient air sample;
- Sample description, which can be input by the user, and has no impact on the analysis;
- The analytical methods to be used by the ATD400 and GC;
- The software method to be used to process the raw data;
- The names of the files where the raw and processed data should be stored;
- Details of the calibration method to be used.

The software method can be defined as 'calnext' or 'sampnext'. Sampnext instructs the system that the next analysis should be normal ambient air sampling and analysis, while 'calnext' results in the air sampler drawing the calibration standard through the system. The

software then uses the analysis results to recalibrate the data processing procedure. An example of part of a sequence spreadsheet is shown in Figure 3.17. Different parameters are defined in each of the columns, such as the 'type' column where the analysis type (sample or calibration) is defined. Other columns include the 'Inst' (instrument) column where the method to be used by the ATD and GC are defined, and the 'data' column, where the filepath for the data storage for each analytical run is defined.



Row	Type	Study	Name	Samp #	Vial	Inst	Proc	Calib	Rpt	Data	ACR	
1	Sample	Template S		1	1	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
2	Sample	Template S		2	2	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
3	Sample	Template S	Calnext	3	3	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
4	Cal:Replace	Template S	Calibratio	4	4	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	N	NP
5	Cal:Replace	Template S	Calibratio	5	5	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	N	NP
6	Cal:Replace	Template S	Calibratio	6	6	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O	N	NP
7	Sample	Template S		7	7	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
8	Sample	Template S		8	8	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
9	Sample	Template S		9	9	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
10	Sample	Template S		10	10	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
11	Sample	Template S		11	11	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
12	Sample	Template S		12	12	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
13	Sample	Template S		13	13	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
14	Sample	Template S		14	14	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
15	Sample	Template S		15	15	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
16	Sample	Template S		16	16	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		
17	Sample	Template S		17	17	SAMP_NXT	C:\TC4\O	C:\TC4\O	C:\TC4\O	C:\TC4\O		

Figure 3.17 Sample sequence spreadsheet from the Turbochrom analytical software

3.2.8 System Maintenance

Regular maintenance of the monitoring system is essential if an adequate level of accuracy is to reliably achieved. It is important to check the gas cylinders regularly and to replace them before they run out. If a gas cylinder unexpectedly runs out on site it may be several days before a new cylinder can be delivered, during which time no monitoring can be carried out. When changing the gas cylinders, the valve on the regulator should be turned off before the valve on the gas cylinder. This preserves the pressure in the supply lines to the instruments. Analysis can then continue while the gas bottles are changed over (bottles must be changed within about 30 - 40 seconds), rather than shutting down and restarting the complete system. There is a set sequence of events for shutting down or starting up the system

and it is important to follow this, in order to prevent damage to valves in the ATD and air sampler. Occasionally the FID collector and cap, shown in Figure 3.18, may need to be cleaned. The collector and cap can be cleaned simply using a lint free cloth and some distilled water.

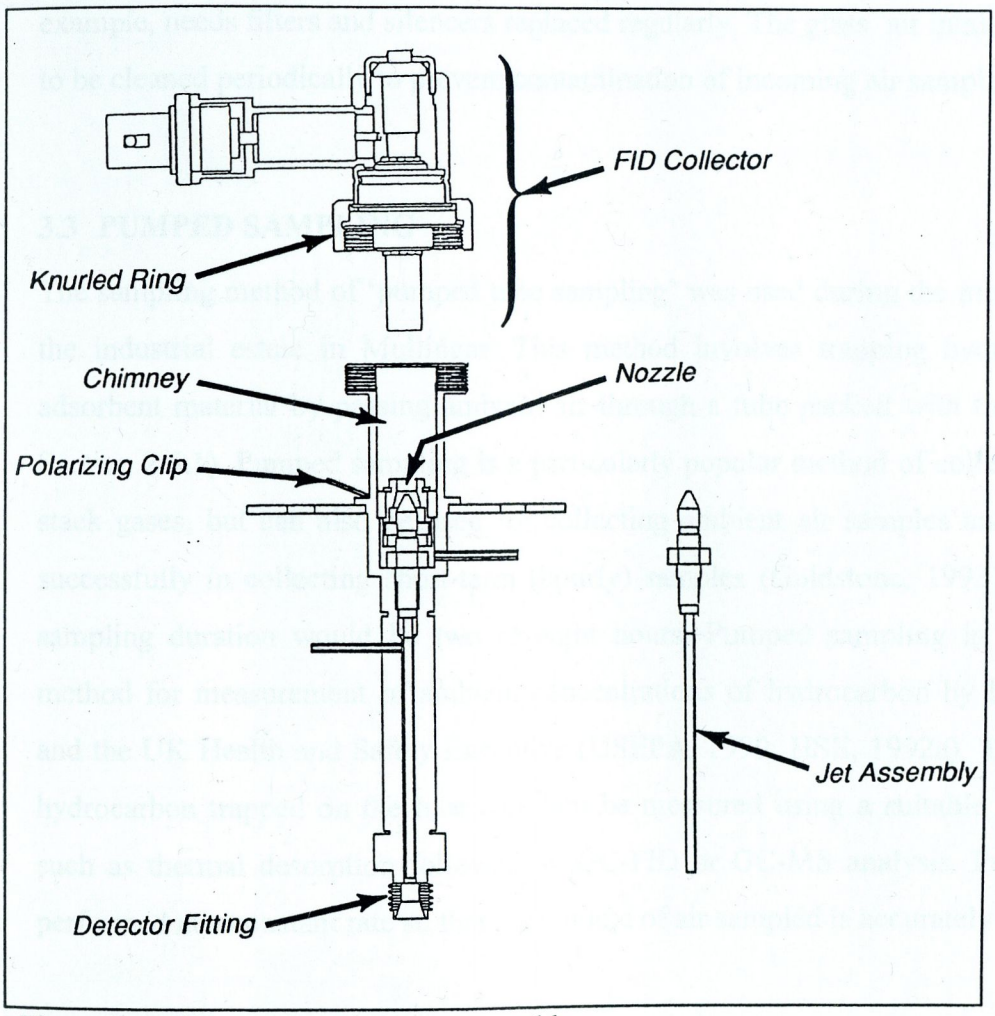


Figure 3.18 FID collector and cap assembly

If the dew point of the air is not up to standard, i.e. the dew point is too high, then the cold trap may ice up due to the excessive water vapour in the air. The cold trap can also ice up due to the seals on the cold trap box being damaged; these must then be replaced. The seals which seal the sample tube into the carrier gas circuit may also need to be replaced at regular intervals. A leak test is performed before every sample run. If the leak test fails on a regular basis, the seals must be replaced. However, one single failure of a leak test does not necessarily mean that the seals need replacement.

Major maintenance operations should be carried out by the manufacturer. Examples of such procedures carried out during this project include replacing the cold trap in the ATD

and the capillary columns in the GC. It is important to manage data file storage on the hard disk of the host computer as during the course of a lengthy analysis, thousands of data files can be created. Data files should be periodically transferred onto an external storage device.

Other parts of the system may also need periodic maintenance. The air generator, for example, needs filters and silencers replaced regularly. The glass air intake manifold needs to be cleaned periodically to prevent contamination of incoming air samples.

3.3 PUMPED SAMPLING

The sampling method of 'pumped tube sampling' was used during the monitoring study at the industrial estate in Mullingar. This method involves trapping hydrocarbons on an adsorbent material by passing ambient air through a tube packed with the adsorbent (see Section 2.6.1). Pumped sampling is a particularly popular method of collecting samples of stack gases, but can also be used for collecting ambient air samples and has been used successfully in collecting short-term (hourly) samples (Goldstone, 1993), though typical sampling duration would be two to eight hours. Pumped sampling is a recommended method for measurement of ambient concentrations of hydrocarbon by both the USEPA and the UK Health and Safety Executive (USEPA, 1999; HSE, 1992a). The mass of each hydrocarbon trapped on the tube can then be measured using a suitable analysis method such as thermal desorption followed by GC-FID or GC-MS analysis. Pumping must be performed at a constant rate so that the volume of air sampled is accurately known.

3.3.1 Sampling Unit

The pumped sampler used during this study was a 'Perkin-Elmer Sequential Tube Sampler (model STS-25) for the ATD400'. The sampler is shown in Figure 3.19. The 'carousel' in the sampler is capable of taking up to 24 sampling tubes and the sampling time can be set between seconds and tens of hours, depending on the study, however, the same sampling time must be used for each of the tubes.

The system does not come complete with a sampling pump, hence an external pump is required. Personal sampling pumps are compatible with the system, as long as they are of

the 'constant speed' or 'constant flow' variety. A constant flow pump is recommended, as this type of pump can compensate for differences in flow impedance.

Personal sampling pumps are operated from an internal battery, which have a limited lifetime. However, this battery can be charged from the 12 volt battery which is used to power the sampling unit operations. This battery is supplied in a shower-proof case, however, any 12 volt battery (e.g. car battery) can power the system. The system can also be powered directly from the mains using the battery charger supplied with the unit.



Figure 3.19 Perkin-Elmer STS 25 sequential tube sampler on-site

The entire sampling unit (sampler, pump, and battery) is easily portable (the pump can be placed inside the sampling unit) and compact, which allows sampling to be carried out in a

variety of relatively inaccessible locations (where the mobile monitoring unit could not be operated).

Up to 24 tubes can be loaded in the carousel of the STS-25 at one time. One end of each tube is sealed in the carousel, while a 'diffusion-limiting cap' is placed on the other end of the tube. The diffusion-limiting cap consists of a tube cap with a narrow bore tube passing through the cap. A schematic of a sampling tube in the carousel is shown in Figure 3.20.

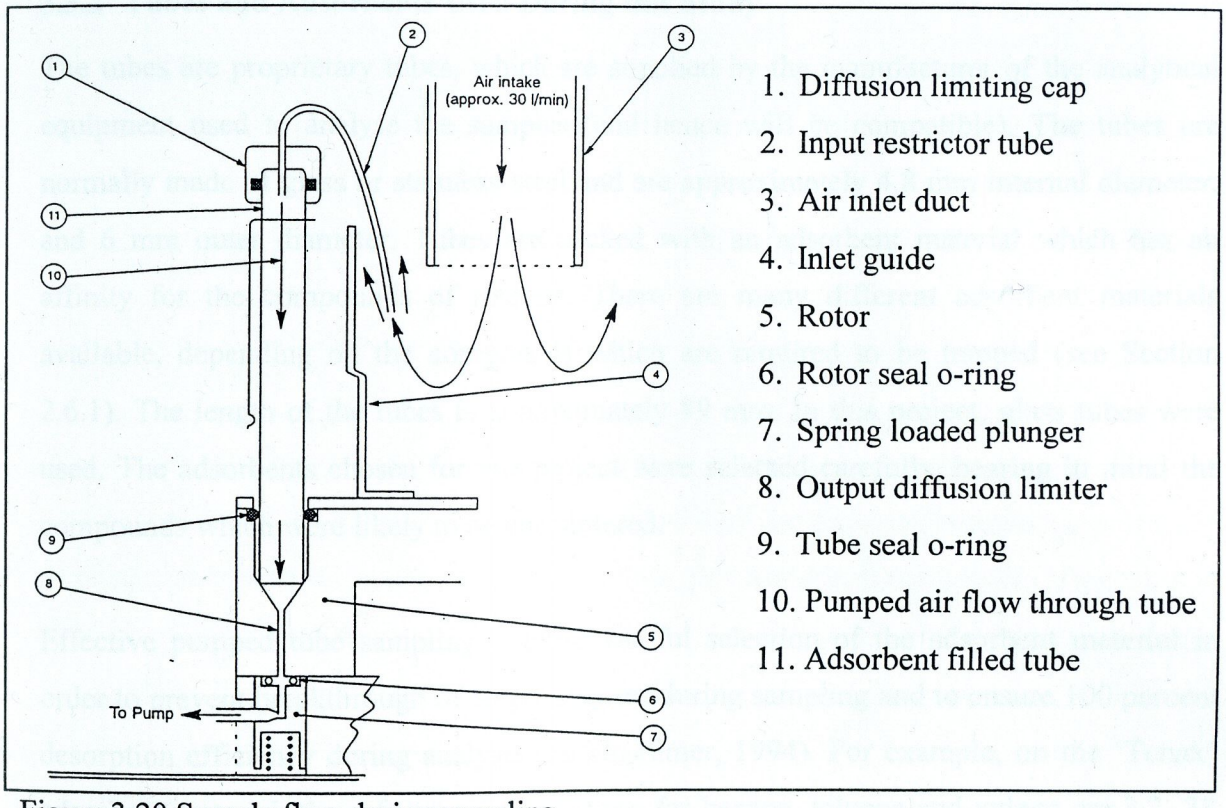


Figure 3.20 Sample flow during sampling

When the sampling time is finished, the carousel rotates to the next tube position, and the previously sampled tube is effectively sealed, by the diffusion-limiting cap at one end and the o-ring seal at the other. A very small amount of air does continue to diffuse through both ends of the tube (approximately 0.63 ml/hour), however, for most sampling rates this small diffusion rate will have no impact on the results of the analyses.

As mentioned previously, the sample flow is an extremely important parameter, which should be accurately known and checked before and after sampling to assess any possible changes in the pump flow rate. Before sampling was initiated, the pump flow rate was set in the laboratory and then checked immediately before and after sampling. The pump flow

rate must be set in conditions as close as possible to actual sampling conditions. Hence, the sampling train must be set up as during sample collection. The sample flow rate for the system used during this study was initially calibrated in the laboratory using a film flowmeter. Once the flow rate has been set to the desired value, the flow should be checked three more times and the average value taken as the flow rate. The same procedure can be used to check the flow rate before and after sampling.

3.3.2 Tubes and Adsorbents Used During this Study

The tubes are proprietary tubes, which are supplied by the manufacturer of the analytical equipment used to analyse the samples (and hence will be compatible). The tubes are normally made of glass or stainless steel and are approximately 4.8 mm internal diameter, and 6 mm outer diameter. Tubes are packed with an adsorbent material which has an affinity for the compounds of interest. There are many different adsorbent materials available, depending on the compounds which are required to be trapped (see Section 2.6.1). The length of the tubes is approximately 89 mm. In this project, glass tubes were used. The adsorbents chosen for this project were selected carefully, bearing in mind the compounds which were likely to be encountered.

Effective pumped tube sampling requires careful selection of the adsorbent material in order to prevent breakthrough of target analytes during sampling and to ensure 100 percent desorption efficiency during analysis (Perkin-Elmer, 1994). For example, on the 'Tenax' adsorbent material, the safe sampling volumes for hexane, toluene and xylene are 3.2, 38 and 300 litres, respectively (Perkin-Elmer, 1994; HSE, 1992a). The safe sampling volume is a conservative estimate of the ability of an adsorbent to retain a given compound, and is calculated as 50 percent of the Retention Volume (RV) of a given adsorbent / analyte combination (Woolfenden, 1997).

During sampling at Mullingar, the maximum volume passed through a pumped sampling tube was 18 litres, hence the SSV for toluene and xylene would not be exceeded. However, the volume of the sample exceeds the SSV for hexane, therefore this adsorbent alone is not suitable for trapping hexane (which was one of the main compounds of interest at the monitoring location in Mullingar). One of the advantages of pumped sampling over passive tube sampling is that more than one adsorbent can be used in series, facilitating the

retention of a wider range of volatile compounds (Perkin-Elmer, 1991). For monitoring at Mullingar, a stronger adsorbent, Spherocarb (Perkin-Elmer, 1993), was also used to ensure that the SSV for hexane was not exceeded. A schematic of the tubes used for pumped sampling is given in Figure 3.21.

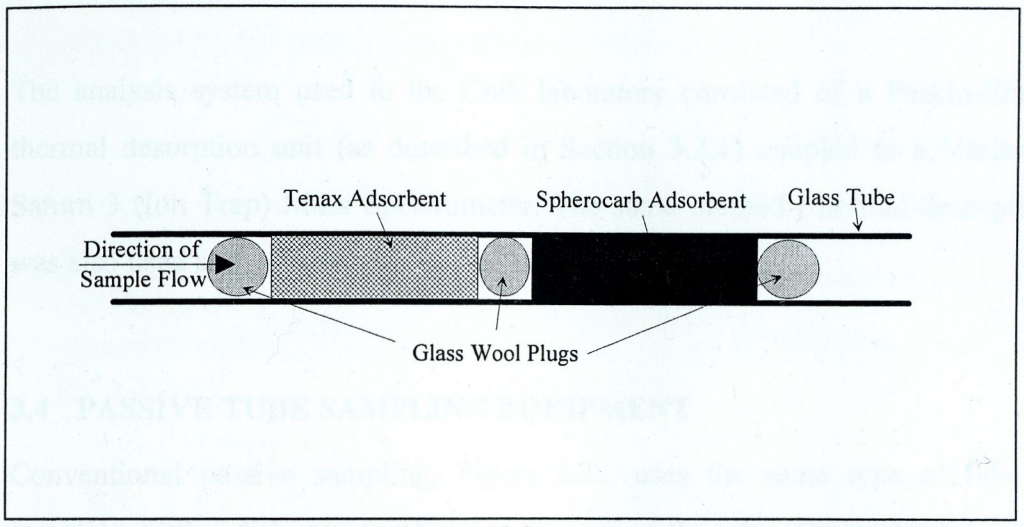


Figure 3.21 Adsorbent filled tubes used for pumped sampling at Mullingar

When using multiple 'beds' of adsorbents such as these, it is important to note that the sample must always be drawn through the sorbents in order of increasing adsorbent strength and subsequently desorbed using reverse flow (Perkin-Elmer, 1993). Prior to, and after sampling, the tubes must be sealed with Swagelok-type caps and PTFE (polytetrafluoroethylene) ferrules.

3.3.3 System Maintenance

The pumped sampling equipment requires very little maintenance. The o-rings which seal the sample tubes into the carousel must be changed after every 200 samples. A large o-ring at the base of the carousel also needs to be changed approximately every 200 operations. This is particularly important as any leaks at this o-ring would lead to leaks in all tubes in the carousel. The diffusion-limiting caps must be checked occasionally to ensure that there are no blockages or crimps in the tube. Also, when placing the caps onto the tubes, care must be taken to ensure that the end of the diffusion tube is not caught between the cap and the top of the sampling tube. The air intake filter, located on the lid of the STS-25 must also be checked occasionally to ensure there are no blockages.

3.3.4 Analysis of Pumped Tubes

As the automated sampling and analysis system described in Section 3.2 was in use during the hydrocarbon monitoring study at Mullingar, analysis of the pumped sampling tubes was carried out elsewhere. The majority of the analyses were carried out at the EPA laboratory in Cork, with one tube being analysed at the Enterprise Ireland laboratory in Dublin.

The analysis system used in the Cork laboratory consisted of a Perkin-Elmer ATD400 thermal desorption unit (as described in Section 3.2.1) coupled to a Varian 3400 GC / Saturn 3 (Ion Trap) Mass Spectrometer. The same method (thermal desorption, GC/MS) was also used at the Enterprise Ireland laboratory.

3.4 PASSIVE TUBE SAMPLING EQUIPMENT

Conventional passive sampling, Figure 3.22, uses the same type of tube as pumped sampling, with a diffusion cap fitted to one end of the tube. The problem with this method is that the rate of diffusion is very low, as only a small surface area at the end of the tube is presented to the polluted atmosphere. These passive sampling tubes are also highly sensitive to windspeed, with overestimation of the actual ambient concentration being observed at higher speeds (Muthusubramanian *et al.,* 1997).

3.4.1 Conventional and Radiello Passive Sampling Theory

Fick's law can be used to describe the diffusion along the length of the adsorbent in an axial diffusive sampler as follows:

$$\frac{dm}{dt} = DA\frac{dC}{dx} \qquad 3.1$$

dm/dt = rate of mass transfer

D = diffusion coefficient

A = cross-sectional surface area

dC/dx = concentration gradient along the axis

Integration of the above equation results in the following solution:

$$\frac{m_t}{t} = \frac{DA}{L}(C_o - C_a) \qquad 3.2$$

m_t = mass transferred in time t

L = diffusion path length

C_o = ambient air concentration

C_a = concentration just above the adsorbent surface

As m_t is directly proportional to the surface area (A) and the sampling duration (t), the value of m_t will be small for short sampling periods (e.g. less than one week).

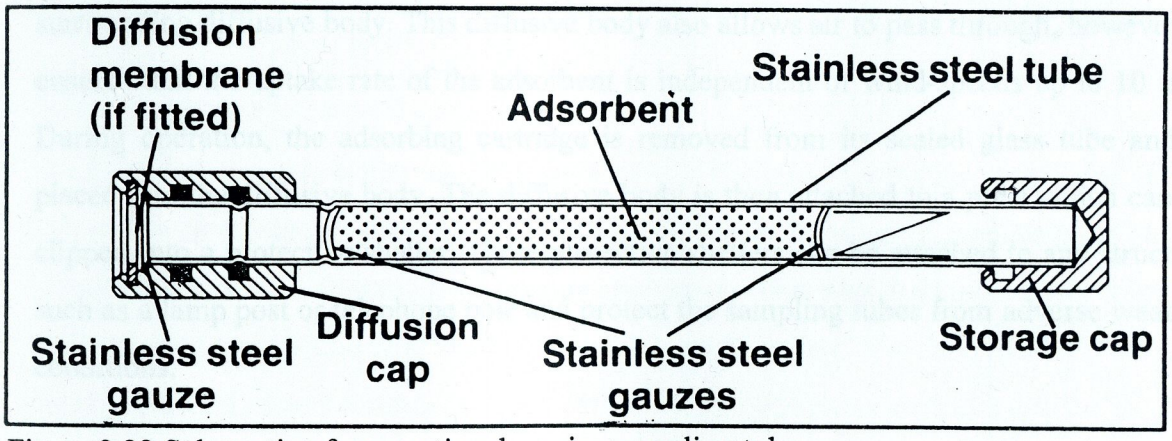


Figure 3.22 Schematic of conventional passive sampling tube

During this study, a recently developed diffusive sampling method was employed which allows radial diffusion over the entire outer area of the tube. This system, known as 'Radiello', was developed in Italy and has a much higher quoted uptake rate than conventional passive sampling techniques. A schematic of the Radiello passive sampler is given in Figure 3.23. The cylindrical diffusive surface of Radiello allows a much greater sampling rate. Integration of Fick's law, based on the geometry of the Radiello passive sampler, results in the following solution:

$$\frac{m_t}{t} = D2\pi h \frac{(C_o - C_a)}{Ln(r_o / r_a)} \qquad 3.3$$

r_o = radius of the outer diffusive body

r_a = radius of the inner adsorbent cartridge

h = length of the cylinder

Ln (r_o/r_a) is a constant which is close to unity, hence m_t is proportional to h, which is the length of the adsorbent body, and significantly greater than A in equation 3.2. For example,

the theoretical uptake rate for benzene on Radiello can be over two orders of magnitude greater than that for commercially available axial sampling tubes, depending on the diffusive body which is used. Hence, sampling duration for Radiello tubes can be significantly less than for axial sampling tubes.

3.4.2 Radiello Passive Sampling Equipment

The main parts of the sampling system are shown in Figure 3.23. The adsorbent material is contained in a cylindrical gauze which allows passage of ambient air through the adsorbent. The adsorbent filled gauze assembly, known as the adsorbing cartridge, is protected by a surrounding diffusive body. This diffusive body also allows air to pass through, however, it ensures that the uptake rate of the adsorbent is independent of wind-speeds up to 10 m/s. During operation, the adsorbing cartridge is removed from its sealed glass tube and is placed into the diffusive body. The diffusive body is then attached to a plate which can be clipped into a protective shelter. These protective shelters can be attached to any structure such as a lamp post or telephone pole and protect the sampling tubes from adverse weather conditions.

Different adsorbent materials can be employed, depending on the compounds of interest. Different diffusive bodies can also be chosen, depending on whether personal workplace sampling or ambient air sampling is required. The sampling rates of 'Radiello' passive tubes are reported to be around 20 cm^3 / minute compared to typical sampling rates of 0.5 to 0.8 cm^3 / minute for traditional passive sampling tubes. For hydrocarbon monitoring, the adsorbent material used is graphitised carbon (Carbotrap B). Standard sampling rates are specified at 25 °C, and corrective factors are applied for lower or higher temperatures.

Once sampling has been completed, the inner adsorbent filled gauze is designed to fit neatly into a normal glass or stainless steel sampling tube compatible with the ATD400 thermal desorption unit (Section 3.2.1). This tube can then be sealed with airtight Swagelok fittings for transportation to the laboratory. Recommended analytical methods are supplied with the sampling tubes. The adsorbing cartridges and diffusive body can be re-used many times, however, care must be taken to ensure that all components are desorbed from the cartridge before re-use.

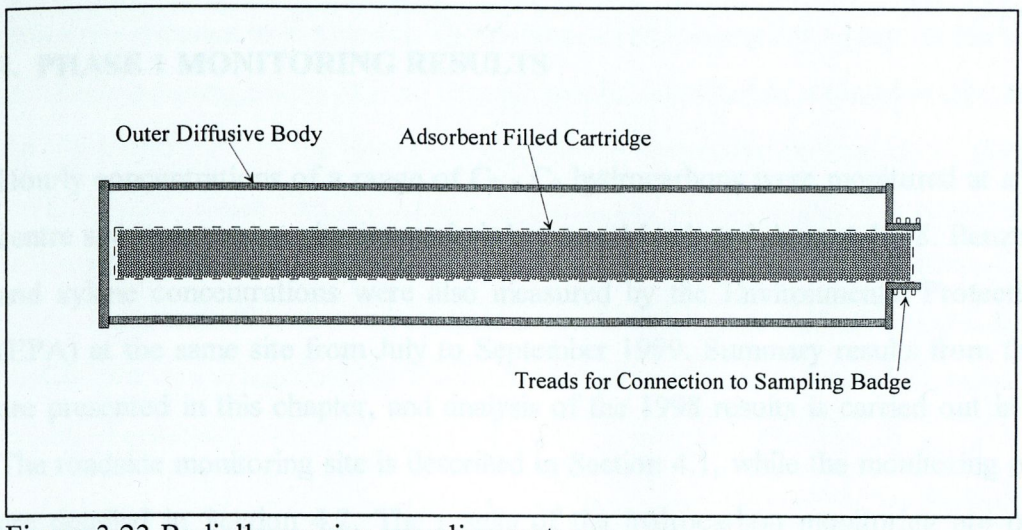


Figure 3.23 Radiello passive sampling system

3.4.3 Analysis of Passive Tubes

Analyses were carried out at the EPA laboratory in Cork and also at the Enterprise Ireland laboratory in Dublin, as described for the pumped sampling tubes in Section 3.3.4. At the Enterprise Ireland Laboratory, several of the tubes were analysed twice to check the efficiency of the thermal desorption method (to check for any contaminants remaining on the tubes). The second analysis showed that all of the hydrocarbons had been successfully desorbed during the first analysis.

The analytical system used at the Cork Laboratory had been originally set-up for the purposes of analysing samples collected at stack exits, with consequently larger masses of contaminants collected on the tubes. Therefore, one of the objectives of the tube sampling (which was carried out as part of an EPA project), was to assess the performance of the EPA analytical facility in the analysis of ambient samples, as under the EU air quality framework directive (CEC, 1996), significantly more ambient air quality monitoring will be required, and the EPA is responsible for this work. Although no ambient pumped or passive samples had previously been analysed, the laboratory participates in the Workplace Analysis Scheme for Proficiency (WASP) run by the UK Health and Safety Executive, and good performance has been achieved in respect of BTX assays at concentrations characteristic of this study.

4. PHASE 1 MONITORING RESULTS

Hourly concentrations of a range of C_2 - C_9 hydrocarbons were monitored at a Dublin city centre site over two monitoring periods between March and August 1998. Benzene, toluene and xylene concentrations were also measured by the Environmental Protection Agency (EPA) at the same site from July to September 1999. Summary results from these studies are presented in this chapter, and analysis of the 1998 results is carried out in Chapter 5. The roadside monitoring site is described in Section 4.1, while the monitoring programmes are detailed in Section 4.2. The results of the hydrocarbon monitoring are presented in Section 4.3, along with initial statistical analysis of these data. Meteorological data were also collected on-site and are presented in Section 4.4. These are compared to official Met Eireann meteorological data from Dublin airport. A primary aim of this chapter is to assess the accuracy and reliability of monitoring methods used and results obtained.

4.1 SITE DESCRIPTION

The monitoring site was located in Dublin city centre. Dublin, situated on the eastern seaboard, is the capital city of Ireland and is the centre of business and industry in the country as well as the most highly populated of Ireland's 26 counties. Of the 3,621,000 inhabitants of Ireland (in 1996) 1,057,000 (28.3 percent) live in Dublin County and Borough area (Central Statistics Office, 1996), shown in Figure 4.1.



Figure 4.1 Map of the greater Dublin area

The monitoring site was located in Dublin city centre on a busy cross city route (from the south side to the north side of the city). A map of the city centre, with the monitoring site

indicated, is shown in Figure 4.2. The distance from the monitoring unit to the road was 4.5 m, with a sampling height of 3 m. This site can be described as a roadside site, as defined by the UK Department of the Environment guidance note on monitoring for air quality (DETR, 1998a), which states that a roadside sampling site will be within five metres of the road, with a sampling height of two to three metres. The monitoring unit was located behind a 1.5 metre high wall (for security reasons) which was not expected to interfere with the measured hydrocarbon concentrations. A schematic of the area around the monitoring site is given in Figure 4.3.

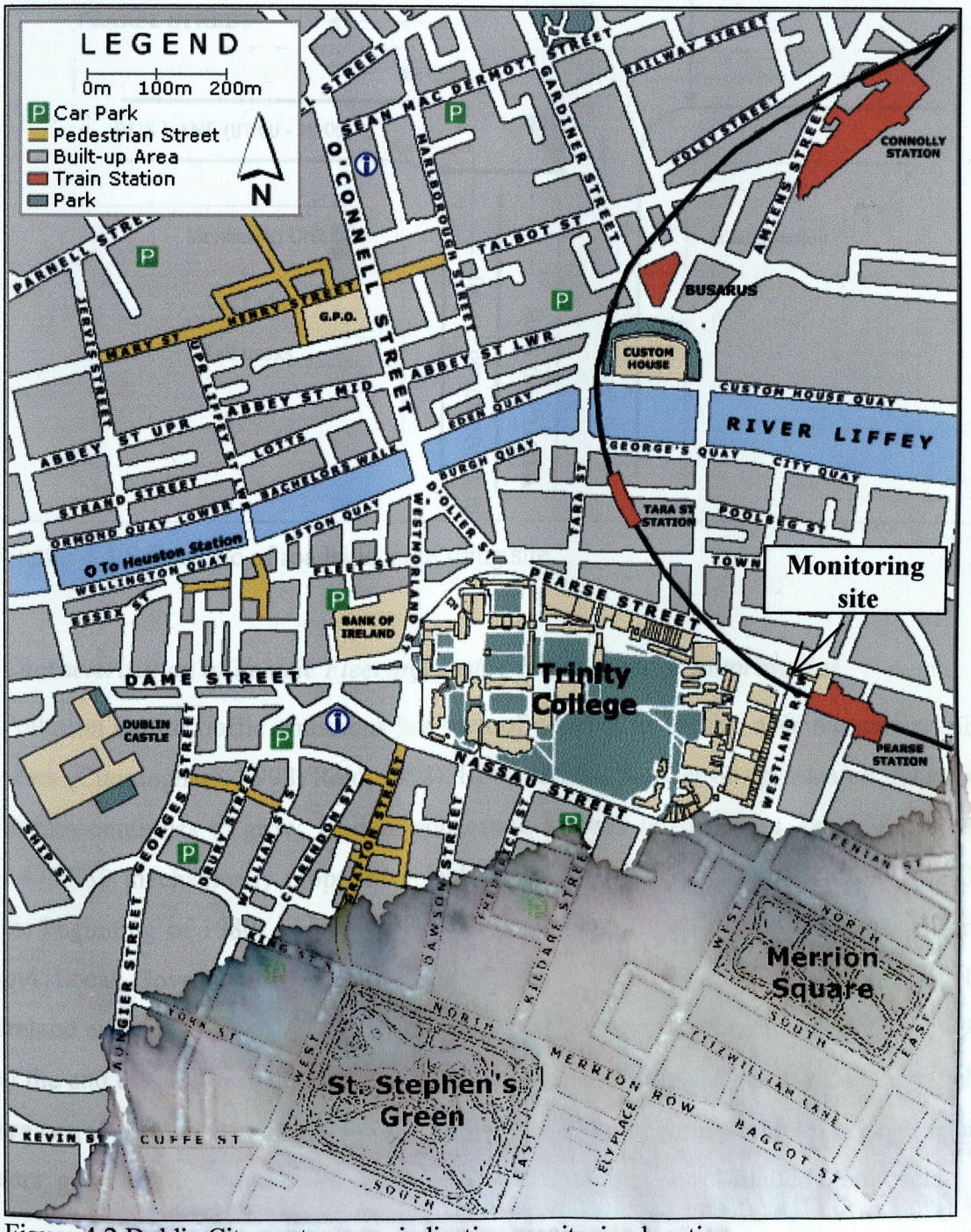


Figure 4.2 Dublin City centre map, indicating monitoring location

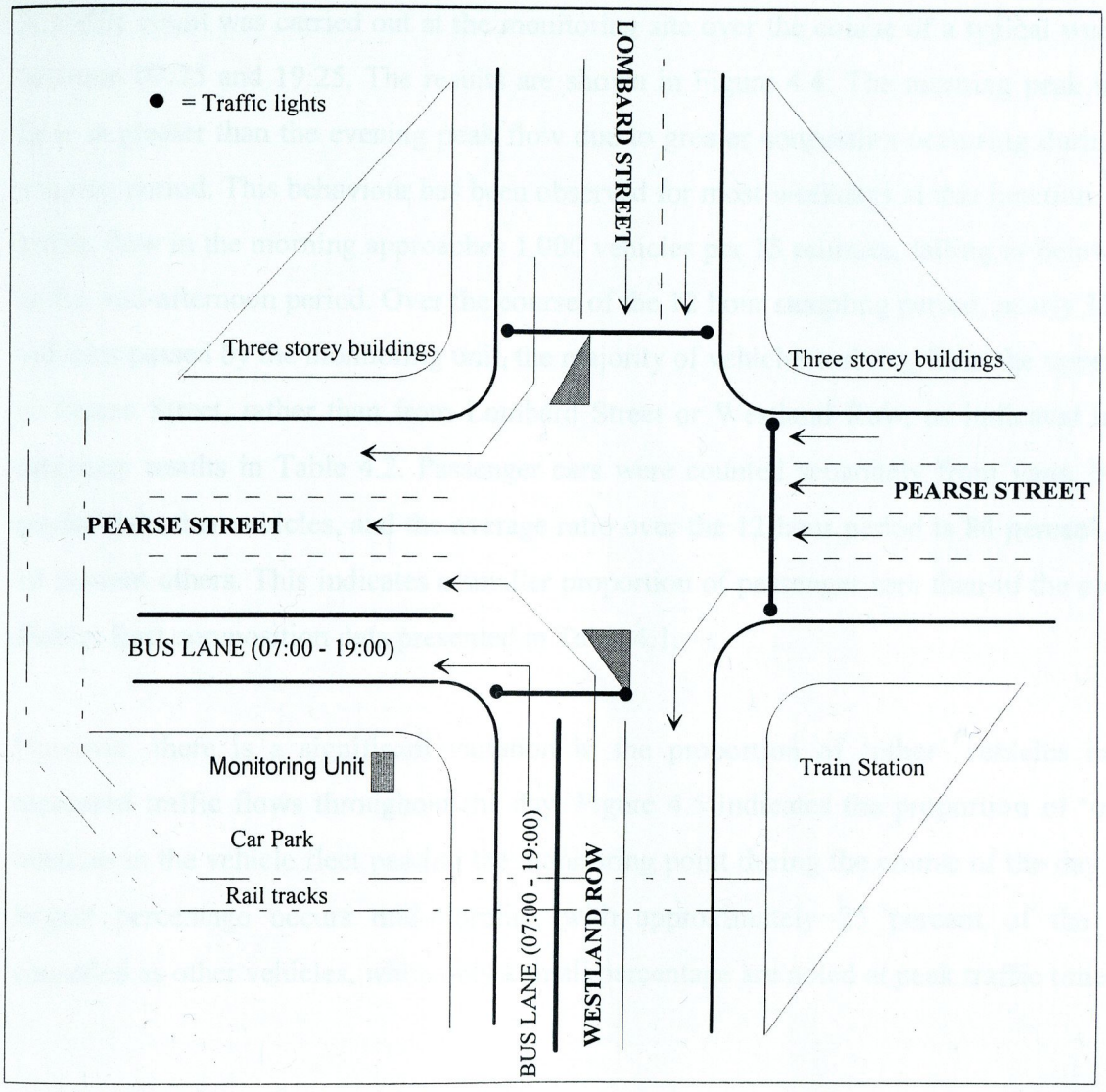


Figure 4.3 Schematic of roadside monitoring site

Characterisation of Vehicle Fleet and Traffic Flows at the Monitoring Site

Pollution due to traffic emissions has been of concern in Dublin over the past number of years (Cunningham, 1998; Reid, 1998). However, the number of vehicles on the streets of Dublin continues to grow, as does congestion at peak traffic times. In 1998, there were 1,432,330 mechanically propelled vehicles registered in Ireland, compared to 911,031 at the beginning of 1980; an increase of nearly 60 percent (Department of the Environment and Local Government, 1998). Approximately 27 percent of the licensed vehicles in Ireland are registered in the Dublin area. A breakdown of the vehicles registered in Dublin at the end of 1998 is given in Table 4.1, indicating that almost 82 percent of these vehicles are petrol-fuelled passenger cars. The majority of the remaining vehicles are diesel-fuelled cars, goods vehicles and buses, with a small percentage of petrol-fuelled motorcycles.

A traffic count was carried out at the monitoring site over the course of a typical weekday between 07:25 and 19:25. The results are shown in Figure 4.4. The morning peak traffic flow is greater than the evening peak flow due to greater congestion occurring during the evening period. This behaviour has been observed for most weekdays at this junction. Peak traffic flow in the morning approaches 1,000 vehicles per 15 minutes, falling to below 700 in the mid-afternoon period. Over the course of the 12 hour sampling period, nearly 37,000 vehicles passed by the monitoring unit, the majority of vehicles arriving from the upper end of Pearse Street, rather than from Lombard Street or Westland Row, as indicated in the summary results in Table 4.2. Passenger cars were counted separately from vans, buses, trucks and other vehicles, and the average ratio over the 12 hour period is 84 percent cars, 16 percent others. This indicates a smaller proportion of passenger cars than in the overall Dublin fleet composition data presented in Table 4.1.

However, there is a significant variation in the proportion of 'other' vehicles in the measured traffic flows throughout the day. Figure 4.5 indicates the proportion of 'other' vehicles in the vehicle fleet passing the monitoring point during the course of the day. The largest percentage occurs mid-morning, with approximately 25 percent of the fleet classified as other vehicles, while only a small percentage are noted at peak traffic times.

Table 4.1 Fleet Composition for the Greater Dublin area in 1998 (Reynolds and Broderick, 1998)

	Petrol	Diesel	LPG	Total
Cars	320,707 (93.29 %)	22,823 (6.64 %)	245 (0.07 %)	343,775 (87.57 %)
LGV	1,302 (4.18 %)	29,850 (95.76 %)	21 (0.07 %)	31,173 (7.94 %)
HGV	59 (0.93 %)	6,251 (99.02 %)	3 (0.05 %)	6,313 (1.61 %)
Buses				2,253 (0.57 %)
MC				8,976 (2.29 %)
Mopeds				69 (0.02 %)
Total	322,068	58,924	269	392,559

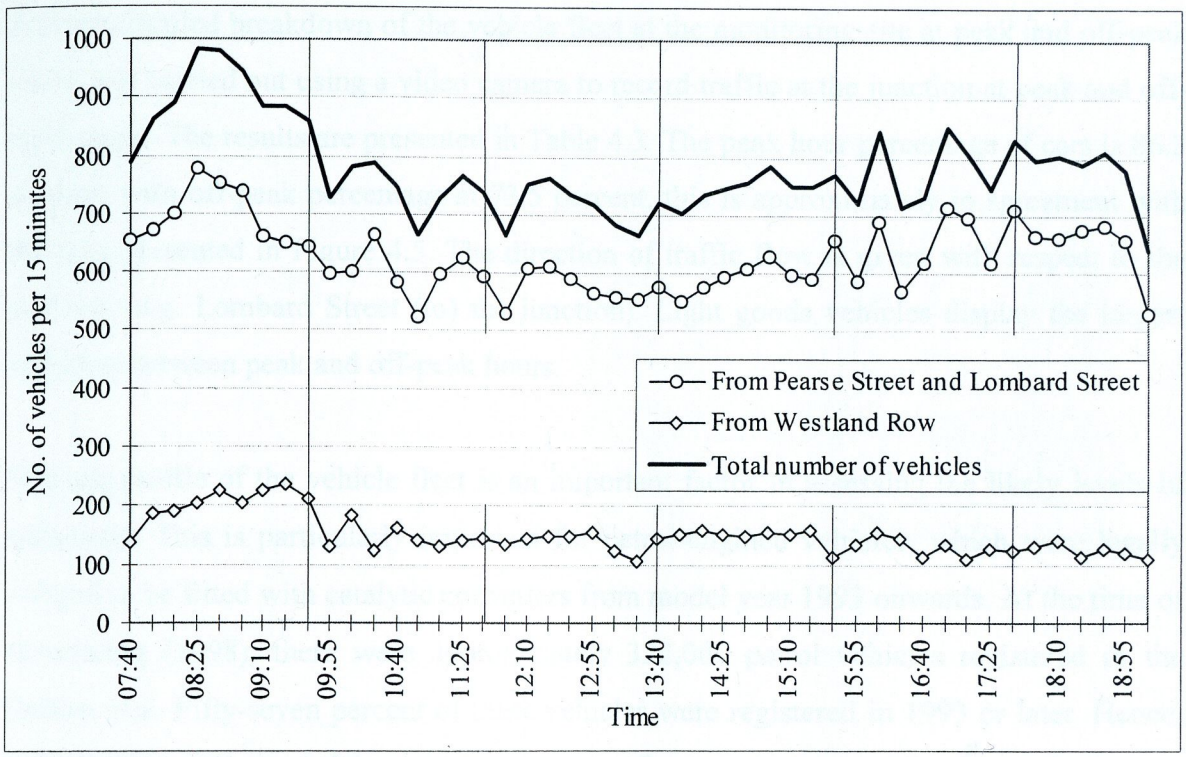


Figure 4.4 Results of traffic count

Table 4.2: Summary results of traffic count

From Pearse Street and Lombard Street			From Westland Row			Total
Cars	Other	Sub-total	Cars	Other	Sub-total	All types
24,758	4,746	29,504	5,966	1,089	7,055	36,559
67.72 %	12.98 %	80.70 %	16.32 %	2.98 %	19.30 %	100 %

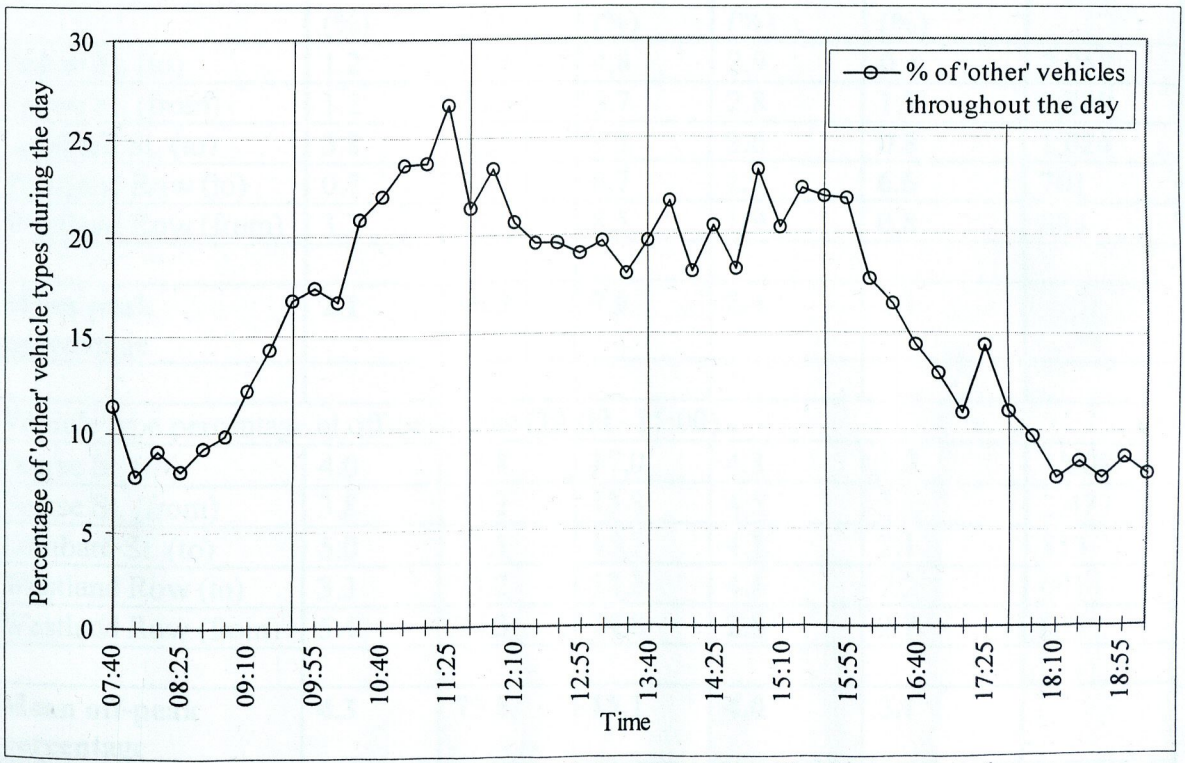


Figure 4.5 Proportion of 'other' vehicles in the measured traffic flow over a day

A more detailed breakdown of the vehicle fleet at the monitoring site at peak and off-peak hours was carried out using a video camera to record traffic at the junction at peak and off-peak times. The results are presented in Table 4.3. The peak hour percentage of cars is 86.3 percent, with off-peak percentage at 73.5 percent, this is approximately in agreement with the data presented in Figure 4.5. The direction of traffic flow is given with respect to the junction (e.g. Lombard Street (to) the junction). Light goods vehicles display the largest variation between peak and off-peak hours.

The age profile of the vehicle fleet is an important factor in assessing the likely levels of emissions. This is particularly important for petrol-engined vehicles, which were legally obliged to be fitted with catalytic converters from model year 1993 onwards. At the time of monitoring (1998), there were approximately 322,000 petrol vehicles registered in the Dublin area. Fifty-seven percent of these vehicles were registered in 1993 or later. Hence, at least this percentage of the petrol-engined car fleet can be expected to be equipped with catalytic converters at the time of monitoring.

Table 4.3 Classification of vehicle types passing the monitoring location at peak and off-peak hours (Reynolds and Broderick, 2000)

	Vehicle Type					
Vehicle type percentage at peak time (08:00 - 09:00)						
Direction of travel	MCs[1] (%)	Cars (%)	LGVs[2] (%)	HGVs[3] (%)	Buses (%)	Total
Pearse St. (to)	1.2	90.7	4.8	2.9	0.4	2,057
Pearse St. (from)	1.2	88.3	5.7	2.8	1.9	2,898
Lombard St. (to)	3.8	83.5	9.3	2.6	0.8	1,024
Westland Row (to)	0.7	84.2	6.7	1.9	6.6	701
Westland Row (from)	3.7	85.1	8.5	1.9	0.8	884
Mean peak percentage	**2.1**	**86.3**	**7.0**	**2.4**	**2.1**	
Vehicle type percentage at off-peak time (14:00 - 15:00)						
Pearse St. (to)	4.0	73.8	17.0	4.3	1.0	1,608
Pearse St. (from)	3.8	73.2	15.8	4.5	2.7	2,477
Lombard St. (to)	5.0	73.1	15.7	4.1	2.1	813
Westland Row (to)	3.3	73.2	12.2	4.1	7.2	691
Westland Row (from)	5.4	74.3	14.8	2.8	2.7	635
Mean off-peak percentage	**4.3**	**73.5**	**15.1**	**4.0**	**3.1**	

[1]MC = Motorcycle
[2]LGV = Light goods vehicles (e.g. medium sized vans)
[3]HGV = Heavy goods vehicles (trucks)

The age profile of the Dublin vehicle fleet at the end of 1998 is presented in Figure 4.6. For reasons of clarity, LPG-fuelled vehicles and petrol-fuelled light goods vehicles have not been included. As can be seen from Table 4.1, the number of these vehicle types registered in Dublin is very small. With the exception of buses, most of the vehicle groups follow similar profiles.

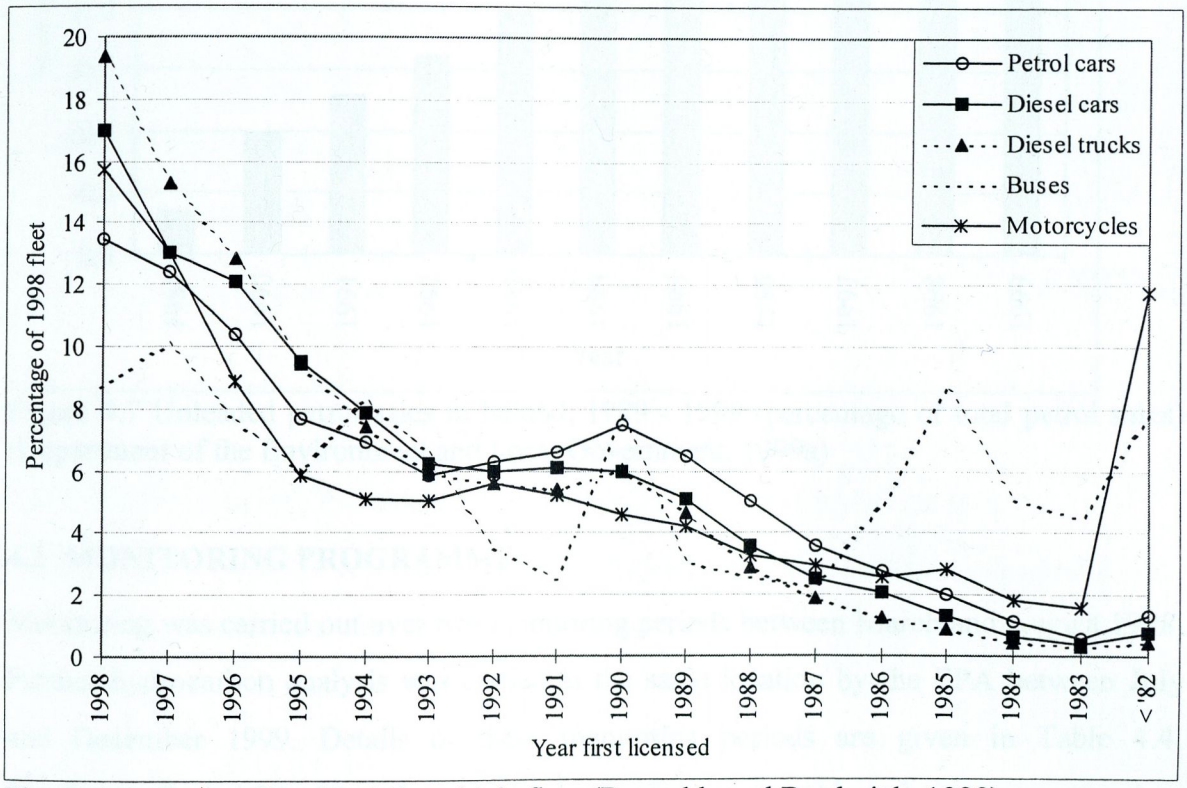


Figure 4.6 Age profile of Dublin vehicle fleet (Reynolds and Broderick, 1998)

Although only approximately 57 percent of the petrol engined car fleet were fitted with catalytic converters in 1998, fuel sales at the time did not indicate a similar split between leaded and unleaded fuel. Variations in annual petrol sales are detailed in Figure 4.7. At the time of monitoring approximately 84 percent of petrol sales were of unleaded petrol. Leaded petrol was required to be completely phased out by 2000 (Department of the Environment and Local Government, 1999a).

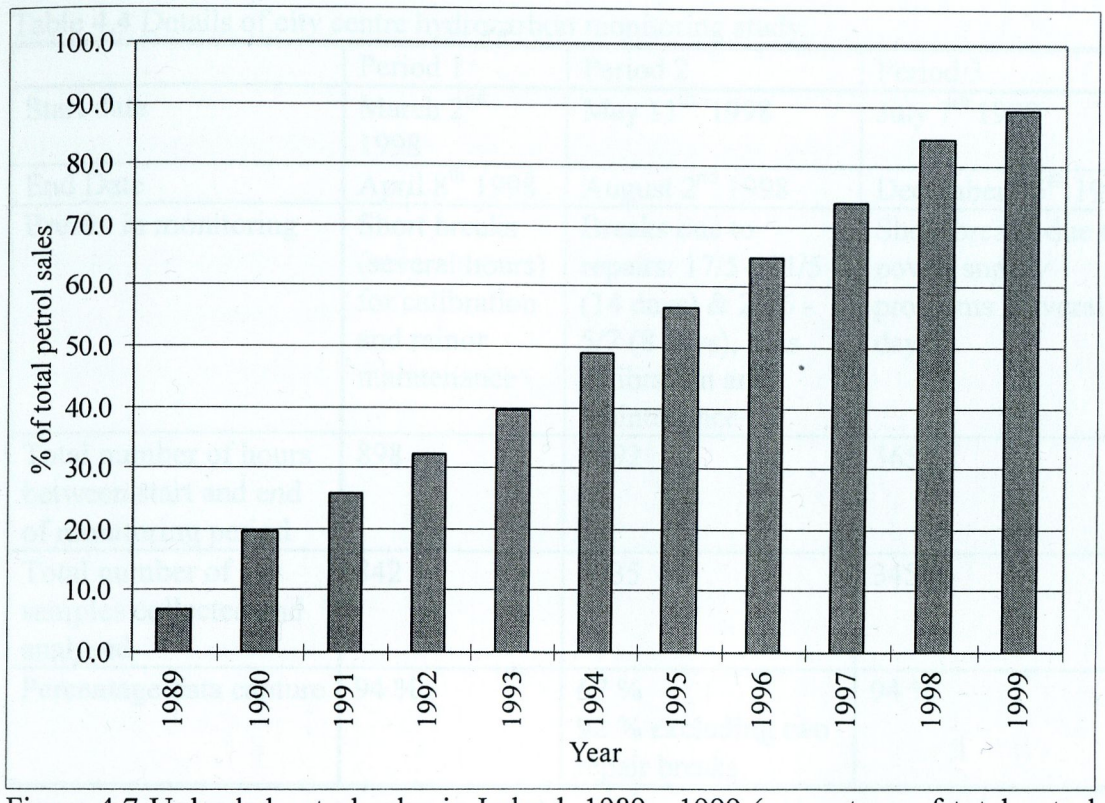


Figure 4.7 Unleaded petrol sales in Ireland, 1989 - 1999 (percentage of total petrol sales) (Department of the Environment and Local Government, 1999a)

4.2 MONITORING PROGRAMME

Monitoring was carried out over two monitoring periods between March and August 1998. Further hydrocarbon analysis was carried at the same location by the EPA between July and December 1999. Details of these monitoring periods are given in Table 4.4. Monitoring Period 2 had two short breaks due to equipment problems being encountered.

During the first monitoring period, a full range of hydrocarbons was measured, as detailed in Table 3.1. During the second monitoring period a smaller range of hydrocarbons were measured, as problems were encountered with one of the capillary columns in the GC (see Section 4.2.2). The compounds measured during the second monitoring period consisted of alkanes and alkenes and acetylene (alkyne) only, as the malfunctioning column was responsible for separation of the aromatics and two of the heavier alkanes (n-heptane and n-hexane). Details of the compounds separated by each column are given in Table 3.1. The EPA measured BTX (benzene, toluene and xylene) during the third monitoring period.

Although the monitoring system is capable of operating unattended, the equipment was checked on a daily basis to ensure that any data loss due to possible malfunctions was minimised.

Table 4.4 Details of city centre hydrocarbon monitoring study

	Period 1	Period 2	Period 3
Start date	March 2nd 1998	May 11th 1998	July 7th 1999
End Date	April 8th 1998	August 2nd 1998	December 15th 1999
Breaks in monitoring	Short breaks (several hours) for calibration and minor maintenance	Breaks due to repairs: 17/5 - 31/5 (14 days) & 27/6 - 5/7 (8 days), plus calibration and maintenance	Short breaks due to power supply problems (several days)
Total number of hours between start and end of monitoring period	898	1992	3659
Total number of samples collected and analysed	842	1335	3456
Percentage data capture	94 %	67 % 92 % excluding two repair breaks	94 %

4.2.1 Calibration and Evaluation of System Chromatographic Performance

Calibration was carried out using a 27 component calibration mixture supplied by the National Physical Laboratory (NPL). Calibration was carried out approximately every 14 days. The calibration standard was passed through the system for five consecutive analyses. For the first two analyses, the calibration gas was analysed as a sample rather than as a calibration standard. There were two reasons for this. Firstly, any contaminants present in the calibration gas line would be flushed through the system before the last three analyses were used to actually calibrate the system. Secondly, analysing the calibration gas as a sample allowed assessment of the analytical drift experienced by the system between calibrations. Although all three calibration runs produced very similar responses from the FID, averaging over three calibration analyses reduced any possible discrepancy between analyses. Each calibration chromatogram was also checked individually to ensure that compounds had been properly identified by the software.

Prior to the beginning of each monitoring campaign, the system was conditioned by heating the oven in the GC and the ATD400 to full operating temperature for an extended period, to purge any impurities from the cold trap in the ATD and the capillary columns in the GC. Conditioning is normally required if the system has been out of operation for a number of

weeks. After conditioning, the system can be operated for several months before further conditioning may be required. Conditioning helps to ensure good peak definition and consistent retention times. Examples of chromatograms from an unconditioned and a conditioned system are given in Figure 4.8 and Figure 4.9, respectively. Figure 4.9 illustrates the characteristic flat baseline and good peak resolution of the monitoring system. These results are from the PLOT column which separates the alkenes and most of the alkanes. A sample chromatogram from channel B (BP column), after system conditioning, is shown in Figure 4.10. All of the aromatics are separated on this column. As can be seen in Figure 4.9 and Figure 4.10, the peak resolution, R_S (resolution describes the degree of separation between a pair of adjacent peaks (Tipler, 1993) is very good for most compounds. It can be calculated using the formula:

$$R_S = \frac{t_{R2} - t_{R1}}{W_{h1} + W_{h2}} \qquad 4.1$$

t_{R1} and t_{R2} = retention times of the two peaks (seconds)
W_{h1} and W_{h2} = widths of peaks 1 and 2, respectively, at half their height (seconds)

For example, in Figure 4.9 the resolution between isopentane and n-pentane is approximately 5.84 (t_{R1} = 31.95, t_{R2} = 32.82, W_{h1} = 0.082, W_{h2} = 0.067). A minimum resolution of 1 is recommended for any peaks of interest in the chromatogram (Tipler, 1993). In Figure 4.9, all of the compounds, with the exception of 2-methylpentane and 3-methylpentane are reasonably well resolved (only 2-methylpentane is labelled in Figure 4.9, as 3-methylpentane is located very closely to the right of 2-methylpentane). These two compounds are shown in detail in Figure 4.11. For these two compounds the resolution is 1.08, which is close to the suggested minimum resolution for qualitative and quantitative identification. Compound resolution for the second capillary column (Figure 4.10) is also good for most compounds, with the exception of m-xylene and p-xylene. These two compounds co-elute (i.e. are not separated), and therefore are identified as a summed concentration (m+p-xylene). The co-elution of these two compound is illustrated in Figure 4.12 where different eluted peaks are just distinguishable.

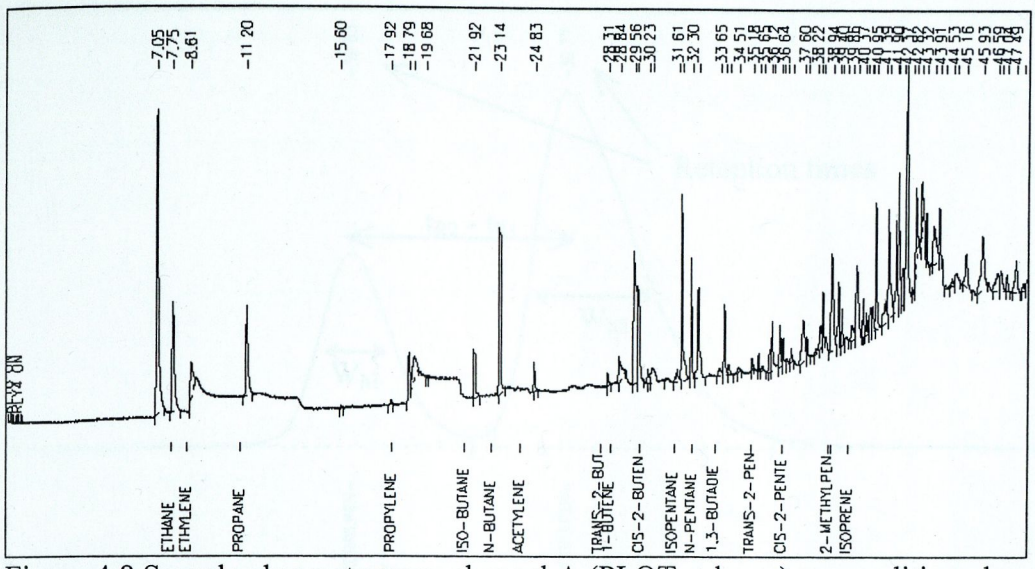


Figure 4.8 Sample chromatogram, channel A (PLOT column), unconditioned system

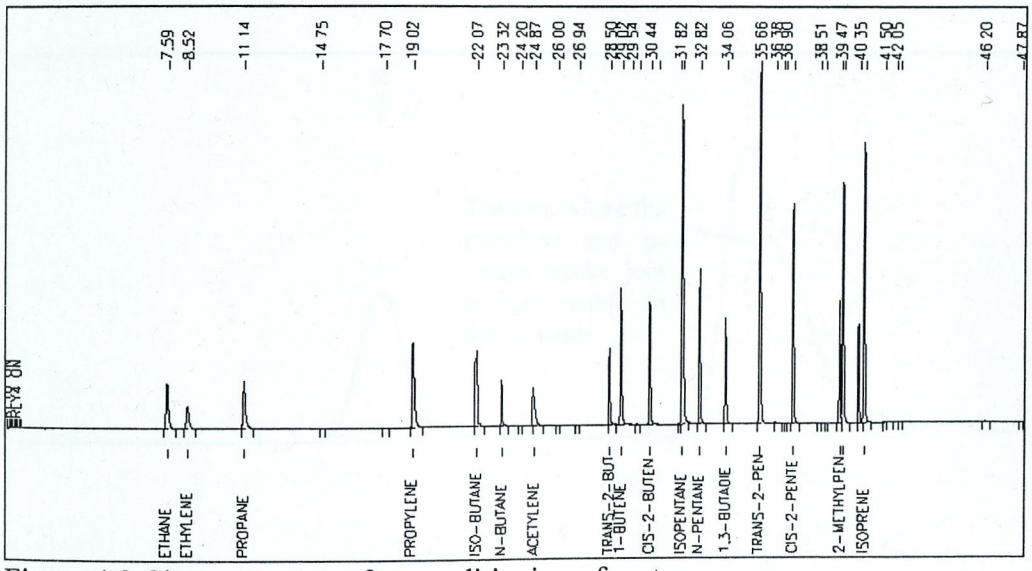


Figure 4.9 Chromatogram after conditioning of system

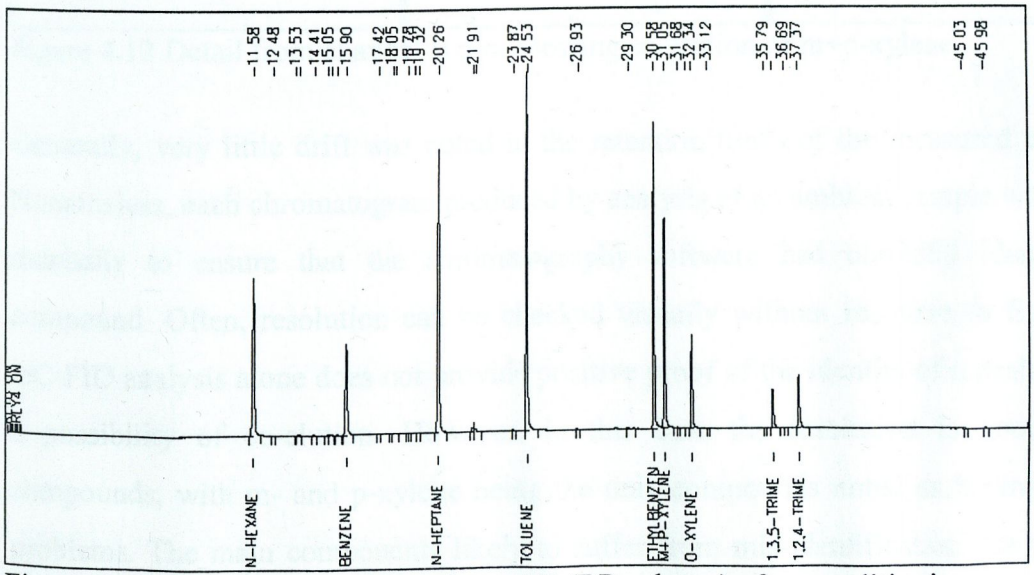


Figure 4.10 Chromatogram from channel B (BP column) after conditioning

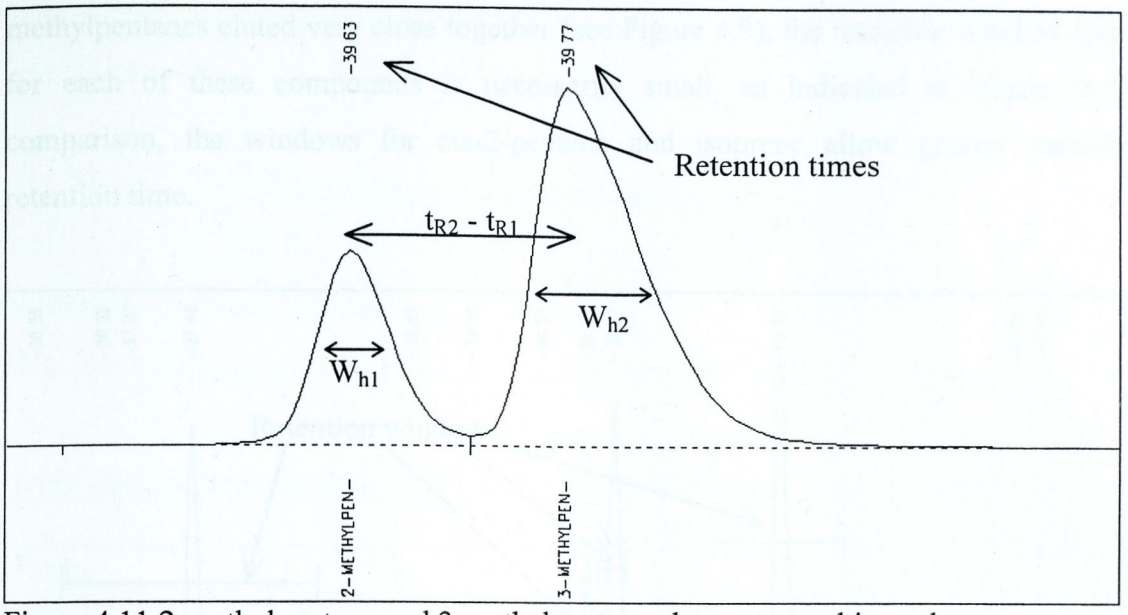


Figure 4.11 2-methylpentane and 3-methylpentane chromatographic peaks

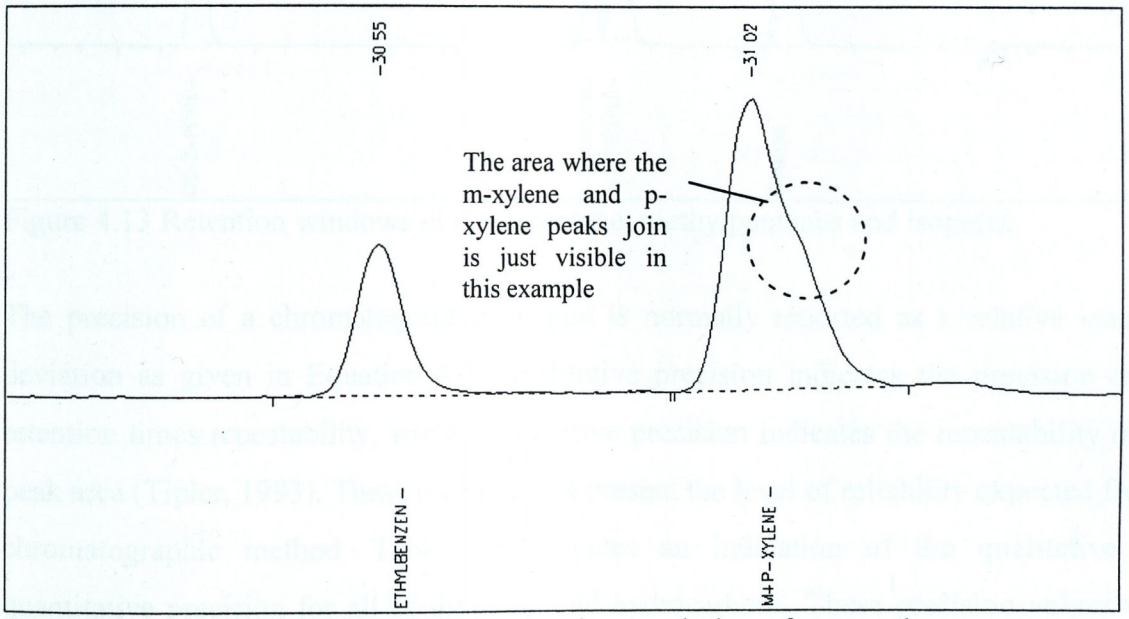


Figure 4.12 Detail from channel B plot showing co-elution of m+p-xylene

Generally, very little drift was noted in the retention times of the measured compounds. Nonetheless, each chromatogram produced by analysis of an ambient sample was inspected manually to ensure that the chromatography software had correctly identified each compound. Often, resolution can be checked visually without recourse to Equation 4.1. GC-FID analysis alone does not provide positive proof of the identity of a peak, as there is a possibility of co-elution. However, in this case the resolution is good for most compounds, with m- and p-xylene being the only compounds noted as having co-elution problems. The main components likely to suffer from mis-identification due to retention time drift were cis-2-pentene, 2-methylpentane and 3-methylpentane. Also, because the

methylpentanes eluted very close together (see Figure 4.9), the retention window specified for each of these compounds is necessarily small, as indicated in Figure 4.13. In comparison, the windows for cis-2-pentene and isoprene allow greater variation in retention time.

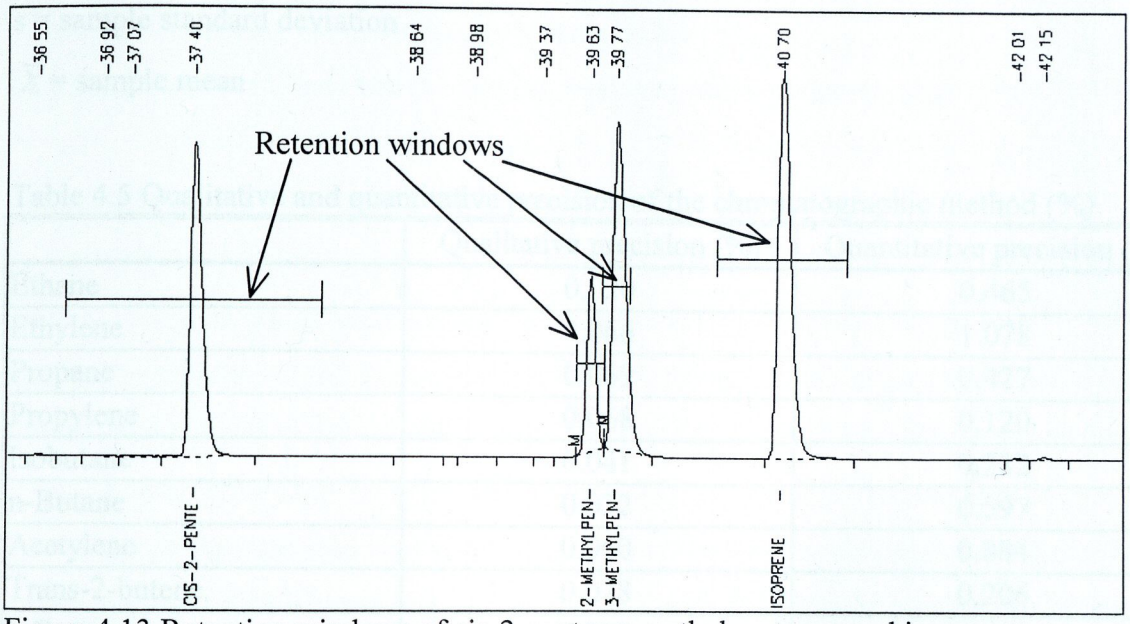


Figure 4.13 Retention windows of cis-2-pentene, methylpentanes and isoprene

The precision of a chromatographic method is normally reported as a relative standard deviation as given in Equation 4.2. Qualitative precision indicates the precision in the retention times repeatability, while quantitative precision indicates the repeatability of the peak area (Tipler, 1993). These parameters represent the level of reliability expected from a chromatographic method. Table 4.5 provides an indication of the qualitative and quantitative precision for all of the measured hydrocarbons. These precision values were calculated from four consecutive analyses of the calibration gas. Tipler suggests that a good chromatographic method will have a qualitative precision of less than 0.05 percent and a quantitative precision of less than 1 percent. The chromatographic method displays good qualitative precision for all of the measured compounds. The quantitative precision for the trimethylbenzenes is lower than for other compounds. It was noted during calibrations that the trimethylbenzenes displayed a smaller peak area for the first (and sometimes the second) calibration analysis. In response to a query, Perkin-Elmer advised that this may be due to some reactions in the transfer line, between the calibration gas cylinder and the air sampling accessory during the initial calibrations, hence, calibrations should only be based on the third analysis onwards, once any possible contaminants had been purged from the

system. This is likely to be the reason for the apparent poorer quantitative precision for the trimethylbenzenes.

$$\text{Relative standard deviation} = \frac{s}{\overline{X}} \qquad 4.2$$

s = sample standard deviation

$\overline{X}$ = sample mean

Table 4.5 Qualitative and quantitative precision of the chromatographic method (%)

	Qualitative precision (%)	Quantitative precision (%)
Ethane	0.020	0.465
Ethylene	0.066	1.078
Propane	0.069	0.427
Propylene	0.068	0.120
Isobutane	0.041	0.282
n-Butane	0.032	0.597
Acetylene	0.060	0.884
Trans-2-butene	0.028	0.206
1-Butene	0.033	0.327
Cis-2-butene	0.026	0.374
Isopentane	0.030	0.455
n-Pentane	0.023	0.377
1,3-butadiene	0.018	0.180
Trans-2-pentene	0.021	0.312
Cis-2-pentene	0.061	0.098
2-methylpentane	0.018	0.633
3-methylpentane	0.020	0.563
Isoprene	0.014	0.573
n-Hexane	0.015	1.218
Benzene	0.026	1.111
n-Heptane	0.016	0.645
Toluene	0.010	0.623
Ethylbenzene	0.005	0.302
m+p-Xylene	0.005	0.173
o-Xylene	0.002	0.297
1,3,5-trimethylbenzene	0.004	2.557
1,2,4-trimethylbenzene	0.002	3.211

The performance of the thermal desorption unit cannot be quantified individually. However, the precision of the chromatographic results suggests that the performance of the ATD is satisfactory with respect to the GC.

4.2.2 Equipment Failures and Malfunctions

In this section, a number of equipment failures which occurred during the monitoring programmes are described. Their description fulfils two purposes:

1) It illustrates the level of operator knowledge and vigilance required to achieve satisfactory results using the on-line system; and
2) It identifies the failures which occurred, their symptoms and remedies.

It is hoped that this information will be of use in future monitoring campaigns.

The first problem which was encountered was the acquisition and connection of a suitable calibration standard. A 57 component hydrocarbon standard was available from the United States; however, the cost of this proved too expensive. A 27 component calibration standard was eventually sourced from the National Physical Laboratory in the UK. Connection of the gas also proved to be a problem due to the fact that a regulator which does not have a built-in pressure gauge was required. This was necessary due to worries over loss of trace hydrocarbons when using a regulator with a built in pressure gauge. A regulator without a gauge was found and the gas was connected as shown in Figure 3.10.

During initial calibration of the system, the trimethylbenzenes present in the calibration gas did not appear on the chromatograms. It was initially feared that there may have been a problem with the regulator leading to loss of these hydrocarbons, as their concentrations in the calibration mixture are low (see Table 3.1). Another fear was that a small amount of grease in the calibration gas line was absorbing the hydrocarbons, as had happened to a similar system in the UK. However, after 4-5 calibration samples were passed through the system, the trimethylbenzenes began to appear on the chromatogram, and after several further samples they had reached a constant peak area. This problem occurred in other calibration analyses, though usually only for the first calibration run, with subsequent analyses indicating good agreement between peak areas.

Rather than using expensive cylinders of zero air, an air generator was installed to provide the large amount of zero air required by the system. However, at the very start of a sequence of sampling, an empty tube must be loaded from the ATD 400 carousel into the air stream in order to complete the pathway for the sample. This pneumatically powered

process required greater pressure than could be supplied by the generator, although the flow rate was adequate for analysis purposes. It was found that this problem could be overcome by lighting the FIDs only after the empty tube had been loaded into the air stream. The extra pressure provided by shutting off the air supply to the FIDs was sufficient to allow the pneumatic processes to operate.

The air sampler accessory, which is connected to the ATD400 in order to draw either an air sample or a calibration sample through the ATD400, also caused some problems. A diaphragm which controls the flow of air through the sampler unit became clogged with 'sticky particulate matter' which was entering the air sampler with the air stream. This caused the sample flow to be reduced from the required 15 ml/min. to 2-3 ml/min as the diaphragm was not able to open fully. A new accessory was fabricated and fitted to the air sampler, which periodically expels a small blast of air towards the diaphragm, thus dislodging the particulate matter, which is then expelled through the sampler exhaust. This problem was responsible for the second break in operation during the second monitoring period.

A problem also occurred with the pneumatic arm which loads the empty tube from the carousel of the ATD400 into the sample pathway. The arm became bent when, during the removal of the tube from the carousel, the arm became caught in the carousel. As the arm retracted it bent before dislodging from the carousel. This arm had to be removed from the ATD400, and a new pneumatic arm installed.

A problem also occurred with the cold trap heater in the ATD400. The heater raises the temperature of the cold trap from -30 °C up to 325 °C in a matter of seconds. However, an error message indicating <TRAP NOT HEATING> appeared on the ATD400 operating screen. The cold trap heater appeared to be unable to heat the cold trap from -30°C to 325°C in the required time. After extensive investigation, it was discovered that a thermocouple had become detached from the trap heater. This meant that the temperature of the cold trap was not being properly measured and the heater appeared not to be able to reach optimum temperature. The trap heater needed to be replaced, as the heating element had burned out attempting to reach the maximum temperature of 325 °C. The cold trap itself also needed to be replaced as this had been damaged by the excessive heating of the element. The cold trap then needed to be conditioned for several hours, and several days of

sampling were required before acceptable chromatograms with well defined peaks were produced.

Further problems were encountered with the zero air generator when its moisture removal system developed a problem, resulting in the first break in operation during the second monitoring period. The water removed from the air is collected in a water trap, which is pneumatically evacuated periodically by a float mechanism. However, this float became lodged at the bottom of the water trap, resulting in the water rising back up into the two desiccant filled drying columns. Hence, moist air was supplied to the ATD400 and to the FIDs. This meant that the moisture was not being properly removed from the ambient air sample when it was passed through the Nafion dryer (which uses the dry air flow to remove the moisture from the sample). Therefore, the air sample was not dry as it passed through the cold trap during sample collection. Air which is supplied to the box in which the cold trap is housed was also moist. The low temperature of the trap (-30 °C) resulted in moisture collecting on the outside and inside of the cold trap, which then formed immediately into ice. This icing up of the cold trap interfered with the efficient heating and cooling process of the cold trap. Initially this problem was not noticed, as the heating process of the cold trap evaporated most of the moisture. However, moisture build-up over a series of analyses resulted in persistent icing of the cold trap, eventually resulting in the trap heater being unable to heat the trap at the required rate. An upgraded water trap had to be fitted to the zero air generator.

Testing of the air generator after the above repairs revealed that further problems were being encountered with pressure loss which were now more serious than before, and that the drying of the air to the specifications required by the monitoring system (a dew point of at least -50 °C is required to prevent icing of the cold trap) was inadequate due to water retention in the drying towers of the generator. It was decided, therefore, to use cylinders of zero-air for the majority of the second monitoring period. The moist air supplied by the air generator, had, however, already resulted in a desiccant-filled filter which was fitted in the air supply line to the ATD becoming saturated. The filter material was dried by placing the desiccant in an oven for 24 hours at 200 °C, and then allowing the desiccant to cool in an evacuated desiccator (to prevent moisture in the air being absorbed by the desiccant) before refilling the filter. During operation of the monitoring system with zero air cylinders, rather

than the zero air generator, no problems were encountered with icing of the cold trap or saturation of the moisture filter in the ATD supply line.

Shortly after the beginning of the second monitoring period, the BP column (which resolves the aromatics and two of the alkanes) began to deteriorate. This was identified as the 'noise' level of the baseline began to increase. Conditioning of the columns did not provide any improvement, and the column performance gradually deteriorated further. Figure 4.14 illustrates a sample chromatogram produced by the BP column after column deterioration. The baseline is not flat, and is noisy, compared to the healthy chromatogram shown in Figure 4.10. As a result of this problem, the results from the BP column for the majority of the second monitoring period could not be reliably used, and thus are not presented in Section 4.3.

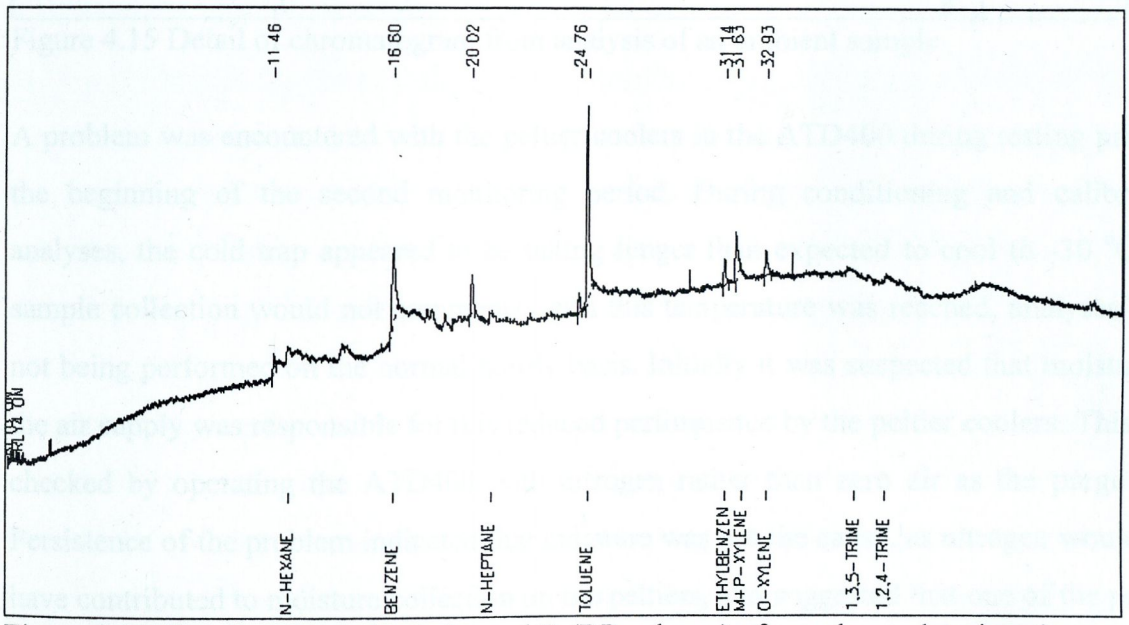


Figure 4.14 Chromatogram from channel B (BP column) after column deterioration

As mentioned in Section 4.2.1, some problems were encountered with the identification of the methylpentanes due to drift in the retention time of these compounds, and due to the fact that these compounds were eluted very close together. Another compound was also eluted very close to the methylpentanes, as shown in Figure 4.15. It is suspected that this compound is 2,3-dimethylbutane although no definite identification could be made. The resolution between this peak and the 2-methylpentane peak is approximately 1.38, which is within the parameters specified in Section 4.2.1. However, there is some co-elution between the two compounds, which may result in some loss of accuracy in the prediction of the 2-methylpentane concentrations. Each chromatogram was manually examined to

ensure correct identification of each compound. A manual identification procedure within the chromatography software allowed any mis-identifications to be remedied.

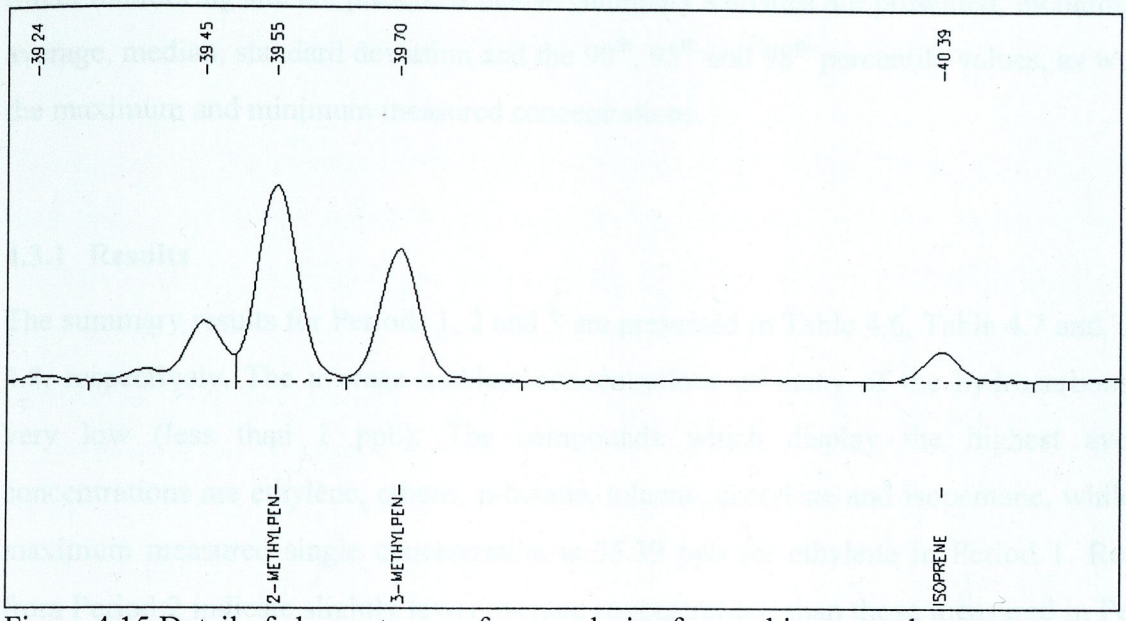


Figure 4.15 Detail of chromatogram from analysis of an ambient sample

A problem was encountered with the peltier coolers in the ATD400 during testing prior to the beginning of the second monitoring period. During conditioning and calibration analyses, the cold trap appeared to be taking longer than expected to cool to -30 °C. As sample collection would not commence until this temperature was reached, analyses were not being performed on the normal hourly basis. Initially it was suspected that moisture in the air supply was responsible for this reduced performance by the peltier coolers. This was checked by operating the ATD400 with nitrogen rather than zero air as the purge gas. Persistence of the problem indicated that moisture was not the cause, as nitrogen would not have contributed to moisture collection on the peltiers, and suggested that one of the peltier coolers was not functioning properly. Several peltier coolers are stacked below the cold trap tube. As it was not possible to identify which of these was not operating, each had to be removed in turn and replaced with a peltier known to be in full working order. The system was then operated to ascertain if the peltier which had been replaced was the faulty item. The non-operational peltier was eventually identified and its replacement allowed the correct cooling rate to be obtained.

4.3 HYDROCARBON MONITORING RESULTS

Summary results from each of the three monitoring campaigns carried out at the Pearse Street monitoring site are presented below. Summary statistics are presented, including the average, median, standard deviation and the 90th, 95th and 98th percentile values, as well as the maximum and minimum measured concentrations.

4.3.1 Results

The summary results for Periods 1, 2 and 3 are presented in Table 4.6, Table 4.7 and Table 4.8, respectively. The average ambient concentrations of many of the hydrocarbons are very low (less than 1 ppb). The compounds which display the highest average concentrations are ethylene, ethane, n-butane, toluene, acetylene and isopentane, while the maximum measured single concentration is 35.39 ppb for ethylene in Period 1. Results from Period 2 indicate slightly lower average concentrations than those measured in Period 1. This is likely to be due to improved atmospheric mixing during the summer months, as has been found in similar hydrocarbon monitoring studies in the UK (PORG, 1993; Field *et al.*, 1994; Derwent *et al.*, 1995; PORG, 1997). Also, exhaust emissions from individual vehicles are reported to decrease with increasing ambient temperature. Farrow *et al.* (1993) observed a halving of emissions when ambient temperature increased from 0 °C to 25 °C.

The only compounds exhibiting higher average concentrations in Period 2 are the alkenes propylene, 1-butene and isoprene. During winter months, the contribution of natural sources to ambient concentrations of isoprene can be expected to be very low, while significant contributions from such sources would be expected during the warmer summer months due to emissions from flora (Reimann *et al.*, 2000). It is possible that emissions from another source were responsible for the higher measured concentrations, though none were identified. Hov *et al.* (1991) observed unusual behaviour for propylene concentrations measured in Norway, with concentrations measured during the summer comparable to, or greater than, winter concentrations. Hov *et al.* (1991) reported that several studies which have measured hydrocarbon concentrations in oceanic air have observed relatively high concentrations of propylene, in reportedly unpolluted air masses. This source may have contributed to the Period 2 propylene concentrations, as easterly winds occurred more frequently, compared to Period 1, with 23 percent of hourly wind direction during Period 1 from the 20 to 160 degree sector (Irish Sea), compared to 27 percent during Period 2 (see

Section 4.4 for description of meteorological data). Goldstone (1993) also noted unusual behaviour for propylene during the warmer summer months, while monitoring in London, with higher average concentrations compared to winter months, though again, no specific source was identified. No sources of 1-butene were identified near the monitoring site.

Comparison of the average benzene concentrations from Period 1 with the UK and EU limit values of 5 ppb and 1.6 ppb, respectively, indicates that the Period 1 average concentration (1.8 ppb) is slightly above the EU limit, but well below the UK limit. These limit values are specified as annual mean concentrations and certain criteria are set for monitoring locations (such as required distance from a junction), hence, a direct comparison of the average benzene concentration for Period 1 should be made cautiously. However, these roadside concentrations provide an indication of the highest concentrations which can be expected due to vehicle emissions.

The average 1,3-butadiene concentration during Period 1 and 2, of 0.38 and 0.24 ppb, respectively, are compliant with the UK annual average limit value of 1 ppb. Though higher hydrocarbon concentrations may be expected during the coldest winter months, it is unlikely that average concentrations above 1 ppb would be measured over the course of a twelve month period. However, as with benzene, comparisons should be made cautiously as the monitoring location and duration do not meet the criteria for application of this limit value.

Comparing the hydrocarbon concentrations measured in Period 1 to the BTX measurements in Period 3 indicates that the measured toluene concentrations are relatively close (Period 3 average is 85 percent of Period 1 average). However, the average benzene concentration measured during Period 3 is only 28 percent of that observed in Period 1. For o-xylene, the concentrations are in good agreement, with the Period 3 average being 90 percent of the Period 1 average. Discussion of these results with the EPA revealed that some problems were encountered during the BTX monitoring, resulting in possible peak misidentification for benzene, due to large variations in the peak retention time. Therefore, the results from Period 3 may not be reliable for benzene.

Table 4.6 Summary statistics for Period 1, ppb

	Average	Minimum	Maximum	Std. dev.	Median	90th percentile	95th percentile	98th percentile
Ethane	**4.34**	1.47	19.29	1.89	4.03	6.09	7.38	10.45
Ethylene	**5.10**	0.20	35.39	4.51	3.81	10.56	13.91	18.72
Propane	**2.14**	0.39	22.09	1.48	1.79	3.26	4.53	6.63
Propylene	**1.58**	0.03	13.57	1.48	1.15	3.39	4.35	5.84
Isobutane	**1.57**	0.11	13.34	1.33	1.26	2.97	3.83	5.05
n-Butane	**3.85**	0.24	29.00	3.33	3.08	7.47	10.27	12.89
Acetylene	**2.81**	0.14	23.70	2.66	1.90	5.90	8.54	10.76
Trans-2-butene	**0.21**	0.00	1.68	0.18	0.16	0.41	0.55	0.71
1-Butene	**0.07**	0.00	1.23	0.18	0.00	0.29	0.48	0.75
Cis-2-butene	**0.19**	0.00	1.56	0.17	0.14	0.38	0.52	0.65
Isopentane	**2.62**	0.04	22.71	2.51	1.99	5.23	7.61	9.77
n-Pentane	**0.90**	0.11	7.05	0.78	0.72	1.73	2.46	2.99
1,3-butadiene	**0.38**	0.03	2.85	0.33	0.29	0.80	1.03	1.30
Trans-2-pentene	**0.27**	0.00	3.13	0.28	0.21	0.54	0.74	0.96
Cis-2-pentene	**0.16**	0.00	1.54	0.16	0.12	0.34	0.46	0.68
2-methylpentane	**0.40**	0.00	4.04	0.45	0.23	0.98	1.41	1.81
3-methylpentane	**0.37**	0.00	3.08	0.36	0.27	0.80	1.08	1.36
Isoprene	**0.13**	0.00	0.84	0.11	0.10	0.26	0.36	0.46
n-Hexane	**0.48**	0.00	4.85	0.44	0.39	0.93	1.20	1.55
Benzene	**1.80**	0.18	16.97	1.66	1.37	3.70	4.90	6.40
n-Heptane	**0.17**	0.00	1.54	0.16	0.12	0.33	0.44	0.63
Toluene	**3.30**	0.20	30.87	3.61	2.10	7.25	9.88	13.78
Ethylbenzene	**0.48**	0.03	3.93	0.43	0.35	1.01	1.33	1.70
m+p-Xylene	**1.56**	0.16	12.49	1.42	1.14	3.32	4.29	5.52
o-Xylene	**0.59**	0.05	4.82	0.54	0.43	1.26	1.62	2.13
1,3,5-trimethylbenzene	**0.42**	0.03	3.30	0.37	0.31	0.89	1.13	1.48
1,2,4-trimethylbenzene	**0.74**	0.08	5.94	0.66	0.53	1.55	2.04	2.58

Table 4.7 Summary statistics for Period 2, ppb

	Average	Minimum	Maximum	Std. dev.	Median	90th percentile	95th percentile	98th percentile
Ethane	**2.71**	0.20	15.33	1.59	2.26	4.20	5.41	7.84
Ethylene	**3.43**	0.00	33.92	3.50	2.26	8.32	11.35	14.54
Propane	**1.37**	0.13	26.52	1.67	0.93	2.40	3.43	5.91
Propylene	**1.92**	0.00	15.74	1.53	1.52	3.46	4.69	6.14
Isobutane	**0.82**	0.00	9.11	0.91	0.55	1.91	2.76	3.59
n-Butane	**2.41**	0.00	19.31	2.53	1.73	5.64	8.15	10.54
Acetylene	**1.77**	0.00	30.06	2.16	1.05	4.30	6.30	8.39
Trans-2-butene	**0.12**	0.00	0.74	0.12	0.09	0.27	0.39	0.49
1-Butene	**0.19**	0.00	1.17	0.16	0.14	0.40	0.55	0.69
Cis-2-butene	**0.12**	0.00	0.71	0.11	0.10	0.27	0.37	0.46
Isopentane	**1.97**	0.00	14.47	1.97	1.40	4.64	6.47	8.31
n-Pentane	**0.69**	0.00	4.25	0.65	0.50	1.56	2.15	2.81
1,3-butadiene	**0.24**	0.02	1.96	0.21	0.17	0.52	0.72	0.90
Trans-2-pentene	**0.13**	0.00	0.86	0.13	0.09	0.27	0.39	0.50
Cis-2-pentene	**0.09**	0.00	0.56	0.08	0.08	0.19	0.26	0.33
2-methylpentane	**0.32**	0.00	4.78	0.32	0.23	0.68	0.87	1.25
3-methylpentane	**0.24**	0.00	2.78	0.34	0.14	0.54	0.91	1.45
Isoprene	**0.16**	0.00	2.02	0.17	0.12	0.35	0.48	0.70

Table 4.8 Summary statistics for Period 3, ppb

	Average	Minimum	Maximum	Std. dev.	Median	90th percentile	95th percentile	98th percentile
Benzene	**0.50**	0.01	6.38	0.61	0.29	1.21	1.70	2.40
Toluene	**2.82**	0.01	27.55	3.52	1.58	6.73	9.95	15.10
o-Xylene	**0.53**	0.00	6.95	0.75	0.26	1.24	1.93	3.01

Mean concentrations measured in other hydrocarbon studies at various locations around the world are presented in Appendix B. Although the sampling periods and locations vary from study to study, a good indication is still given of the range of concentrations which can be expected. In Dublin, the benzene, toluene and xylene data collected by the EPA during a diffusion tube study (site number 29, Appendix B) shows good agreement with the concentrations measured during this study, with the exception of total xylene concentration, which is substantially higher for the EPA study (Henderson *et al.,* 1997). A BTEX measurement study was also carried out as part of the Dublin Air Quality Management Plan (Envirocon, 1997), at both urban and suburban locations (study numbers 30 and 31). High concentrations were reported by this study, and agreement is poor with both the on-line results at Pearse Street and the EPA diffusion tube study. Hydrocarbon data from a selection of urban studies in Appendix B are presented in Table 4.9, along with the average concentrations from Period 1 and 2 monitoring in Dublin.

Results from urban monitoring in Rome (Brocco *et al.,* 1997) indicate very high concentrations in this city, with concentrations of all compounds, except ethane, at least a factor of 4 higher than in Dublin. Measurements from Athens (Rappengluck *et al.,* 1998), a city known for air pollution episodes, is very similar to that in Rome, and again, much higher than that measured in Dublin. Measurements from roadside monitoring in California (Hammond and Cook, 1993) are in better agreement with results from Dublin. The aromatic compounds, in particular, are in excellent agreement with Dublin roadside concentrations during Period 1. Results from the London UCL roadside monitoring site (which is part of the UK automatic network) are in good agreement with Dublin results, though concentrations in Dublin are slightly higher. This can be explained by the fact that the traffic flow is greater on Pearse Street (in Dublin), than at the UCL roadside monitoring site. Very high traffic flow (> 80,000 vehicles / day) is experienced at the roadside monitoring site in Marylebone Road (London). The resulting ambient hydrocarbon concentrations are significantly higher than those measured in Dublin for all of the measured hydrocarbons. Average concentrations are generally three to four times higher than those measured in Dublin, though the traffic flow in Dublin is more than 50 percent of that on Marylebone Road. This suggests greater congestion on Marylebone Road compared to Pearse Street. Results from city centre monitoring in Munich (Rappengluck and Fabian, 1999) indicates that concentrations are approximately one third higher at this site compared

to monitoring data from Dublin, though only a limited range of compounds are reported for Munich.

Table 4.9 Results from urban hydrocarbon monitoring studies

Site	Period 1	Period 2	Rome[1]	Athens[2]	Calif.[3]	London[4]	London[5]	Munich[6]
Ethane	4.34	2.71	9.94	x	4.80	3.67	22.35	x
Ethylene	5.10	3.43	19.24	x	x	2.83	16.10	x
Propane	2.14	1.37	13.01	x	5.77	2.27	6.34	x
Propylene	1.58	1.92	10.54	x	1.93	1.57	5.29	x
Isobutane	1.57	0.82	12.81	x	6.08	1.98	6.46	x
n-Butane	3.85	2.41	14.72	x	in total	3.31	27.52	x
Acetylene	2.81	1.77	28.86	x	x	2.82	4.48	x
Trans-2-butene	0.21	0.12	3.69	x	x	x	0.88	x
Cis-2-butene	0.07	0.19	1.68	x	x	0.18	0.70	x
1-Butene	0.19	0.12	1.76	x	x	0.21	0.93	x
Isopentane	2.62	1.97	24.86	26.30	1.58	2.51	10.62	x
n-Pentane	0.90	0.69	7.78	x	in total	0.64	2.23	x
1,3-butadiene	0.38	0.24	2.05	x	x	0.23	1.05	x
Trans-2-pentene	0.27	0.13	2.06	x	x	0.17	0.76	x
Cis-2-pentene	0.16	0.09	1.03	x	x	0.09	0.44	x
2-methylpentane	0.40	0.32	7.63	x	x	1.36	2.87	1.2
3-methylpentane	0.37	0.24	5.39	4.70	x	in total	1.70	0.5
Isoprene	0.13	0.16	x	x	x	0.16	1.46	x
n-Hexane	0.48	x	4.41	4.10	0.58	0.31	1.33	0.6
Benzene	1.80	x	11.08	11.70	1.77	1.20	3.94	2.8
n-Heptane	0.17	x	2.31	1.30	0.26	0.16	0.66	0.3
Toluene	3.30	x	26.07	21.20	3.10	2.40	8.61	4.6
Ethylbenzene	0.48	x	3.99	4.00	0.51	0.43	1.39	0.6
m+p-Xylene	1.56	x	12.39	11.30	1.69	1.26	4.55	2.2
o-Xylene	0.59	x	5.70	5.50	0.64	0.48	1.64	0.8
1,3,5-trimethylb.	0.42	x	4.53	x	x	x	x	x
1,2,4-trimethylb.	0.74	x	4.21	x	0.56	x	x	x

1: Rome (urban centre), Brocco *et al.*, 1997
2: Athens, Greece (urban roadside), Rappengluck *et al.*, 1998
3: California (roadside), Hammond and Cook, 1993
4: London (roadside, UCL), 1998
5: London (roadside, Marylebone), 1998
6: Munich, Germany (city centre), Rappengluck and Fabian, 1999.

The data which can be compared most directly with the measurements from this study are those collected at the UK monitoring sites at the London urban roadside sites at UCL and Marylebone Road (MB) and at the urban background site in Belfast. These sites also use on-line hydrocarbon systems. The ratio of the Dublin Period 1 data to London and Belfast data are presented in Table 4.10 (no 1997 data is available for Marylebone Road).

The values are similar for each of the compounds, particularly for the London and Dublin data. The main discrepancy between the Belfast and Dublin data is with propane, which

exhibits much higher concentrations in Belfast than in Dublin. The high propane levels at the Belfast monitoring site are reported to be due to leakage from local LPG (liquefied petroleum gas) storage tanks. The relative concentration of some of the alkenes (1,3-butadiene and the pentenes) is higher in Dublin, particularly in 1998. The high reactivity (with the hydroxyl radical) of these compounds may result in some decrease in concentration between the source and the urban background measurement site in Belfast.

The ratios between the Dublin and London UCL data exhibit some discrepancies for 1-butene, acetylene (in 1997), and isoprene. A similar low ratio for 1-butene is observed between the Dublin and Belfast data. The 1-butene concentrations measured in Dublin were very low with a lot of zero concentrations recorded; the above findings may point to some analytical problems either in trapping or identifying 1-butene. The very high acetylene concentrations reported for London are attributable to analytical problems, as difficulties are reported with co-elution of acetylene and isobutane at that monitoring station (Derwent *et al.*, 2000). The same problem does not occur for the 1998 London UCL data. It is likely that the same problems were encountered at Belfast in 1997, as the average concentration dropped by over 50 percent between '97 and '98, which is a larger decrease than for any other compound.

Comparison of the roadside Dublin and London Marylebone hydrocarbon data reveals a constant ratio between the majority of the reported hydrocarbon compounds, with a large number of compounds exhibiting values between 0.3 and 0.4. Indeed the standard deviation for this data is significantly lower than for any of the other data comparisons. Compounds which exhibit a lower than average ratio include ethane, n-butane, cis-2-butene and the methylpentanes, suggesting other possible sources of these compounds in London. Ethane has previously been associated with natural gas leakage in London (Field *et al.*, 1994; Derwent *et al.*, 1995; Derwent *et al.*, 2000). Acetylene exhibits the highest ratio of 0.63. Problems with identification of acetylene in the UK monitoring network have been encountered (Derwent *et al.*, 2000), which may account for the relatively low acetylene concentrations.

As hydrocarbon concentrations at the Dublin and London Marylebone sites are dominated by vehicle emissions, and the vehicle fleets would be expected to be similar at both sites, it is not surprising that such consistency is observed between the two datasets.

Table 4.10 Ratio of London and Belfast HC data to Dublin Period 1 concentrations

	Dublin Belfast 97	Dublin Belfast 98	Dublin London UCL 97	Dublin London UCL 98	Dublin London MB 98
Ethane	1.95	2.05	0.91	1.18	0.19
Ethylene	2.16	2.98	1.12	1.80	0.32
Propane	0.17	0.29	0.70	0.94	0.34
Propylene	1.60	1.74	0.68	1.01	0.30
Isobutane	1.27	1.64	0.45	0.79	0.24
n-Butane	1.38	2.02	0.75	1.16	0.14
Acetylene	0.99	2.05	0.32	1.00	0.63
Cis-2-butene	0.64	0.88	0.29	0.39	0.10
1-Butene	1.12	1.58	0.58	0.90	0.20
Isopentane	1.81	2.91	0.61	1.04	0.25
n-Pentane	1.67	2.14	0.91	1.41	0.40
1,3-butadiene	2.38	3.80	1.00	1.65	0.36
Trans-2-pentene	2.45	5.40	0.96	1.59	0.36
Cis-2-pentene	3.20	8.00	1.07	1.78	0.37
Methylpentanes	1.71	2.33	0.48	0.57	0.17
Isoprene	0.87	1.63	0.35	0.81	0.09
n-Hexane	3.20	4.36	1.12	1.55	0.36
Benzene	1.98	2.61	1.03	1.50	0.46
n-Heptane	1.55	1.70	0.85	1.06	0.26
Toluene	1.98	2.64	0.93	1.38	0.38
Ethylbenzene	1.37	2.00	0.70	1.12	0.35
m+p-Xylene	1.58	2.08	0.79	1.24	0.34
o-Xylene	1.37	1.90	0.76	1.23	0.36
Mean	1.67	2.55	0.75	1.18	0.30
Standard deviation	0.72	1.61	0.26	0.37	0.12

4.3.2 Distribution of Hourly Hydrocarbon Concentrations

Air quality data are inherently random variables because of their dependence on the fluctuations of a variety of meteorological and emissions variables (Georgopoulos and Seinfeld, 1982). However, it has been observed by many researchers in the environmental field that the frequency distribution of pollutant concentrations do not exhibit a normal (or Gaussian) distribution. Instead, the distribution most often applied to air quality data is the 'lognormal' distribution (Munn, 1981; Ott, 1990; Cohen *et al.,* 1991), meaning that the frequency distribution of the logarithm of pollution data is normal. The plot of the frequency distribution (known as a histogram) of lognormal data can also be described as 'right skewed' or 'positively skewed', as the right-hand tail of the distribution tends to be longer than that on the left (primarily because negative values of pollutant concentrations are not possible). Though the lognormal distribution is still the most popularly applied distribution for air pollution data, other distributions (such as gamma, Weibull and beta)

may also be found to represent such data (Benoit *et al.*, 1999). Indeed, Benoit *et al.* indicate that the distribution of air pollution data from a study in Chile is indistinguishable from several different distributions for certain datasets.

Many statistical tests (such as the t-test for comparing mean values) assume that the data being tested are drawn from normally distributed samples. Therefore, any statistical analysis carried out on pollution data must be checked to ensure that the procedure is robust, i.e. that it can be used on non-normal data. Some tests, such as the t-test can indeed be used properly if the sample size is large (30 or more observations) (Haynes, 1996). Other statistical procedures, such as analysis of variance tests, are also reported to be robust (MacBerthouex and Brown, 1994).

The summary statistics presented in Section 4.3 suggest that the hydrocarbon data collected during this study is not normally distributed, as the arithmetic mean and the median are not the same or similar. Histograms of hourly toluene concentrations and the natural logarithm of the same data are presented in Figure 4.16 and Figure 4.17, respectively.

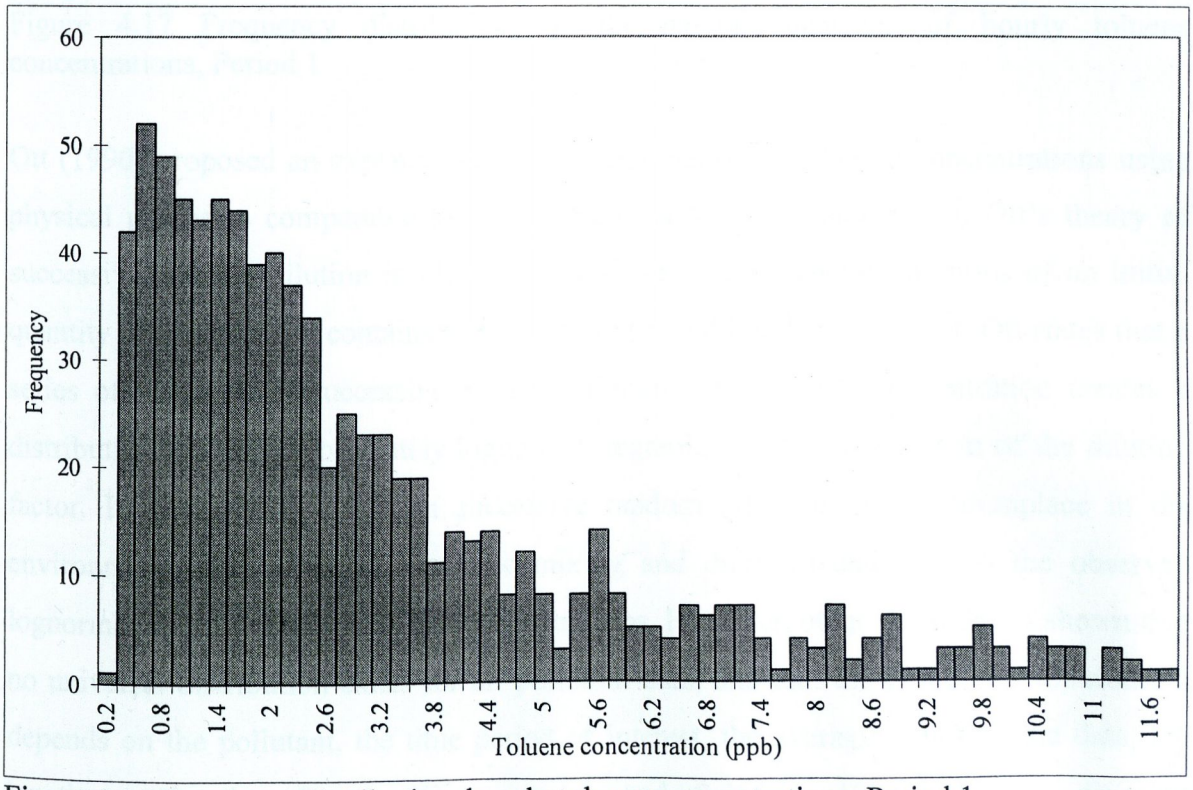


Figure 4.16 Frequency distribution, hourly toluene concentrations, Period 1

The long tail of the frequency distribution in the positive direction in Figure 4.16 is typical of a lognormal distribution. The plot of the logarithmic data is clearly similar to a typical

normal distribution. Another distribution which is often applied to air quality data is the gamma distribution, which is a modification of the standard exponential distribution, and is described in more detail later in this section.

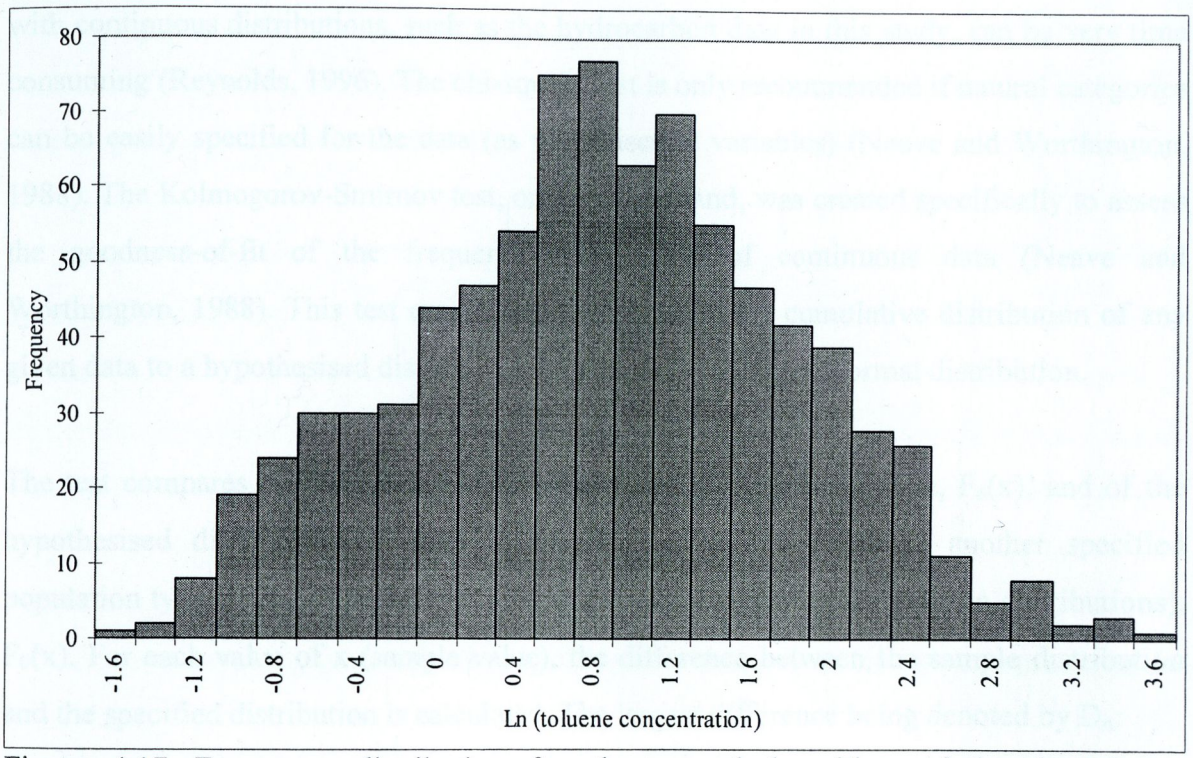


Figure 4.17 Frequency distribution for the natural logarithm of hourly toluene concentrations, Period 1

Ott (1990) proposed an explanation of the lognormality of pollutant concentrations using physical processes comparable to those which occur in the atmosphere. Ott's theory of successive random dilution is illustrated using successive random dilutions of an initial quantity of water which contains a small amount of a diluted contaminant. Ott states that a series of independent successive random dilutions of an initial concentration creates a distribution that is approximately lognormal, regardless of the distribution of the dilution factor. It is proposed that such successive random dilutions are commonplace in the environment (such as in atmospheric mixing and dilution) and lead to the observed lognormal distribution of pollutant concentrations. However, other research has shown that no universal distribution exists for air pollution data, and that the best fitting distribution depends on the pollutant, the time period of interest, the averaging time of the data, the location and other factors (Georgopoulos and Seinfeld, 1982). Because different distributions may be more applicable in certain situations, the most appropriate distribution is best identified by employing standard statistical methods such as the Kolmogorov-Smirnov or chi-square test.

Both the chi-square test and the Kolmogorov-Smirnov test can be used to test if the distribution of a data-set is similar to a specified distribution such as a normal or lognormal distribution (this is known as a goodness-of-fit test) (Haynes, 1996). However, the chi-square test can be awkward to use as categories must be specified for the data, and dealing with continuous distributions, such as the hydrocarbon data in this study, can be very time consuming (Reynolds, 1996). The chi-square test is only recommended if natural categories can be easily specified for the data (as with discrete variables) (Neave and Worthington, 1988). The Kolmogorov-Smirnov test, on the other hand, was created specifically to assess the goodness-of-fit of the frequency distribution of continuous data (Neave and Worthington, 1988). This test can be used to compare the cumulative distribution of any given data to a hypothesised distribution such as a normal or lognormal distribution.

The test compares the cumulative distribution functions of the sample, $F_n(x)$, and of the hypothesised distribution function if the sample were taken from another specified population type (such as normal, lognormal, exponential, gamma or poisson distributions), $F_0(x)$. For each value of x (sample value), the difference between the sample distribution and the specified distribution is calculated, The largest difference being denoted by D_n:

$$D_n = \max [F_n(x) - F_0(x)] \qquad 4.3$$

n = sample size

$F_n(x)$ = cumulative distribution function of the sample

$F_0(x)$ = hypothesised population cumulative distribution function

The value of D_n is compared to available tables of critical values for different confidence intervals, such as those provided in Neave and Worthington (1988). If D_n is greater than the critical value, the goodness-of-fit is poor and the sample data are unlikely to be from the hypothesised population.

The Kolmogorov-Smirnov test was applied to the hourly hydrocarbon concentrations for each of the first two monitoring periods. A significance level of 95 percent was used. The data were analysed in groups, the weekday and weekend hourly data for each week of each monitoring period being analysed separately. The sample cumulative distribution function was compared to hypothesised normal and lognormal functions. Results of the weekday

analysis are presented in Table 4.11. The evidence from the analyses suggests that the hourly hydrocarbon data tend towards lognormal behaviour on the majority of occasions. Several occasions were observed where the hourly hydrocarbon data were not statistically different (at the 95 percent confidence level) from either the normal or lognormal behaviour. Similar results have been observed with other measurements of traffic-related pollutants (Reynolds, 1996). For Period 1, 73 percent (114 of 156) of analyses indicate a tendency towards lognormal behaviour, with 27 percent suggesting normal behaviour. This compares to 69 percent and 31 percent, respectively for Period 2. However, 21 analyses (13.5 percent) showed that the samples were statistically significantly different to both lognormal and normal behaviour during the first period, increasing to 32 percent for the second period. The increased occurrence of non-conformance with either normal or lognormal behaviour in Period 2 is attributable to the fact that measured concentrations during Period 2 were lower than those in Period 1. This lead to a larger number of zero or very low concentration measurements. Compounds which exhibit this behaviour during Period 2 are mainly the butenes, pentenes, 3-methylpentane and isoprene. The histogram for cis-2-butene in Figure 4.18 illustrates the above point. Without the zero readings, the distribution would be a typical lognormal distribution.

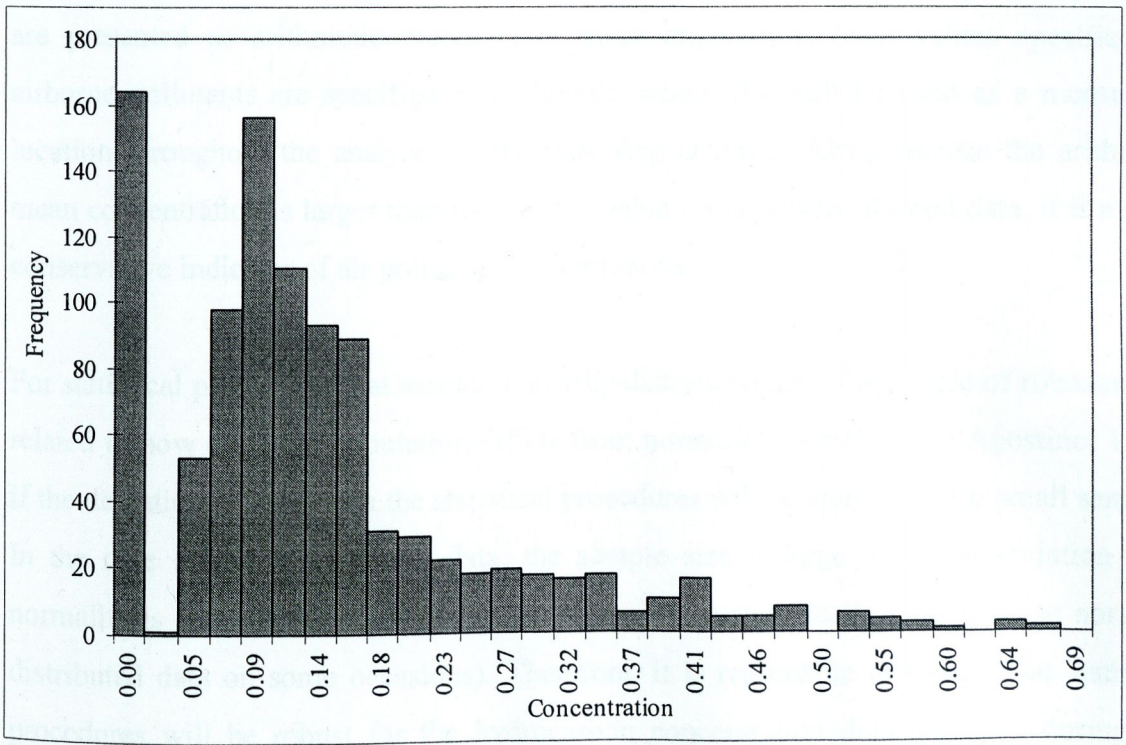


Figure 4.18 Histogram for all cis-2-butene concentrations from Period 2, ppb

Kolmogorov-Smirnov analyses of weekend hydrocarbon data reveals that over 91 percent of weekend data were not statistically different to lognormal behaviour, with only 7 percent

of weekends being statistically different from both normal and lognormal behaviour. This behaviour is different to that observed for the weekday data, where the occurrence of lognormal behaviour is not as frequent. This is likely to be due to a higher frequency of low (but not zero) concentrations at the weekend which promote a 'positively skewed' frequency distribution. Summary data from the weekend Kolmogorov-Smirnov analyses are presented in Table 4.12. Again, the larger number of analyses which conform to neither normal nor lognormal behaviour in Period 2 weekends can be attributed to a greater number of zero readings during the summer months.

From these analyses, it can be concluded that the frequency distributions of the hourly hydrocarbon concentrations measured in Periods 1 and 2 tend towards lognormal behaviour, and the underlying distribution for all compounds is positively skewed. Larger numbers of zero concentrations for certain compounds during the second monitoring period resulted in neither normal nor lognormal behaviour being observed.

These results raise the question of whether the arithmetic mean (average) is the best 'measure of location' for summarising air quality data, or whether the median value should be used in preference. As results from the vast majority of air quality monitoring surveys are presented as arithmetic means, and, more importantly, limit values specified for airborne pollutants are specified as arithmetic means, this will be used as a measure of location throughout the analyses in the following chapters. Also, because the arithmetic mean concentration is larger than the median value for positively skewed data, it is a more conservative indicator of air pollutant concentrations.

For statistical procedures that assume normally distributed data, the degree of robustness is related to how close the population differs from normality (Schiff and D'Agostino, 1996). If the deviation is small then the statistical procedures will be valid even for small samples. In the case of the hydrocarbon data, the sample size is large, and the deviation from normality is not extreme (data have been shown to be statistically equivalent to normally distributed data on some occasions). Therefore, it is reasonable to expect that statistical procedures will be robust for the hydrocarbon concentration data collected during this study.

Table 4.11 Results of Kolmogorov-Smirnov analysis for each week of weekday hourly hydrocarbon concentrations

	Period 1 (six weeks)					Period 2 (9 weeks)					
Hydrocarbon	Lognormal weeks	Normal weeks	Neither	both	More lognormal	Lognormal	Normal	Neither	Both	More lognormal	Remarks
Ethane	4	3	2	3	5	5	3	3	2	8	
Ethylene	5	1	1	1	4	6	3	3	3	7	
Propane	5	1	1	1	6	8	2	1	2	9	
Propylene	5	2	0	1	5	5	3	3	2	5	
Isobutane	4	2	2	2	4	7	2	1	1	7	
n-Butane	4	2	2	2	3	5	2	3	1	6	
Acetylene	6	1	0	1	5	8	2	1	2	7	
Trans-2-butene	4	3	1	2	4	2	2	6	1	5	Period 2, many low and zero concentrations
Cis-2-butene	4	3	1	2	3	1	2	6	0	5	Period 2, many low and zero concentrations
Isopentane	4	2	2	2	4	4	3	2	0	6	
n-Pentane	5	3	0	2	4	8	4	0	3	6	
1,3-butadiene	6	1	0	1	6	7	3	1	2	7	
Trans-2-pentene	4	3	1	2	3	3	2	4	0	3	
Cis-2-pentene	4	1	2	1	5	1	4	4	0	3	
2-methylpentane	4	1	2	1	4	7	2	1	1	7	
3-methylpentane	5	2	1	2	4	2	2	5	0	7	Period 2, many low and zero concentrations
Isoprene	5	2	1	2	5	3	2	5	1	7	Period 2, many low and zero concentrations
n-Hexane	4	4	1	3	3						
Benzene	5	2	0	1	4						
n-Heptane	6	3	0	3	5						
Toluene	6	2	0	2	5						
Ethylbenzene	5	3	0	2	3						
m+p-Xylene	6	1	0	1	6						
o-Xylene	6	2	0	2	5						
1,3,5-trimethylbenzene	4	3	1	2	4						
1,2,4-trimethylbenzene	6	1	0	1	5						
Total	126	54	21	45	114 (of 156)	82	43	49	21	105 (of 153)	

Table 4.12 Summary for all measured compounds of Kolmogorov-Smirnov analyses for hourly weekend hydrocarbon data

	Lognormal weekends	Normal weekends	Both	Neither	More lognormal
Period 1	51	14	14	1	52 (of 52)
Period 2	43	4	2	6	46 (of 51)
Total	94	18	16	7	98 (of 103)

Although the lognormal distribution is most often applied to air quality monitoring data, it has been proposed that the gamma distribution is also representative of such data (Jakeman *et al.*, 1991). The gamma distribution is a modification of the standard exponential distribution and has been used successfully to represent the frequency distribution of hydrocarbon concentrations measured at a roadside location in the US (Zhang *et al.*, 1994). For the gamma distribution :

$$f(x) = \left[\frac{1}{\beta^{\alpha}\,\Gamma(\alpha)}\right] x^{\alpha-1} \exp\left(\frac{-x}{\beta}\right) \qquad 4.4$$

where α and β are the shape parameters of the gamma distribution

To assess the representativity of the gamma distribution, the Kolmogorov-Smirnov test was carried out on the Period 1 weekday data, and compared to the representativity of the lognormal data. Of the 156 tests carried out, 126 were not statistically different from lognormal behaviour, while 120 were not statistically different from the gamma distribution, indicating that both distributions are representative of the hydrocarbon population. Summary results from these analyses are presented in Table 4.13. Ninety-seven of the tests were not statistically different from either the lognormal or gamma distributions. This is not surprising, as Benoit *et al.* (1999) point out that there are situations where several distributions may fit a given set of data equally well. Comparison of the maximum difference between the observed distribution, and the lognormal and gamma distributions, shows that 76 of the tests indicate data tending more towards lognormality, while 80 tend more towards the gamma distribution, again indicating similar representativity of these two distributions.

Only four of the 156 samples tested are statistically different (at the 95 percent confidence interval) to both the gamma and lognormal distributions, indicating that between the two

distributions, the frequency distribution of the data is almost completely represented. Three of these four non-compliances relate to ethane and propane, which are more likely to be normally distributed due to the constant emissions of these compounds from natural gas leakage. The other non-compliance is for cis-2-pentene, and in this case, the observed distribution is very close to lognormal behaviour (it is statistically similar to lognormal behaviour at the 90 percent confidence interval). Twenty-three of the 30 tests which are statistically different to the lognormal distribution, are gamma distributed, while 32 of the 36 tests which are statistically different to the gamma distribution are statistically similar to lognormal behaviour.

Table 4.13 Comparative results from Kolmogorov-Smirnov analysis of Period 1 hydrocarbon data for gamma and lognormal distribution

	Log-normal	Gamma	Not lognormal but gamma	Not gamma but lognormal	Both lognormal and gamma	More lognormal
n-Pentane	5	5	1	1	4	2
Ethane	4	4	0	0	4	5
Ethylene	5	5	1	1	4	2
Propane	5	2	0	3	2	6
Propylene	5	5	1	1	4	2
Isobutane	4	5	2	1	3	2
n-Butane	4	5	2	1	3	2
Acetylene	6	5	0	1	5	4
Trans-2-butene	4	5	2	1	3	2
Cis-2-butene	4	5	2	1	3	2
Isopentane	4	5	2	1	3	2
1,3-butadiene	6	5	0	1	5	4
Trans-2-pentene	4	5	2	1	3	4
Cis-2-pentene	4	4	1	1	3	3
2-methylpentane	4	4	2	2	2	3
3-methylpentane	5	5	1	1	4	1
Isoprene	5	4	0	2	4	3
n-Hexane	4	5	1	1	4	3
Benzene	5	5	1	1	4	2
n-Heptane	6	3	0	3	3	4
Toluene	6	4	0	2	4	4
Ethylbenzene	5	5	1	1	4	2
m+p-Xylene	6	5	0	1	5	2
o-Xylene	6	5	0	1	5	3
1,3,5-trimethylb.	4	5	1	1	4	3
1,2,4-trimethylb.	6	5	0	1	5	4
Total (of 156 tests)	126	120	23	32	97	76

This analysis indicates that both of these distributions can equally well represent the frequency distribution of urban hydrocarbon measurements. Although previous analysis has

suggested that the gamma distribution is the most representative distribution for air pollution data (Jakeman *et al.,* 1991), this analysis suggests that both distributions are representative, and indeed, complement each other by describing the distribution of data which may not conform with the other distribution.

4.4 METEOROLOGICAL DATA

Meteorological data were collected at the monitoring site using the equipment described in Section 3.2.2. Meteorological data from the synoptic monitoring station at Dublin Airport (collected by Met Eireann, the national meteorological service) were also obtained for the monitoring periods at Pearse Street. The results from both sites were expected to be different due to the differing site conditions. For example, the city centre measurements were taken relatively close to buildings, at a junction of streets and near to passing cars, buses and goods vehicles, all of which may have some impact on the wind direction and speed measurements (Croxford and Penn, 1996). Wind direction, windspeed and temperature measured at both stations are briefly presented and compared in the following sections.

Summary results for the meteorological data collected in Dublin over each of the monitoring periods are presented in Table 4.14. The most significant difference between Periods 1 and 2, is for temperature data, where higher average temperatures are measured during the warmer summer months.

Very little confidence can be placed in the meteorological data collected during the third monitoring period. The meteorological monitoring equipment was situated at the roof level of the monitoring unit, thus measurements are likely to be affected by the sheltering effects of the side of the monitoring unit, and the turbulence caused by eddy currents generated by the monitoring unit itself.

Table 4.14 Summary statistics for meteorological data collected at Pearse Street

Period 1				
	Airport temperature	Local temperature	Airport windspeed	Local windspeed
Average	7.93	9.5	2.6	2.0
Minimum	-1.1	1.6	0.0	0.2
Maximum	14.6	16.8	7.2	5.7
Standard deviation	2.63	2.4	1.4	1.0
Period 2				
	Airport temperature	Local temperature	Airport windspeed	Local windspeed
Average	13.3	14.8	2.4	1.8
Minimum	3.7	7.1	0.3	0.1
Maximum	22.0	22.3	6.4	4.6
Standard deviation	2.9	2.6	1.1	0.8
Period 3				
	Airport temperature	Local temperature	Airport windspeed	Local windspeed
Average	11.9	13.6	5.2	1.8
Minimum	-0.7	1.4	0.5	0.3
Maximum	23.5	25.3	16.5	5.2
Standard deviation	4.3	4.3	2.7	0.7

4.4.1 Wind Direction Data

Wind direction data measured at the airport and at the city centre monitoring site differ due to the reasons outlined above. Also, the airport directional data are given in ten degree bands while the data measured at the monitoring site are given to the nearest degree. The meteorological data are presented separately for each of the three monitoring periods in Figure 4.19, Figure 4.20 and Figure 4.21, respectively. The data are presented as the number of hourly frequencies of each ten degree wind sector. Figure 4.19 and Figure 4.20 show similar differences between the airport and local wind direction data in each period. However, Figure 4.21, for the third monitoring period, displays a very different relationship, even though the airport wind direction rose is largely the same as in the first and second monitoring periods. This suggests that the low height of the meteorological monitoring equipment during the third monitoring period has had an effect on the measured wind directions. The wind direction results from the third monitoring period are, therefore,

assumed to be inaccurate, as the wind direction measurements from the first two periods were known to be well calibrated.

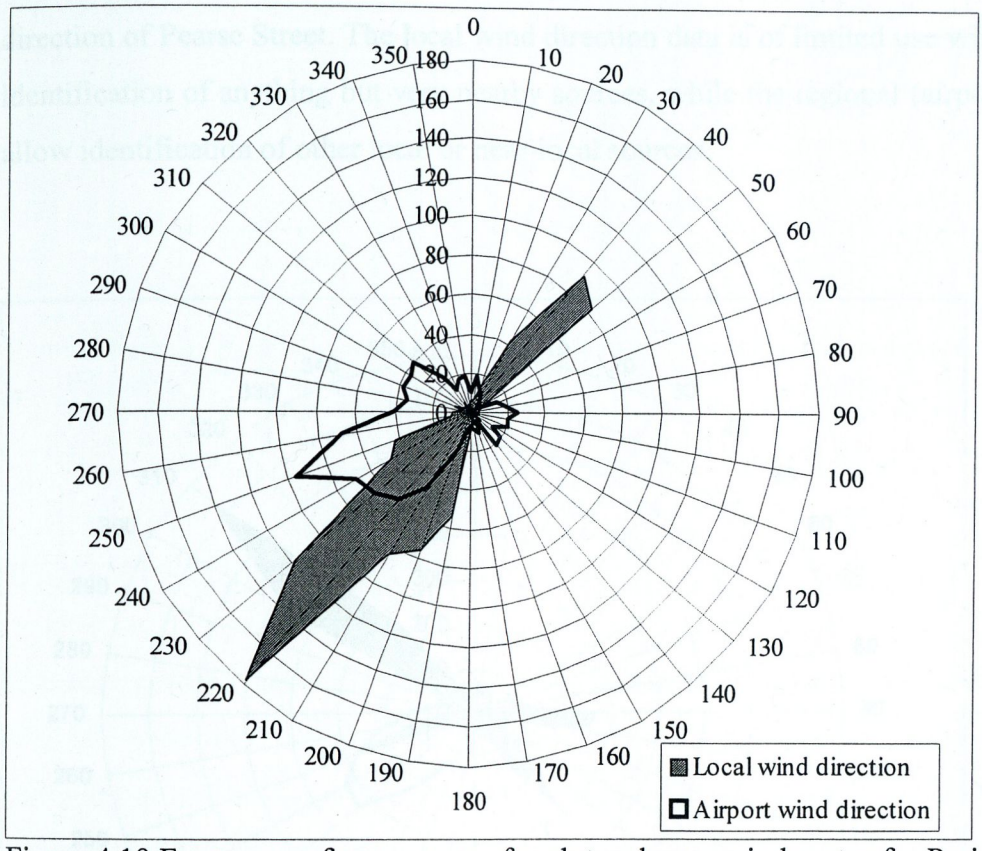


Figure 4.19 Frequency of occurrence of each ten degree wind sector for Period 1

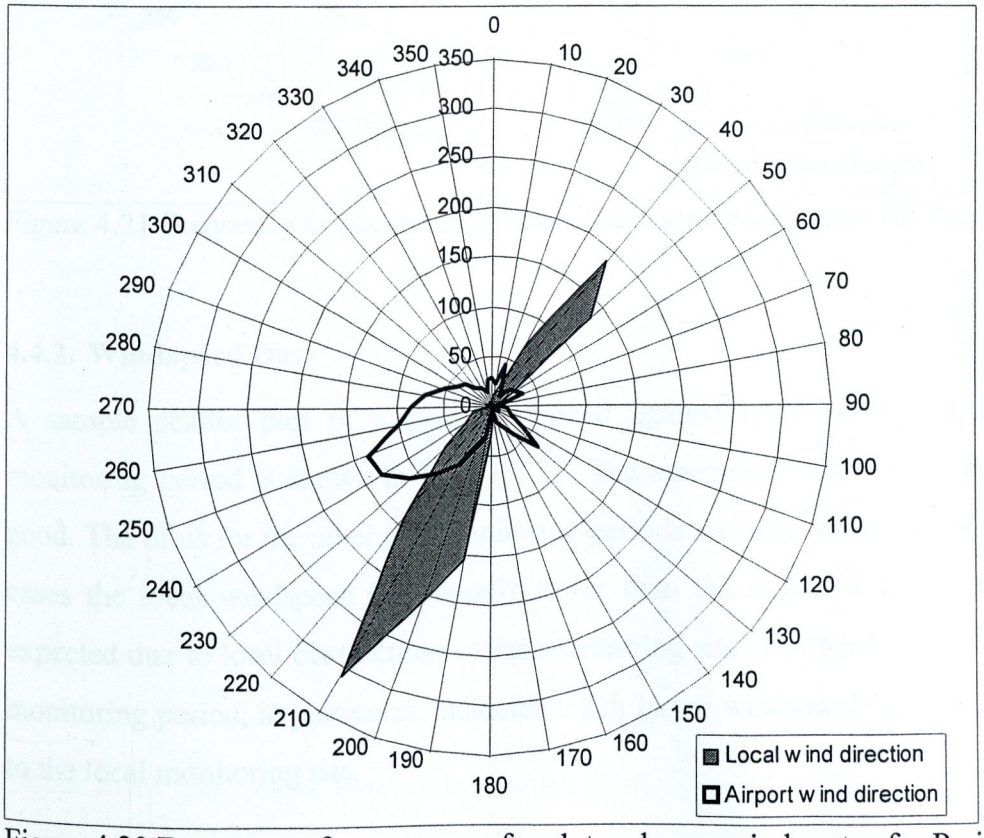


Figure 4.20 Frequency of occurrence of each ten degree wind sector for Period 2

The results from the first two monitoring periods points to the possibility of the prevailing wind being tunnelled along the Lombard Street / Westland Row direction. The orientation of each of these streets is illustrated in Figure 4.3. The local wind flow rarely follows the direction of Pearse Street. The local wind direction data is of limited use with regard to the identification of anything but very nearby sources, while the regional (airport) data should allow identification of other local or near-local sources.

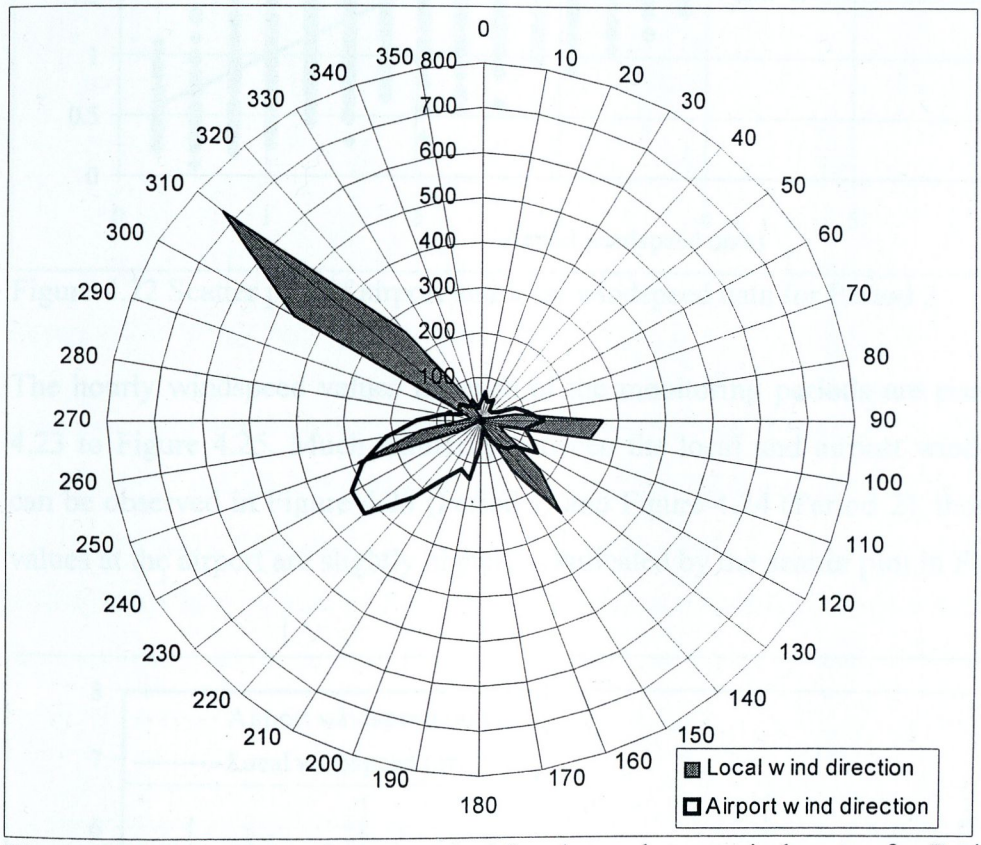


Figure 4.21 Frequency of occurrence of each ten degree wind sector for Period 3

4.4.2 Windspeed Data

A sample scatter plot of airport windspeed against local windspeed for the second monitoring period is shown in Figure 4.22. The agreement between the data is generally good. The plots for the other two monitoring periods are very similar. However, in all three cases the local windspeed is generally lower than the airport windspeed. This is to be expected due to local obstructions at the monitoring site. The windspeed data for the third monitoring period, in particular, indicates much larger windspeeds at the airport compared to the local monitoring site.

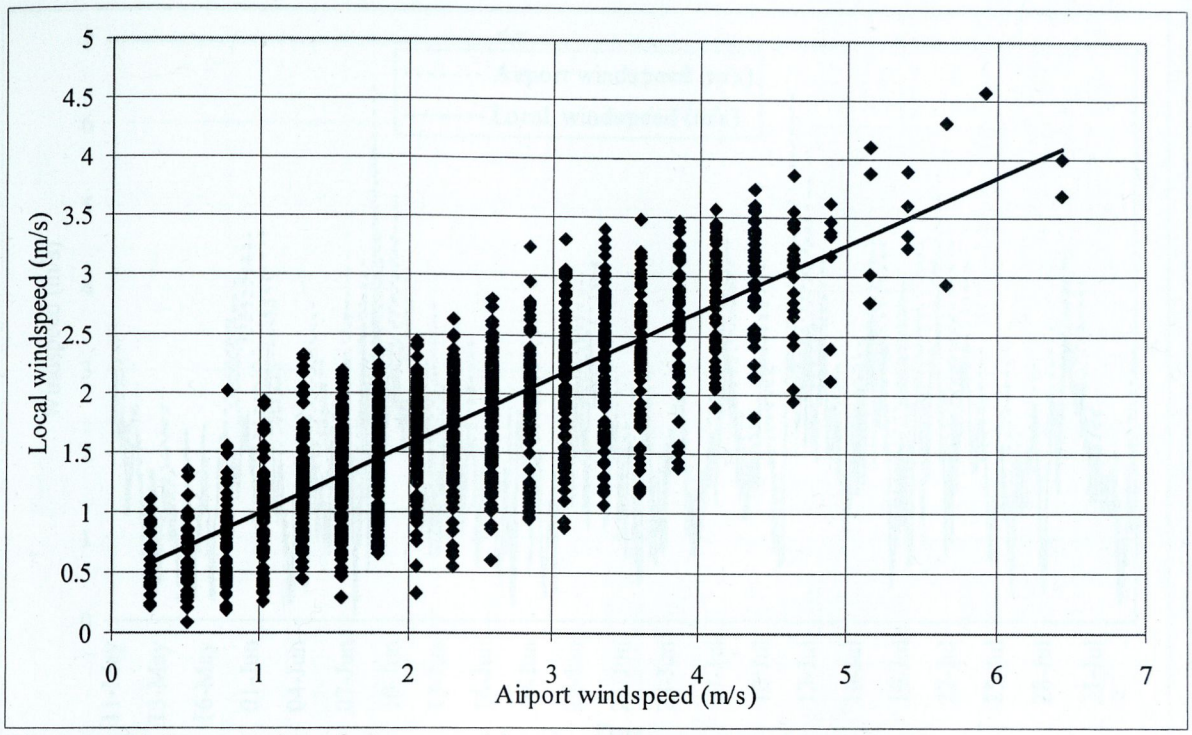


Figure 4.22 Scatter plot of airport and local windspeed data for Period 2

The hourly windspeed values for each of the monitoring periods are presented in Figure 4.23 to Figure 4.25. Much similarity between the local and airport windspeed variations can be observed in Figure 4.23 (Period 1) and Figure 4.24 (Period 2), though the absolute values at the airport are slightly higher, as indicated by the scatter plot in Figure 4.22.

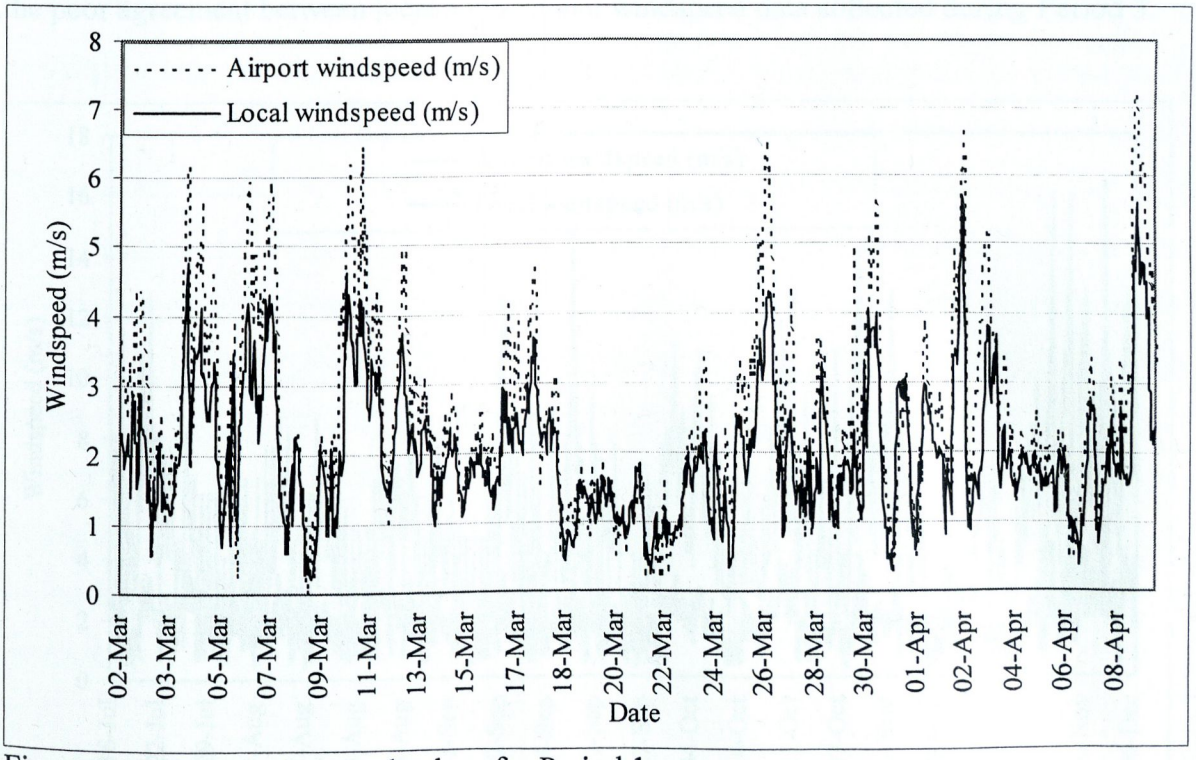


Figure 4.23 Hourly windspeed values for Period 1

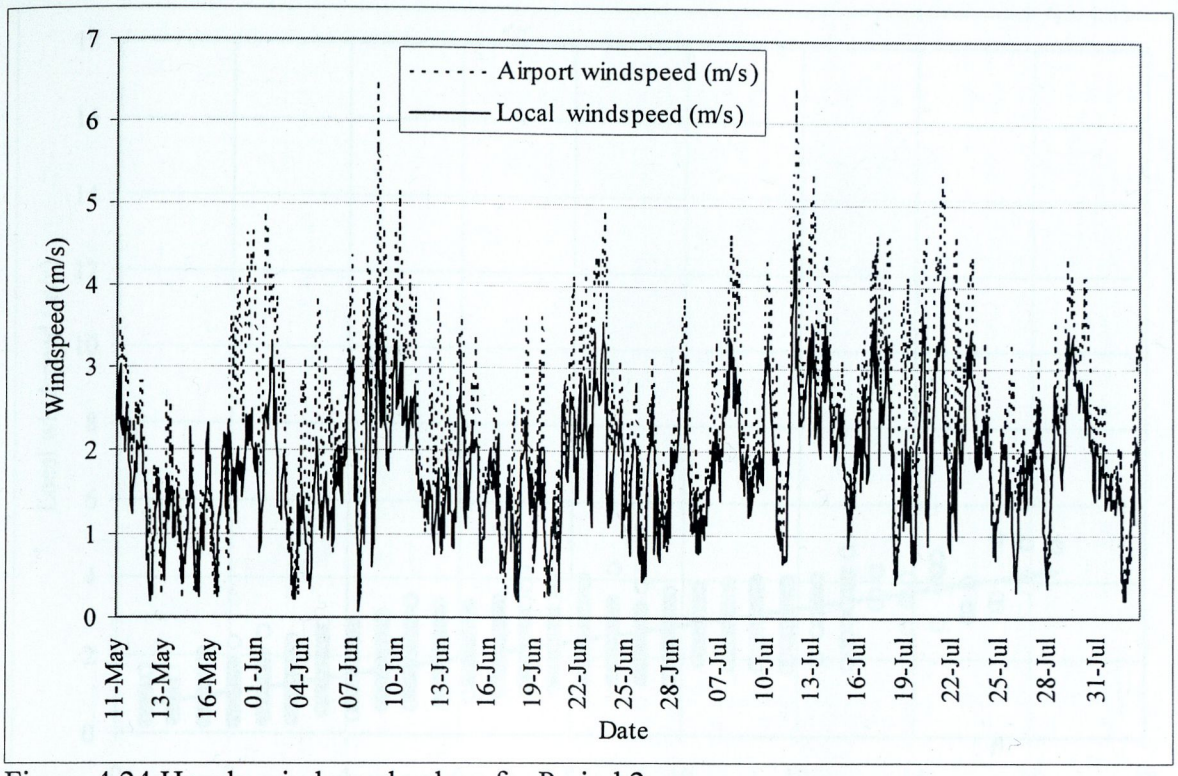


Figure 4.24 Hourly windspeed values for Period 2

However, any such similarity is harder to identify in Figure 4.25 (Period 3), as the magnitude of the airport data is much greater than the local windspeed data. The airport windspeed data presented in Figure 4.25 are much greater than the typical airport windspeeds observed during Periods 1 and 2. The scatter plot in Figure 4.26 also illustrates the poor agreement between local and regional windspeed data collected during Period 3.

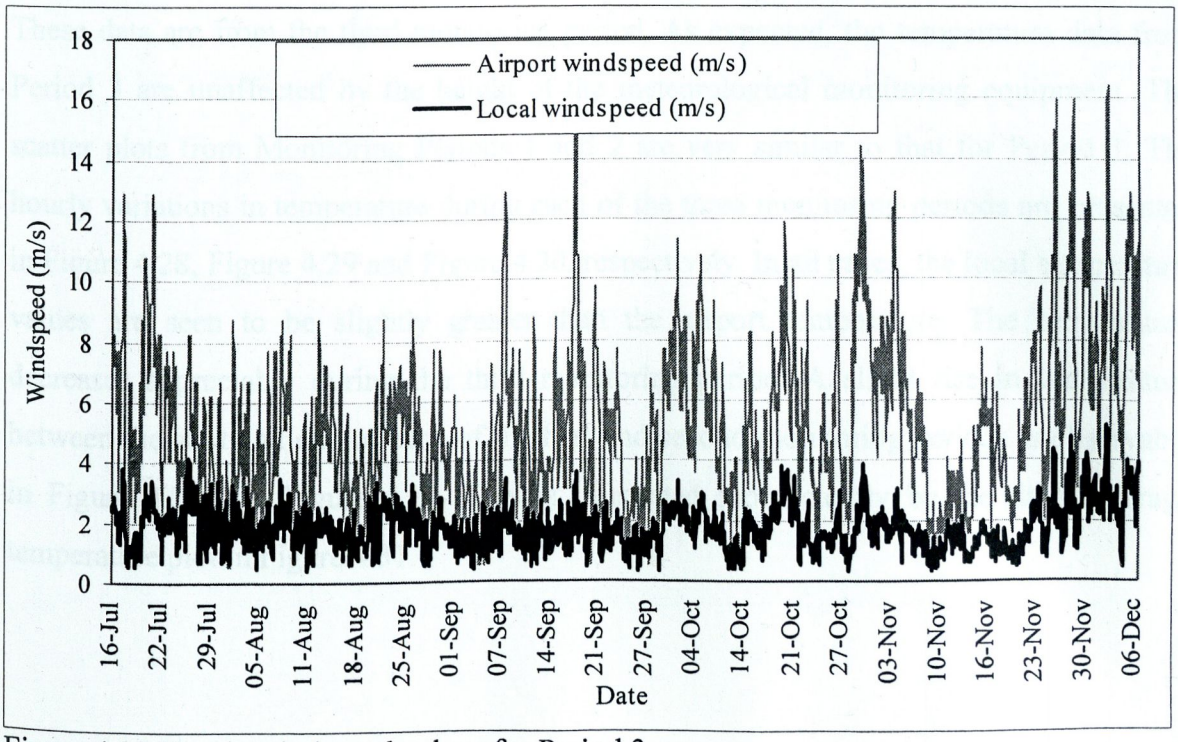


Figure 4.25 Hourly windspeed values for Period 3

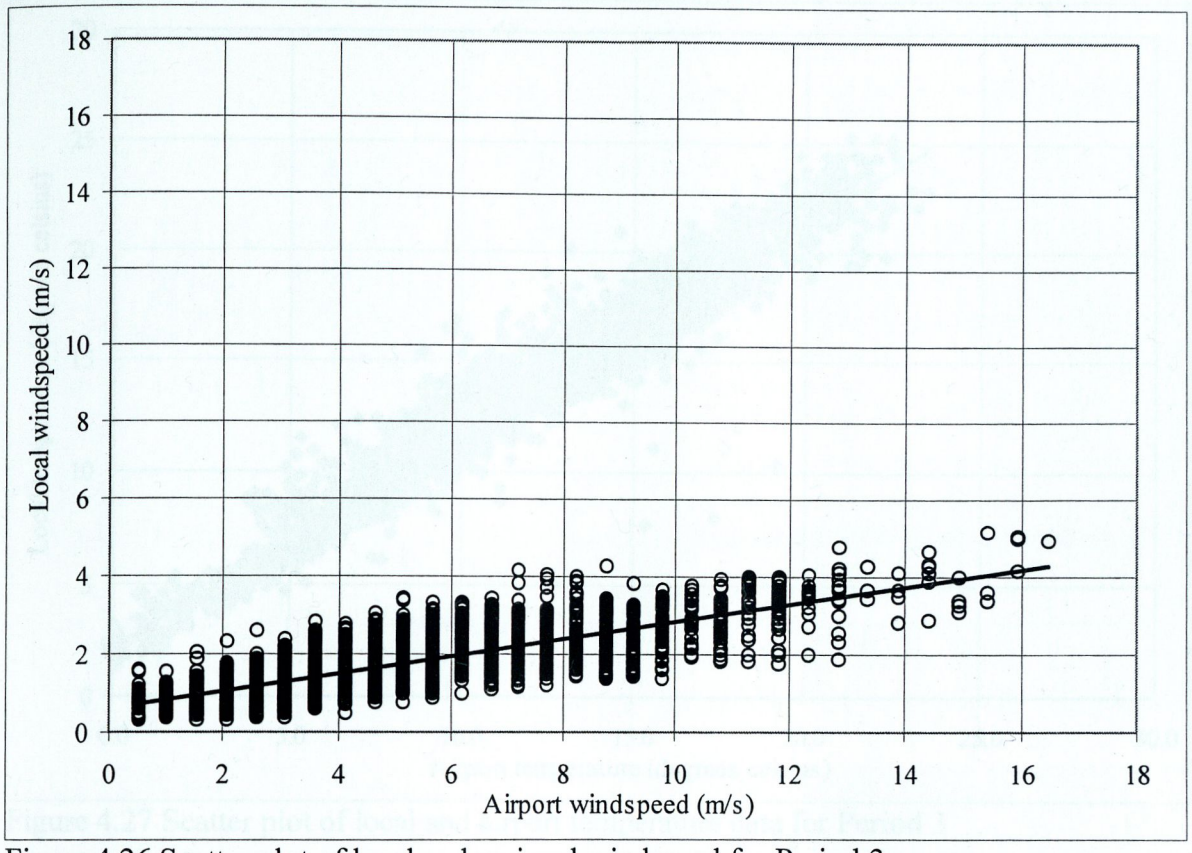


Figure 4.26 Scatter plot of local and regional windspeed for Period 3

4.4.3 Temperature Data

The agreement between the airport and local temperature data is generally very good, with the local data tending to be slightly higher than the airport data. An example of the correlation between the airport and local temperature data is presented in Figure 4.27. These data are from the third monitoring period. As expected, the temperature data from Period 3 are unaffected by the height of the meteorological monitoring equipment. The scatter plots from Monitoring Periods 1 and 2 are very similar to that for Period 3. The hourly variations in temperature during each of the three monitoring periods are presented in Figure 4.28, Figure 4.29 and Figure 4.30, respectively. In all cases, the local temperature values are seen to be slightly greater than the airport temperature. The temperature decreases appreciably during the third monitoring period. A slight rise in temperature between the start and end of each of the first and second monitoring periods is observable in Figure 4.28 and Figure 4.29. This is illustrated more clearly by the daily average temperature plot in Figure 4.31.

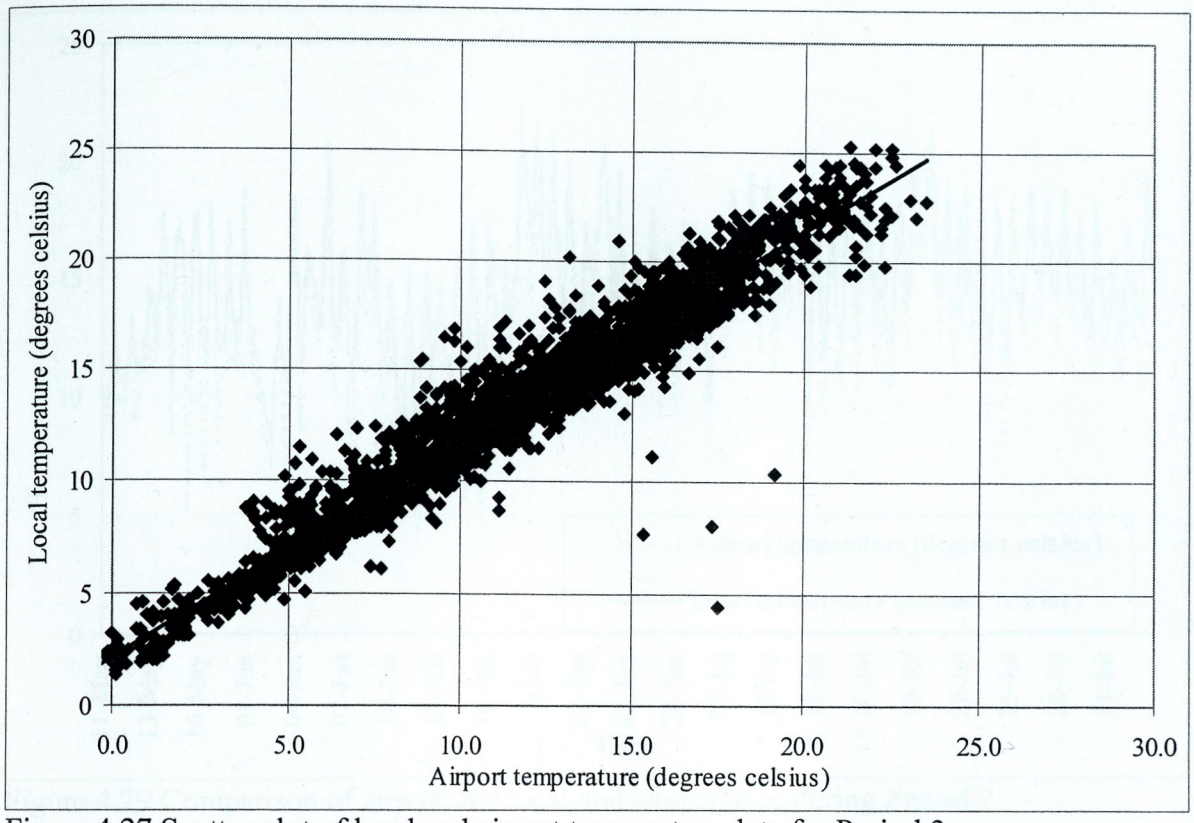


Figure 4.27 Scatter plot of local and airport temperature data for Period 3

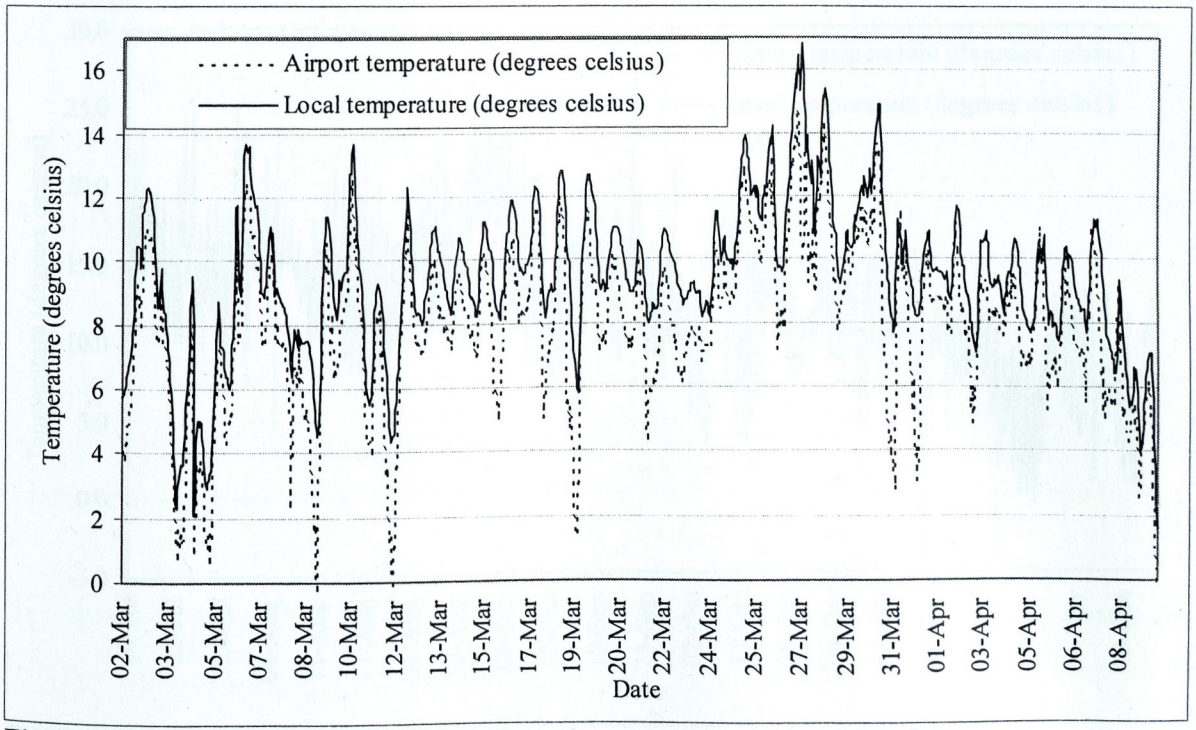


Figure 4.28 Comparison of local and airport temperature during Period 1

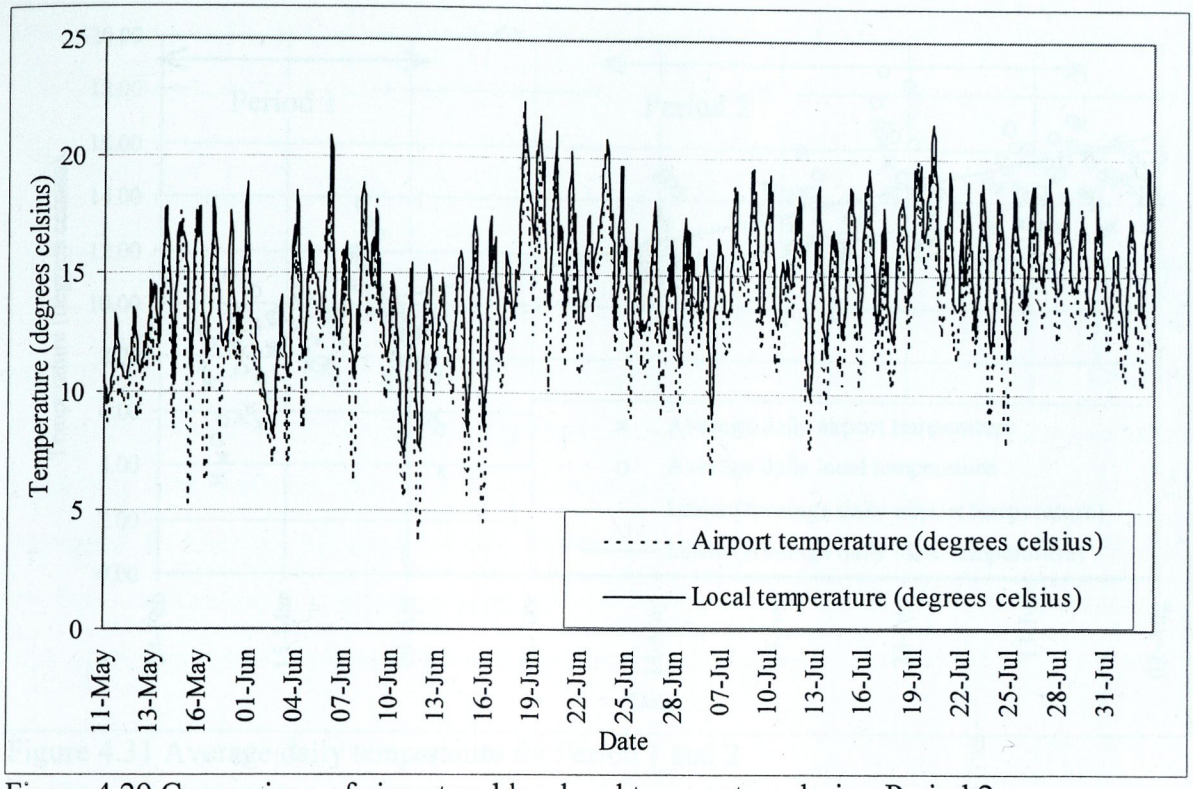


Figure 4.29 Comparison of airport and local and temperature during Period 2

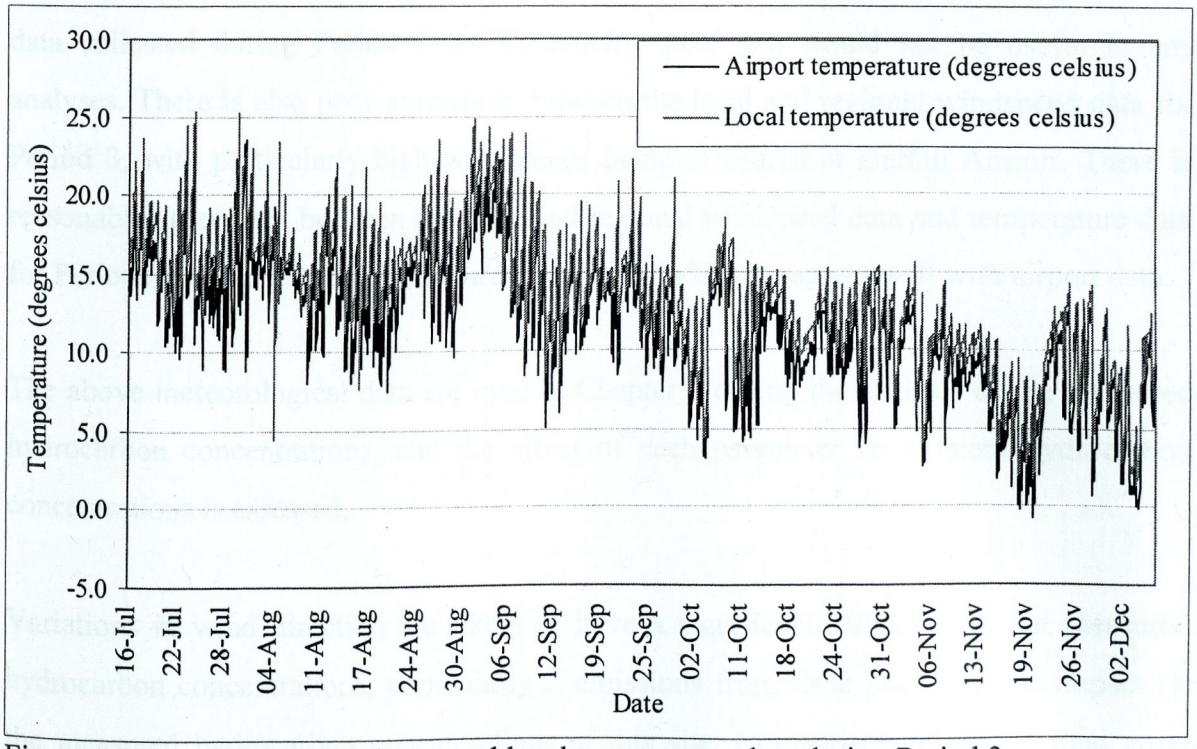


Figure 4.30 Comparison of airport and local temperature data during Period 3

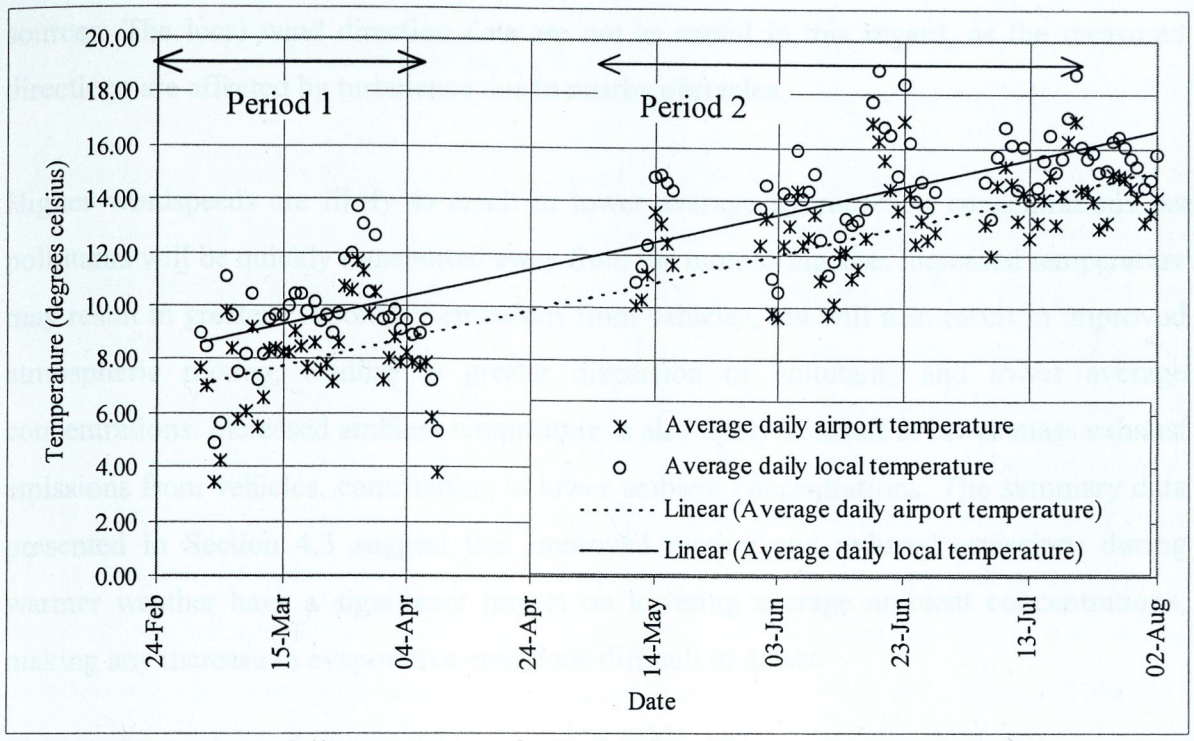


Figure 4.31 Average daily temperature for Period 1 and 2

4.4.4 Implications

As would be expected, poor agreement is seen between the local and regional wind direction data, due to local measurements being taken in a built-up area. The wind direction data collected during Period 3 are particularly poor and would not be useful in any analyses. There is also poor agreement between the local and regional windspeed data for Period 3, with particularly high windspeeds being measured at Dublin Airport. There is reasonable agreement between the local and regional windspeed data and temperature data for Periods 1 and 2. Local temperature data for Period 3 also agrees well with airport data.

The above meteorological data are used in Chapter 5 during the analysis of the measured hydrocarbon concentrations, and the effect of each parameter on ambient hydrocarbon concentrations is assessed.

Variations in wind direction are likely to have a significant influence on the measured hydrocarbon concentrations, particularly if emissions from local point sources impact on the measured hydrocarbon concentrations at this site. Comparison of the regional wind direction and hydrocarbon concentration data should allow identification of any such

sources. The local wind direction data are not as useful in this regard, as the measured directions are affected by turbulence due to nearby obstacles.

Higher windspeeds are likely to result in lower average hydrocarbon concentrations, as pollutants will be quickly transported away from the monitoring site. Increased temperature may result in greater evaporative emissions from vehicles, but will also result in improved atmospheric mixing, leading to greater dispersion of pollutants and lower average concentrations. Increased ambient temperature is also likely to result in lower mass exhaust emissions from vehicles, contributing to lower ambient concentrations. The summary data presented in Section 4.3 suggest that improved mixing and reduced emissions during warmer weather have a significant impact on lowering average ambient concentrations, making any increase in evaporative emissions difficult to detect.

5. ANALYSIS OF PHASE 1 RESULTS

An analysis of results collected at the Dublin urban roadside monitoring site is presented in this chapter. In Section 5.1, short-term variations in hydrocarbon concentrations are presented for Monitoring Periods 1 and 2, including a comparison of the average day and the so called 'typical' or most representative day. Short-term variations in hydrocarbon concentrations are compared to those in London and Belfast. The correlations between the hourly concentrations of individual hydrocarbons are also examined. Section 5.2 assesses the impact of meteorological conditions (using both local and regional meteorological data) on hydrocarbon concentrations. Hourly wind directions are compared to contemporary hydrocarbon concentrations to identify any possible alternate sources in the area of the monitoring site. The impact of windspeed is investigated, and the effect of seasonal temperature variations on evaporative emissions from vehicles is also considered. Section 5.3 assesses the contribution of vehicle exhaust to the measured urban hydrocarbon concentrations. Firstly, the method of principal component analysis is employed to identify compounds with similar behavioural patterns, thus aiding the identification of the sources of the measured compounds. Measured hydrocarbon concentrations in Dublin are compared to results from tunnel and dynamometer studies carried out in Europe and elsewhere, to assess the similarity between the hydrocarbon ratios at the Dublin roadside location and concentrations known to be vehicle related. Finally, the relationship between fuel hydrocarbon constituents and ambient hydrocarbon concentrations are estimated by comparing the measured ambient concentrations with the results of hydrocarbon analyses of fuel samples collected at petrol stations in Dublin during Period 1.

5.1 ANALYSIS OF SHORT-TERM CONCENTRATION VARIATIONS

The advantage of the automated continuous monitoring system used in this study over traditional sampling methods, such as adsorbent sampling, is its ability to provide hourly concentration values over an extended time period. The concentrations are available in near real-time (approximately 50 minutes after sampling is complete). Such analysis would be both logistically difficult and labour intensive using separate sampling and analysis equipment.

5.1.1 Diurnal Patterns

The diurnal pattern followed by the hourly concentration of a pollutant provides information on the possible sources of a pollutant, its behaviour relative to meteorological conditions (if measurements are available), and the likely short-term peak concentrations.

The diurnal patterns displayed by the hydrocarbons measured during this survey are presented below. Rather than presenting diurnal patterns from individual days, an average day is calculated for each monitoring period using the following equation.

$$\overline{HC}_{d,t} = \frac{\sum_{d=1}^{N_d} HC_{d,t}}{N_d} \qquad 5.1$$

$\overline{HC}_{d,t}$ = the average hydrocarbon (individual hydrocarbon) concentration on day d (where d = Monday, Tuesday, etc.) for the hour ending at time t;

$\Sigma HC_{d,t}$ = sum of all HC concentrations for the hours ending at time t on each day of type d in a given period;

N_d is the number of days, within a given period, of day type d.

Hence, the average concentration on a particular day of the week, at a particular hour, for an individual hydrocarbon is determined. The figures given below present only average weekday and weekend diurnal patterns, as the difference between the diurnal pattern of individual weekdays is small. A number of sample diurnal plots for individual days during Periods 1 and 2 are presented in Appendix A.

Figure 5.1 presents the average measured hydrocarbon concentration (i.e. the sum of all measured hydrocarbon concentrations divided by the number of individual compounds) for each hour of each weekday, for Monitoring Periods 1 and 2. Two distinct peaks are observed on most weekdays (some intermediate peaks can be seen in the data from Period 2); the pattern alters slightly at weekends and tends to exhibit a single significant peak, with much lower concentrations compared to the weekday data. This indicates the significance of vehicle emissions as a source of hydrocarbon emissions at this roadside location.

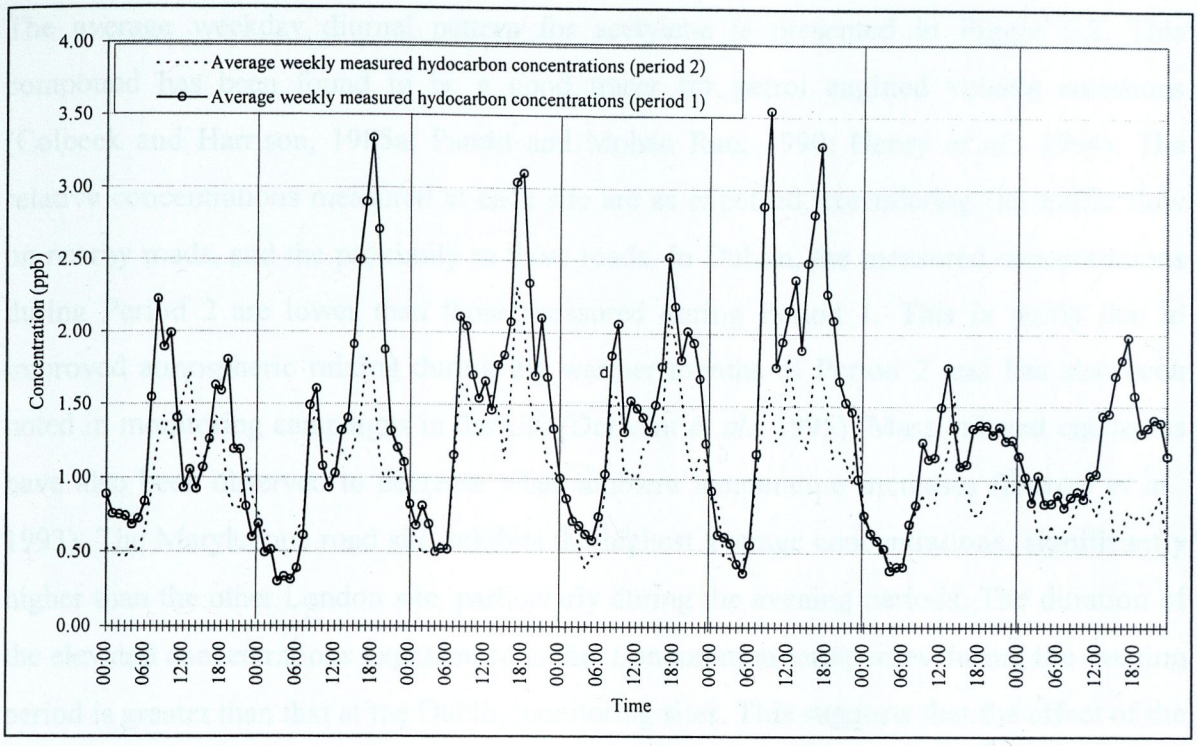


Figure 5.1 Average weekly hydrocarbon concentration for monitoring Periods 1 and 2 (starting with Monday at the left)

The following figures illustrate the average weekday and weekend diurnal patterns of a number of measured hydrocarbons during Period 1 and / or Period 2. For comparison, average weekday and weekend diurnal patterns, for 1998, from a selection of monitoring sites in the UK monitoring network are also presented, namely:

a) Belfast urban background site, which would be expected to exhibit generally lower concentrations due to its location and the fact that Belfast is a smaller city (in terms of population) than Dublin;
b) London UCL, which is a roadside site on a reasonably busy single carriageway road with the monitoring point approximately four metres from the edge of the kerb. The traffic flow is lower than that experienced at the Dublin monitoring site, hence lower concentrations are generally experienced at this site compared to the Dublin site;
c) London Marylebone is defined as a roadside site. However, it is located only one metre from the edge of the kerb of the six lane Marylebone Road, which has a traffic flow of over 80,000 vehicles per day (greater than at the Dublin site). Because of the proximity of the site to the kerbside, and the large traffic flow, very high concentrations are experienced at this site.

The average weekday diurnal pattern for acetylene is presented in Figure 5.2. This compound has been found to be a good tracer for petrol engined vehicle emissions (Colbeck and Harrison, 1985a; Pandit and Mohan Rao, 1990; Henry *et al.,* 1994). The relative concentrations measured at each site are as expected, considering the traffic flow on nearby roads, and the proximity to these roads. In Dublin, the measured concentrations during Period 2 are lower than those measured during Period 1. This is partly due to improved atmospheric mixing during the warmer months of Period 2 and has also been noted in monitoring campaigns in the UK (Derwent *et al.,* 1995). Mass exhaust emissions have also been observed to decrease when ambient temperature increases (Farrow *et al.,* 1993). The Marylebone road site exhibits the highest average concentrations, significantly higher than the other London site, particularly during the evening periods. The duration of the elevated concentrations experienced at the London monitoring sites during the evening period is greater than that at the Dublin monitoring sites. This suggests that the effect of the evening peak travel period persist longer in London than in Dublin.

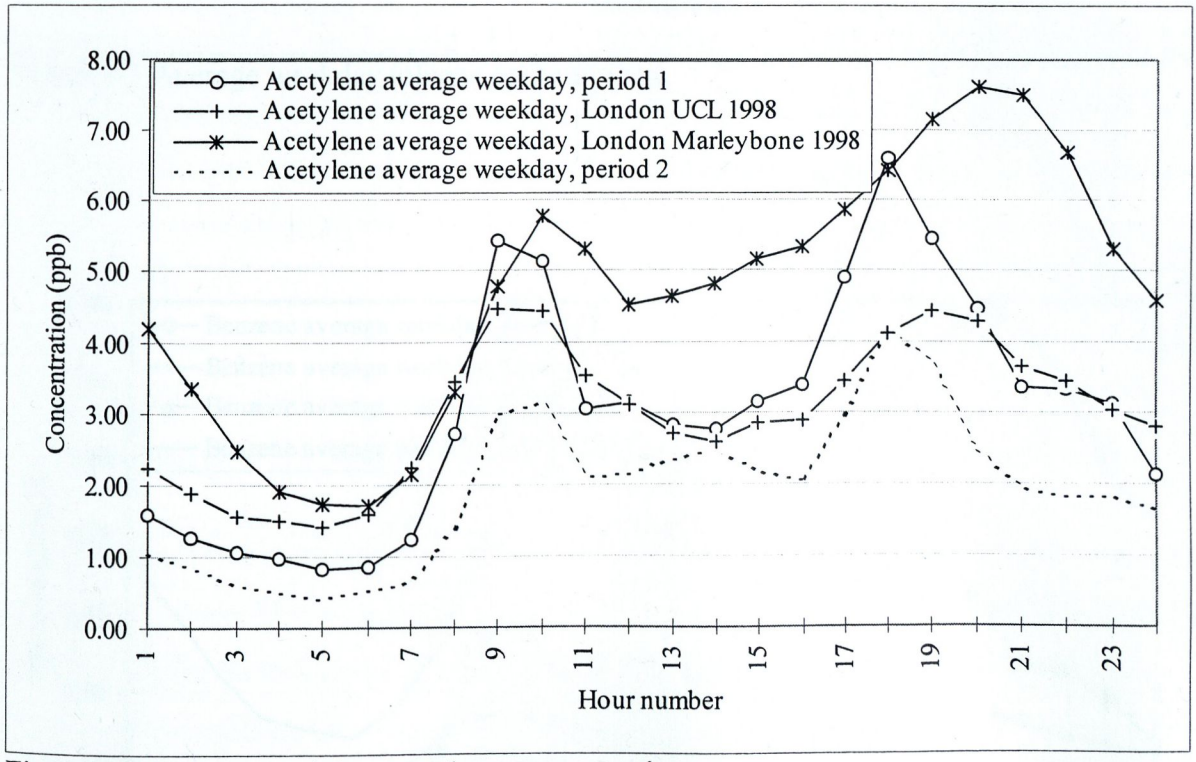


Figure 5.2 Average weekday acetylene concentration

Although acetylene is noted as a vehicle emissions tracer, similar diurnal patterns are observed with toluene, benzene and isopentane (Figure 5.3, Figure 5.4 and Figure 5.5, respectively). The rate of increase in the hydrocarbon concentration at London Marylebone

during the early afternoon is much greater than that exhibited by the Dublin data, which normally remains constant until the onset of the evening rush-hour.

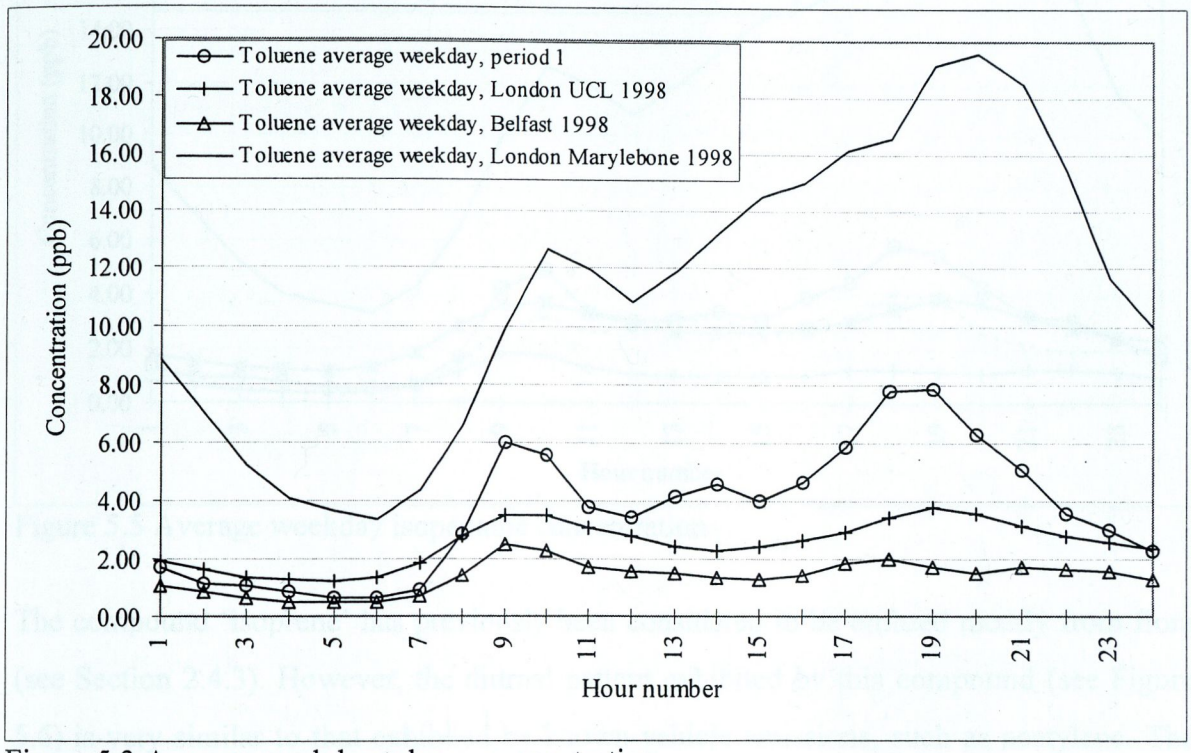


Figure 5.3 Average weekday toluene concentration

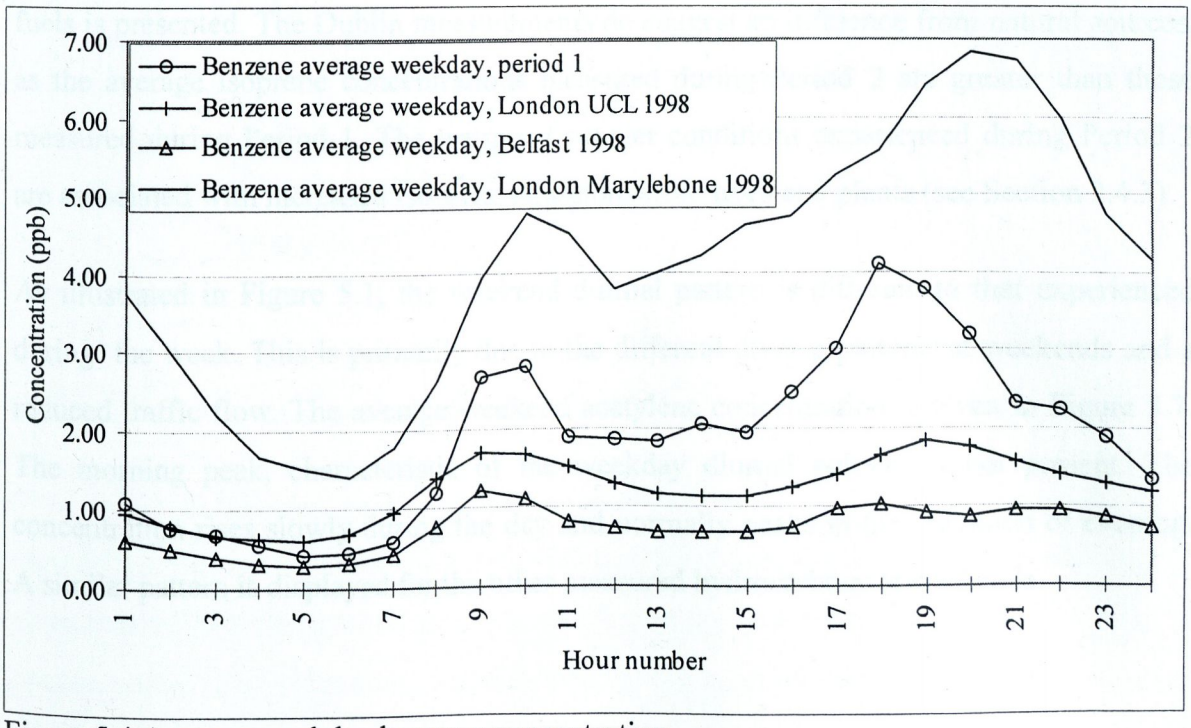


Figure 5.4 Average weekday benzene concentration

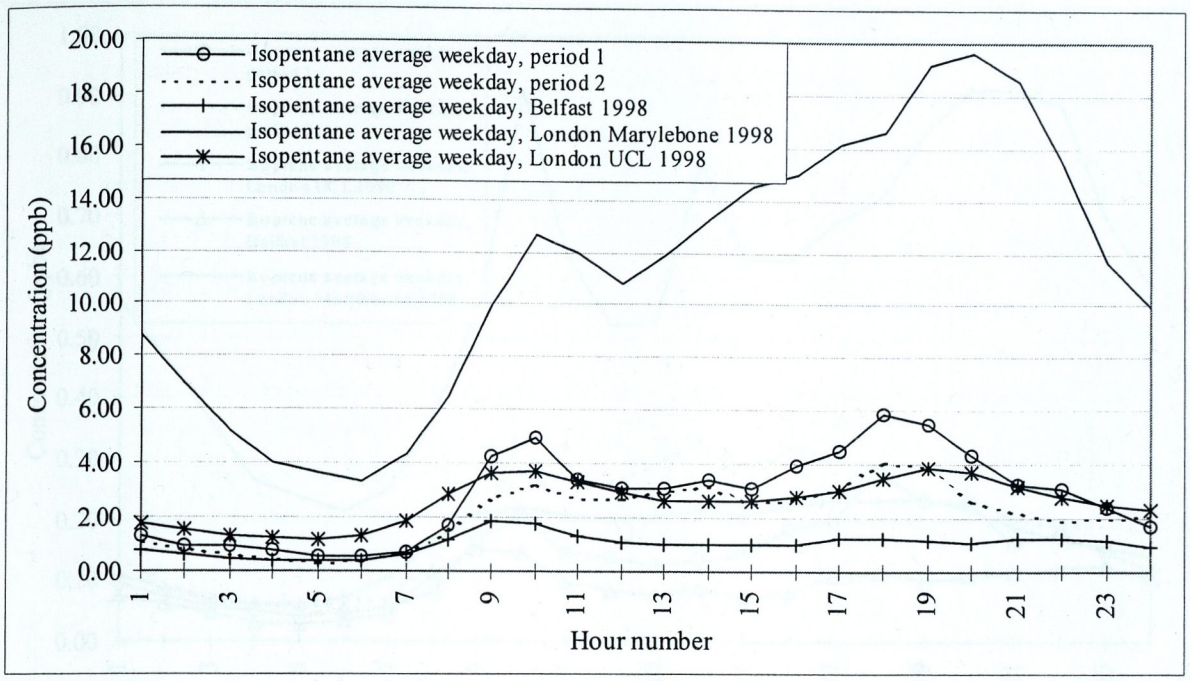


Figure 5.5 Average weekday isopentane concentration

The compound 'isoprene' has previously been considered to be emitted mostly from flora (see Section 2.4.3). However, the diurnal pattern exhibited by this compound (see Figure 5.6) is very similar to that exhibited by known vehicle emissions, such as acetylene. The fact that the busier roadside site at London Marylebone exhibits larger concentrations than London UCL also suggests a contribution from vehicle exhausts. However, isoprene is not found in vehicle fuels; as described in Section 5.3.3, where a typical composition of Irish fuels is presented. The Dublin measurements do suggest an influence from natural sources, as the average isoprene concentrations measured during Period 2 are greater than those measured during Period 1. The warmer / sunnier conditions experienced during Period 2 are associated with increased isoprene emissions from trees and plants (see Section 2.4.3).

As illustrated in Figure 5.1, the weekend diurnal pattern is different to that experienced during the week. This is primarily due to the different driving patterns at weekends and a reduced traffic flow. The average weekend acetylene concentration is given in Figure 5.7. The morning peak, characteristic of the weekday diurnal pattern, is not present. The concentration rises slowly during the day and normally peaks in the afternoon or evening. A similar pattern is displayed for the other measured hydrocarbons at weekends.

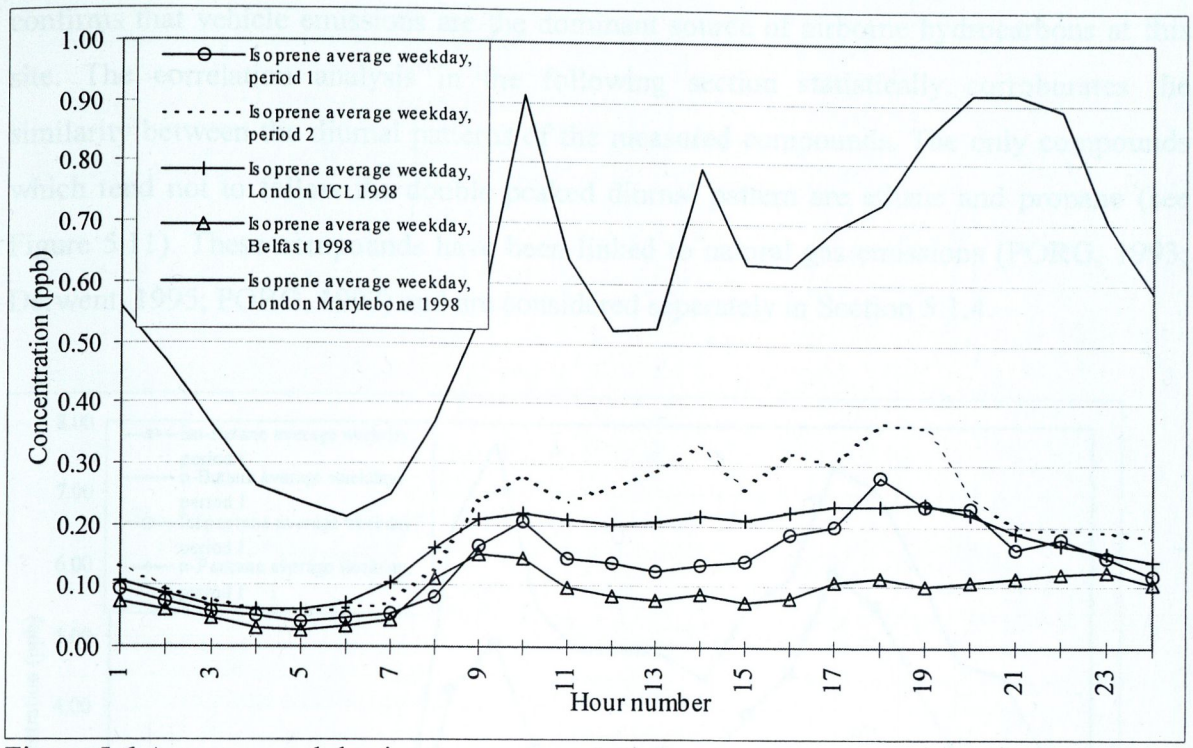


Figure 5.6 Average weekday isoprene concentration

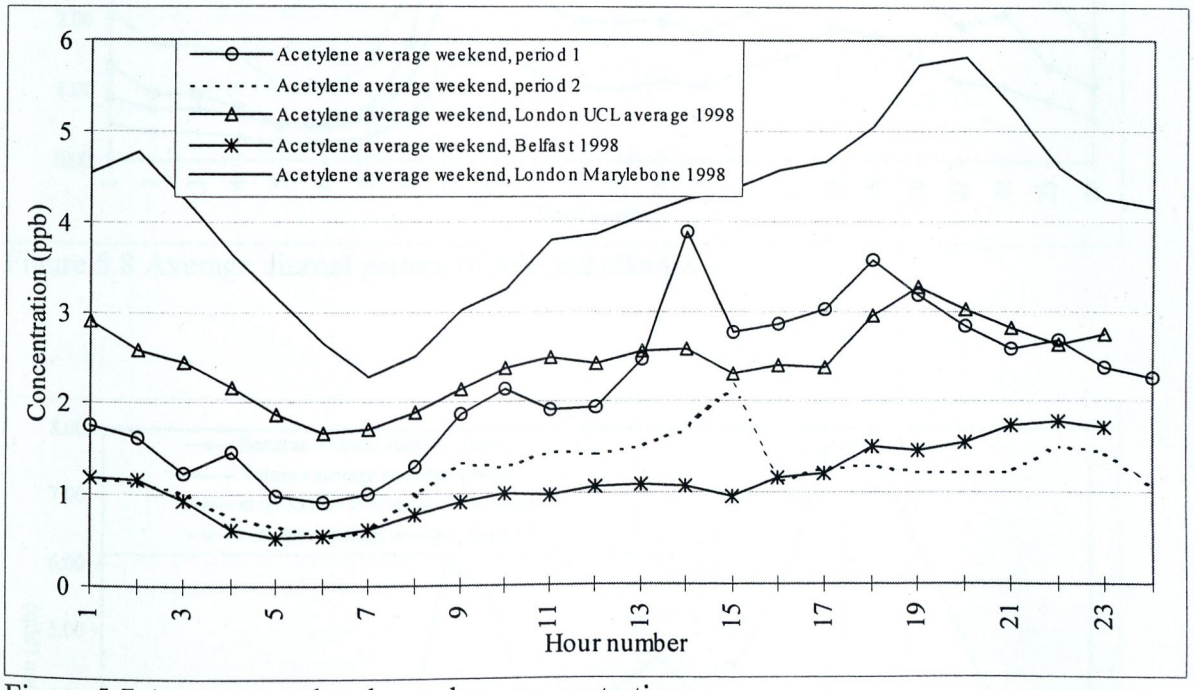


Figure 5.7 Average weekend acetylene concentration

Compounds in the same hydrocarbon groups display very similar diurnal properties. The diurnal concentration pattern of several alkanes are plotted in Figure 5.8. These display almost identical patterns, although the magnitude of the concentrations is different. Similar double peaked diurnal patterns are followed by the aromatics and alkenes, though some characteristics of the diurnal patterns are particular to each group (see Figure 5.9 and Figure 5.10). The double peaked diurnal pattern displayed by nearly all of the compounds

confirms that vehicle emissions are the dominant source of airborne hydrocarbons at this site. The correlation analysis in the following section statistically corroborates the similarity between the diurnal patterns of the measured compounds. The only compounds which tend not to follow the double peaked diurnal pattern are ethane and propane (see Figure 5.11). These compounds have been linked to natural gas emissions (PORG, 1993; Derwent, 1995; PORG, 1997) and are considered separately in Section 5.1.4.

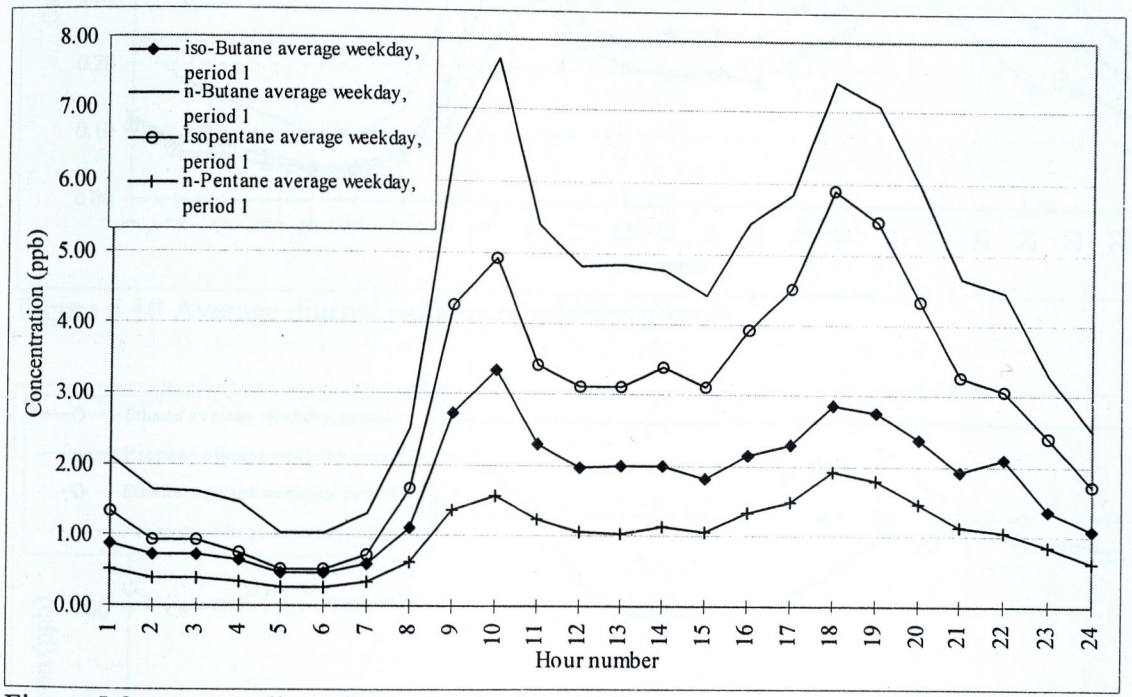


Figure 5.8 Average diurnal pattern of selected alkanes

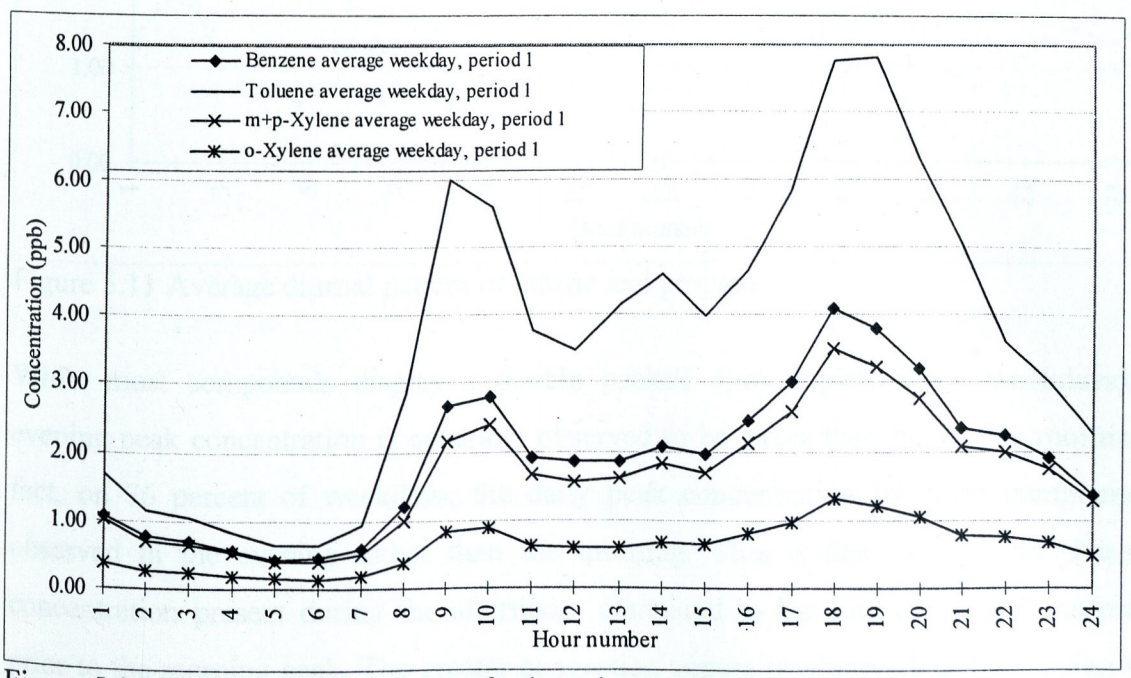


Figure 5.9 Average diurnal patterns of selected aromatics

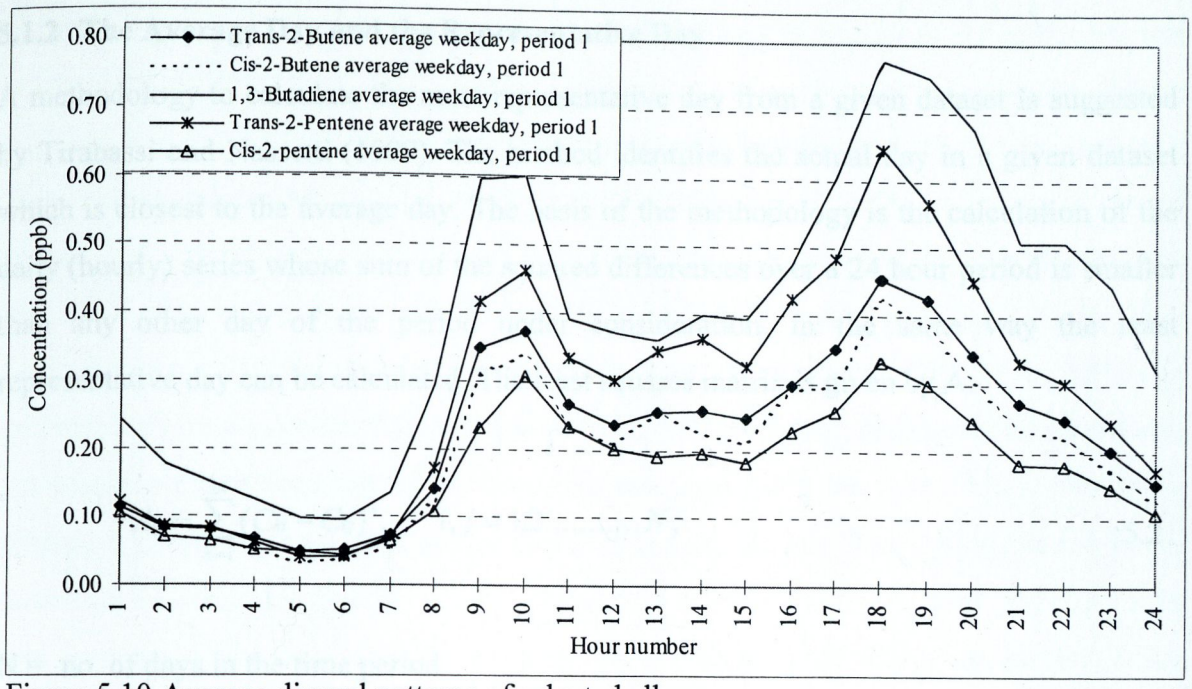


Figure 5.10 Average diurnal patterns of selected alkenes

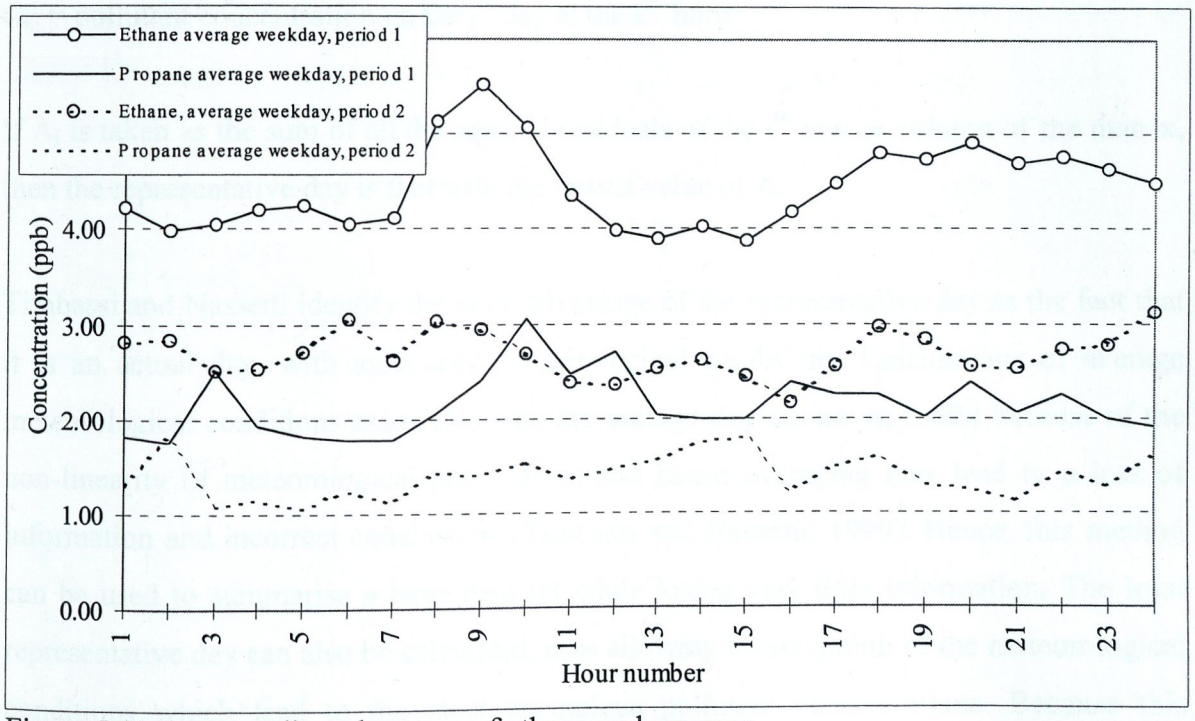


Figure 5.11 Average diurnal pattern of ethane and propane

While most compounds display a double peaked diurnal pattern (on weekdays), the evening peak concentration is generally observed to be larger than that in the morning. In fact, on 76 percent of weekdays, the daily peak concentration for most compounds is observed in the evening rather than the morning. This is due to a higher 'baseline' concentration present during the afternoon, compared to the low concentrations present prior to the morning peak. The greater congestion generally observed at the evening rush-hour may also contribute to elevated evening concentrations.

5.1.2 The Average Day and the Representative Day

A methodology to calculate the most representative day from a given dataset is suggested by Tirabassi and Nassetti (1999). The method identifies the actual day in a given dataset which is closest to the average day. The basis of the methodology is the calculation of the daily (hourly) series whose sum of the squared differences over a 24 hour period is smaller than any other day of the period under consideration. In the same way the least representative day can be calculated. The least squares matrix is given by A:

$$A_{ij} = \sum_{k=1}^{24} (C_{ki} - C_{kj})^2, \qquad i, j = 1,2.....N, \tag{5.2}$$

N = no. of days in the time period

C_{ki} = pollutant concentration on the ith day at the kth hour

C_{kj} = pollutant concentration on the jth day at the kth hour

If A_i is taken as the sum of all the squared residuals of the ith row or column of the matrix, then the representative day is that with the lowest value of A_i.

Tirabassi and Nassetti identify the main advantage of the representative day as the fact that it is an actual day, with associated meteorological conditions. Calculations of average meteorological conditions associated with the average day are not as useful because of the non-linearity of meteorological phenomena, and hence averaging may lead to a loss of information and incorrect conclusions (Tirabassi and Nassetti, 1999). Hence, this method can be used to summarise a large data set while losing very little information. The least representative day can also be calculated, thus allowing investigation of the meteorological conditions which lead to the most anomalous pollutant concentrations. Because this method identifies an actual day, more detailed emission parameters, such as traffic flow data or stack emissions data can be taken into account.

This method was applied to the hydrocarbon data collected in Dublin during Period 1. The method was applied to each hydrocarbon individually, to identify if the same representative day would be calculated for each pollutant. Any differences between individual compounds could indicate the influence of a non-traffic related source. The proximity of the monitoring point to the roadside means that hydrocarbon reaction is unlikely to be an important factor

in determining the pollutant concentration measured, hence if emissions are traffic related, it would be expected that each pollutant would have the same representative day. Figure 5.12 and Figure 5.13 illustrate the representative day for ethylene and toluene, respectively. The least representative day for ethylene and toluene are presented in Figure 5.14 and Figure 5.15, respectively. In the case of ethylene, the representative day and the average day are similar. However, the similarity in the toluene plots is not as strong. This is likely to be due to the fact that toluene concentrations can vary significantly due to the influence of emissions from a non-traffic related source (see Section 5.2.1), while ethylene emissions are wholly traffic related and tend to be similar from one day to the next. The probability of finding a highly representative day is therefore greater for ethylene. As the period under investigation increases in duration, the probability of encountering a more representative day for toluene increases. This implies that the 'representativity' of a given representative day can be dependent on the source of the pollutant, and more importantly, on the characteristics of the source emissions, such as the level of variability associated with the emissions.

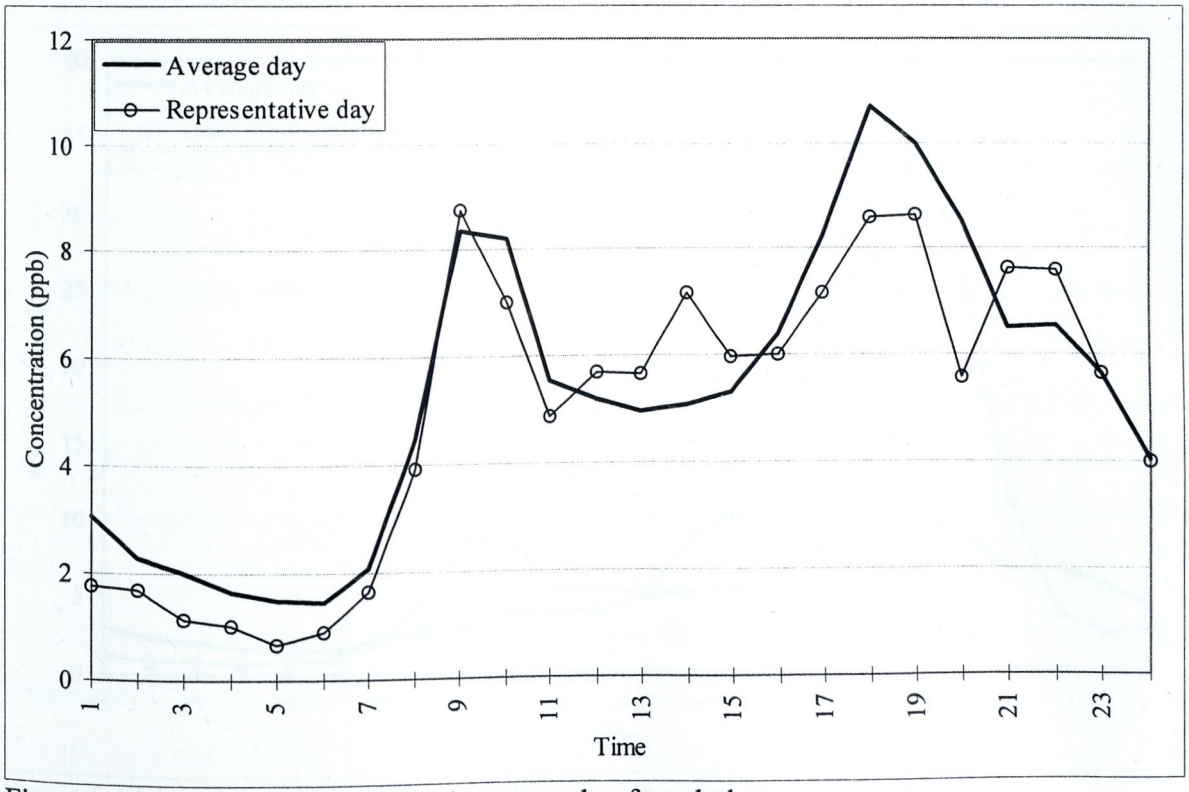


Figure 5.12 Representative day and average day for ethylene

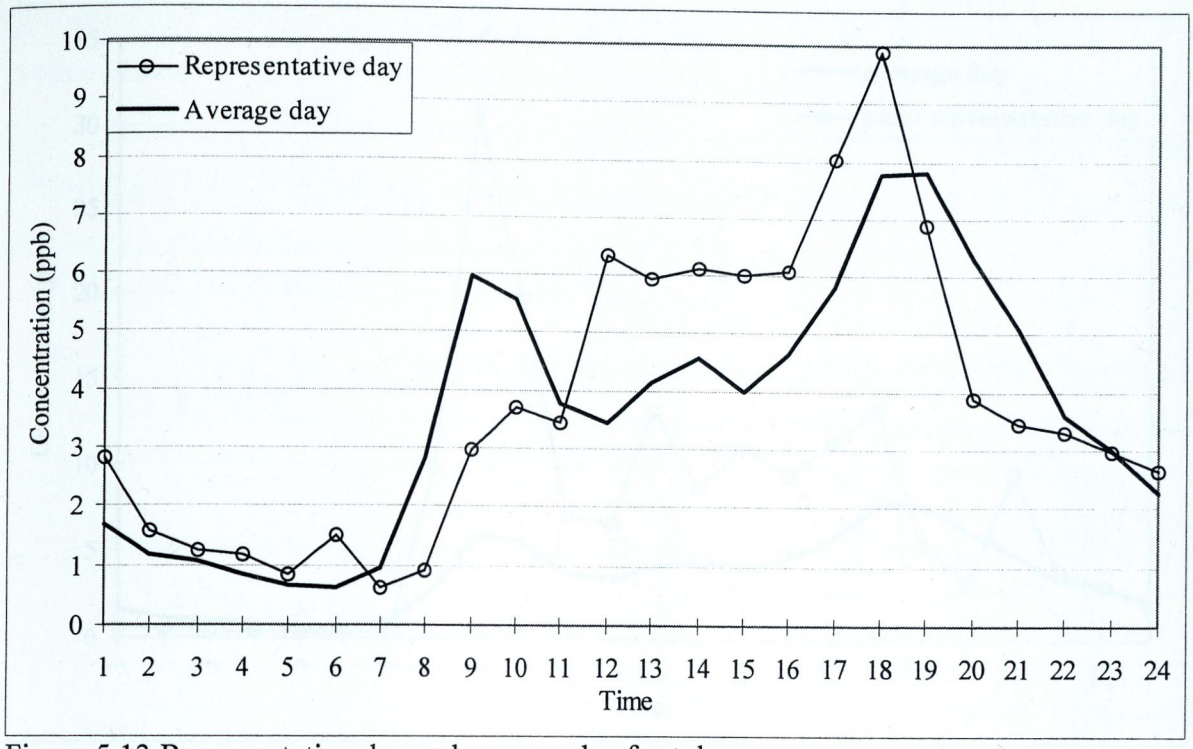


Figure 5.13 Representative day and average day for toluene

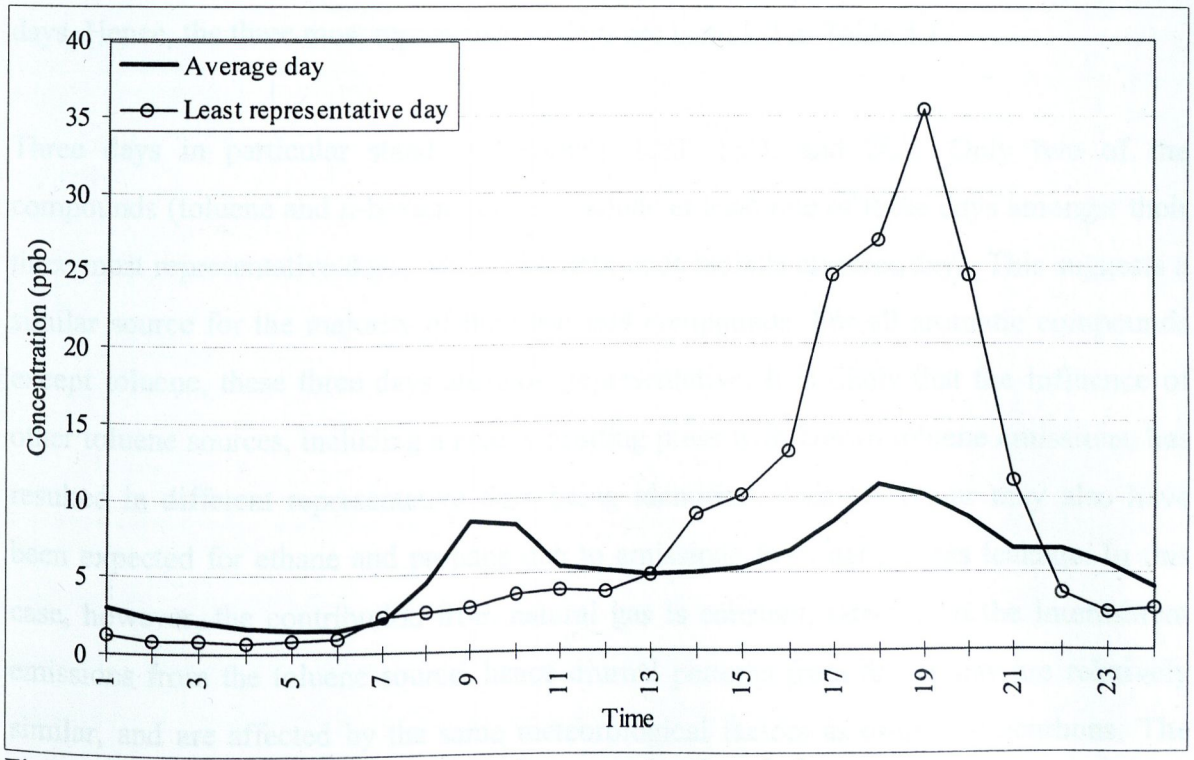


Figure 5.14 Least representative day and average day for ethylene

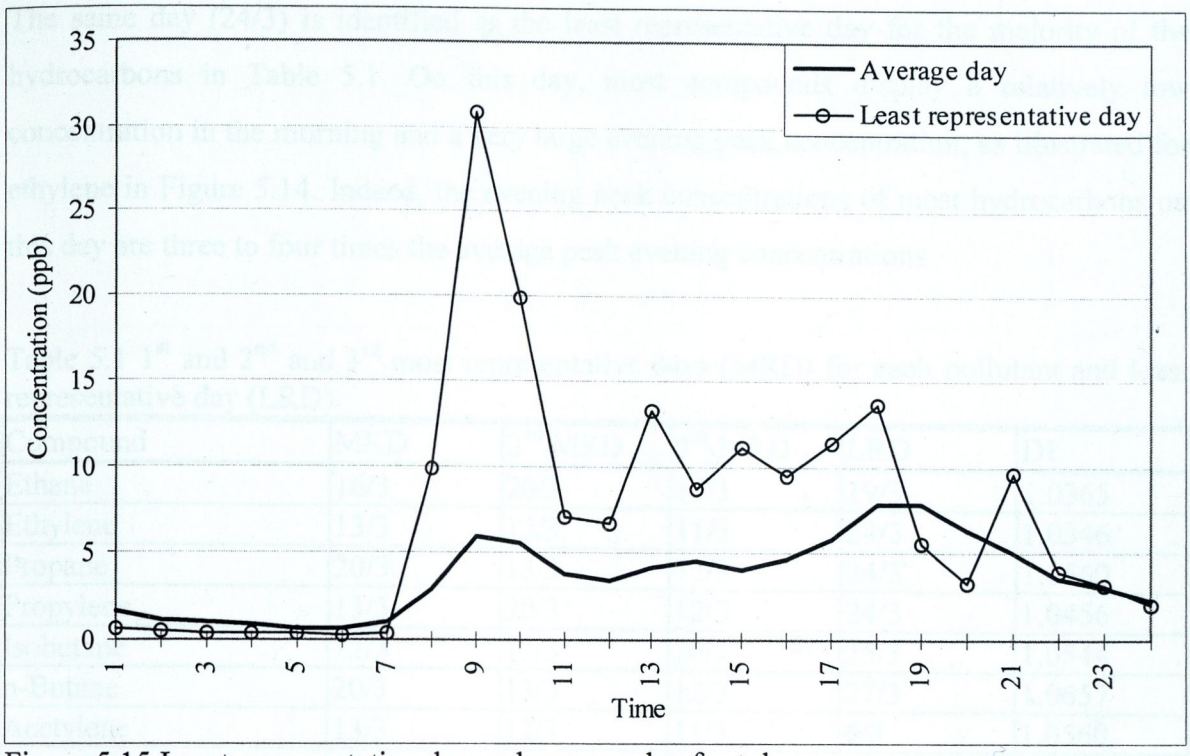


Figure 5.15 Least representative day and average day for toluene

Table 5.1 details the representative day for each compound, indicating that many of the compounds share the same representative day. For many compounds, the value of the sum of the squared residuals is very similar on the first, second and third most representative days. Hence, the three most representative days are included in Table 5.1.

Three days in particular stand out, namely 12/3, 13/3, and 20/3. Only two of the compounds (toluene and n-hexane) do not include at least one of these days amongst their three most representative days, while 14 compounds include all three days. This suggests a similar source for the majority of the measured compounds. For all aromatic compounds except toluene, these three days are most representative. It is likely that the influence of other toluene sources, including a nearby printing press with known toluene emissions, has resulted in different representative days being identified. This behaviour may also have been expected for ethane and propane due to emissions from natural gas leakage. In this case, however, the contribution from natural gas is constant, rather than the intermittent emissions from the toluene source, hence diurnal patterns from day to day are relatively similar, and are affected by the same meteorological factors as other hydrocarbons. The data provided in Table 5.1 also suggest another source of n-hexane in the vicinity of the monitoring location, although no sources were identified.

The same day (24/3) is identified as the least representative day for the majority of the hydrocarbons in Table 5.1. On this day, most compounds display a relatively low concentration in the morning and a very large evening peak concentration, as illustrated for ethylene in Figure 5.14. Indeed, the evening peak concentrations of most hydrocarbons on this day are three to four times the average peak evening concentrations.

Table 5.1 1st and 2nd and 3rd most representative days (MRD) for each pollutant and least representative day (LRD)

Compound	MRD	2nd MRD	3rd MRD	LRD	DI
Ethane	16/3	20/3	13/3	19/3	1.0365
Ethylene	13/3	12/3	11/3	24/3	1.0346
Propane	20/3	13/3	12/3	24/3	1.0560
Propylene	13/3	20/3	12/3	24/3	1.0456
Isobutane	12/3	13/3	20/3	25/3	1.0544
n-Butane	20/3	13/3	12/3	27/3	1.0657
Acetylene	13/3	12/3	11/3	6/3	1.0560
Trans-2-butene	12/3	13/3	20/3	24/3	1.0355
Cis-2-butene	20/3	12/3	13/3	6/3	1.0493
Isopentane	20/3	13/3	25/3	24/3	1.0543
n-Pentane	20/3	13/3	25/3	24/3	1.0506
1,3-butadiene	11/3	13/3	12/3	24/3	1.0360
Trans-2-pentene	20/3	25/3	23/3	24/3	1.0357
Cis-2-pentene	20/3	19/3	2/4	9/3	1.0487
2-methylpentane	12/3	11/3	13/3	6/3	1.0325
3-methylpentane	13/3	12/3	20/3	24/3	1.0466
Isoprene	23/3	20/3	13/3	24/3	1.0686
n-Hexane	2/4	30/3	23/3	24/3	1.0763
Benzene	13/3	20/3	12/3	24/3	1.0524
n-Heptane	12/3	11/3	13/3	24/3	1.0838
Toluene	2/4	4/3	10/3	11/3	1.0861
Ethylbenzene	20/3	13/3	12/3	24/3	1.0485
m+p-Xylene	13/3	12/3	20/3	24/3	1.0439
o-Xylene	13/3	12/3	20/3	24/3	1.0404
1,3,5-trimethylbenzene	13/3	20/3	12/3	24/3	1.0440
1,2,4-trimethylbenzene	20/3	13/3	12/3	24/3	1.0426

Analysis of meteorological conditions on this day reveals a possible explanation for this behaviour, namely a sudden change in wind direction during the afternoon. A plot of the benzene concentration for this day, and the corresponding hourly wind directions, is given in Figure 5.16. The change in wind direction between the morning and afternoon is approximately 180 degrees. The wind direction during the evening period (50 degrees) is directly from the junction, resulting in the transportation of vehicle emissions from evening

peak traffic directly towards the monitoring location, while the morning wind direction (230 degrees) would tend to transport vehicle emissions in the opposite direction. The wind direction then reverts back to the prevailing south westerly direction in the late evening, which results in slightly elevated concentration during the early morning of March 25th.

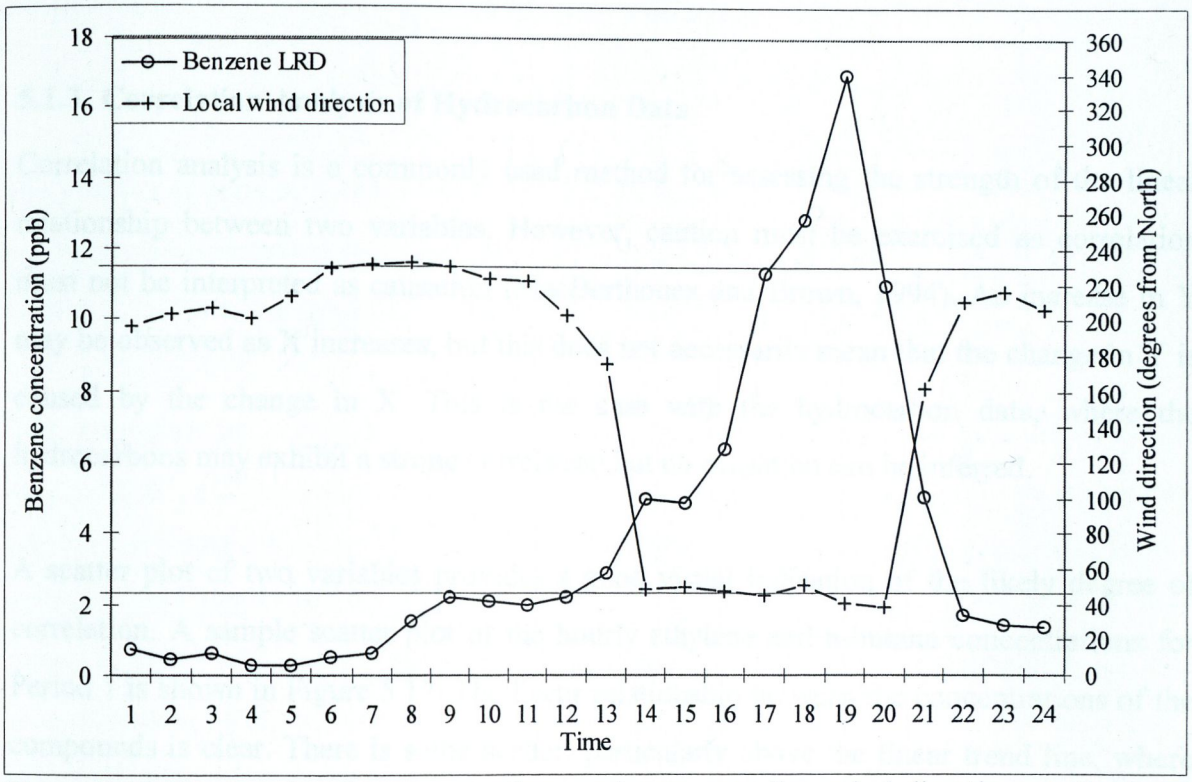


Figure 5.16 Benzene hourly concentrations and corresponding wind direction on the least representative day

Tirabassi and Nassetti (1999) also suggest a measure of the "representativity" of the representative day given by Equation 5.3.

$$DI = \frac{\sqrt{\sum_{i=1}^{N}\sum_{k=1}^{24}(\Gamma_k - c_{ik})^2}}{\sqrt{\sum_{i=1}^{N}\sum_{k=1}^{24}(\overline{C} - c_{ik})^2}} \qquad 5.3$$

$\overline{C}_k$, Γ_k = mean hourly concentrations at the kth hour of the average and representative day

c_{ik} = pollutant concentration on the ith day at the kth hour

The closer the value of DI (Daily Index) to unity, the more representative is the specified representative day, i.e. a value of 1.00 implies a perfect match. DI values for the MRDs of each of the hydrocarbons are given in Table 5.1. All of the values are very close to unity

(between 1.03 and 1.09), making initial assessment of this 'normalising factor' difficult. However, those compounds with values closest to unity are associated with representative days which are 'more representative' than hydrocarbons which have higher DI values. A good example is ethylene and toluene, given in Figure 5.12 and Figure 5.13, respectively. The representative day for ethylene appears more representative than that of toluene.

5.1.3 Correlation Analysis of Hydrocarbon Data

Correlation analysis is a commonly used method for assessing the strength of the linear relationship between two variables. However, caution must be exercised as correlation must not be interpreted as causation (MacBerthouex and Brown, 1994). An increase in Y may be observed as X increases, but this does not necessarily mean that the change in Y is caused by the change in X. This is the case with the hydrocarbon data, where the hydrocarbons may exhibit a strong correlation but no causation can be inferred.

A scatter plot of two variables provides a good visual indication of the likely degree of correlation. A sample scatter plot of the hourly ethylene and n-butane concentrations for Period 1 is shown in Figure 5.17. The linear relationship between the concentrations of the compounds is clear. There is some scatter, particularly above the linear trend line, where elevated n-butane concentrations do not coincide with elevated ethylene concentrations, suggesting a possible secondary source of n-butane.

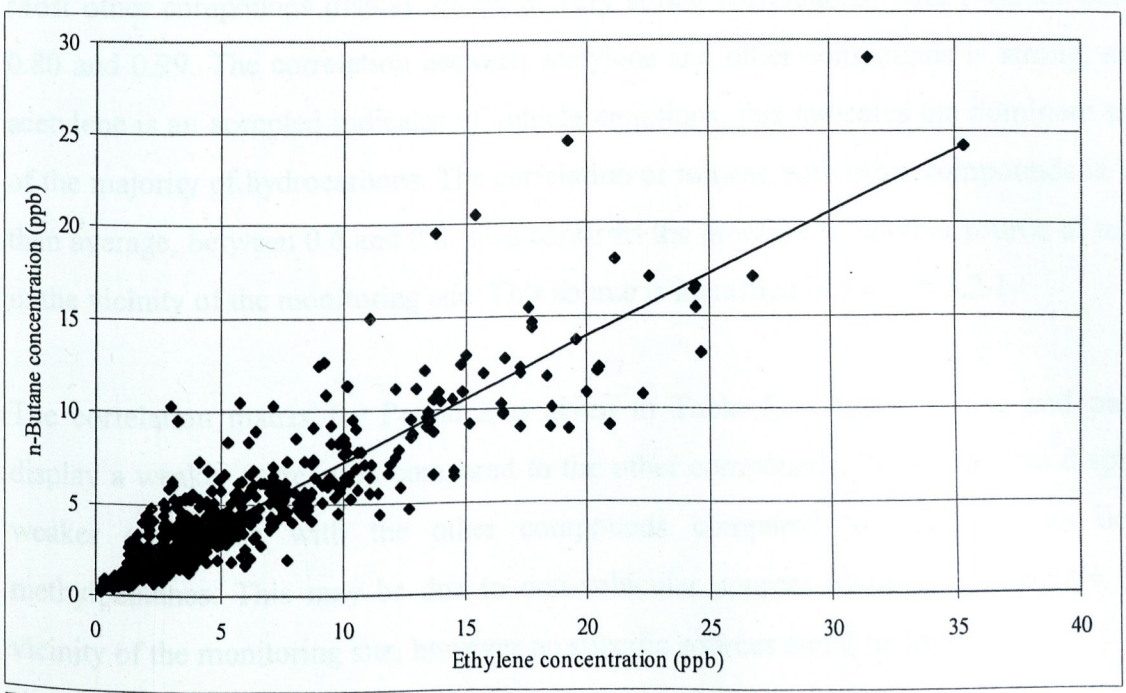


Figure 5.17 Ethylene and n-butane scatter plot for Period 1

The correlation coefficient, r, is given by Equation 5.4. A coefficient close to one indicates a strong correlation, while a value close to zero indicates a weak correlation. The correlation matrix for all measured compounds during Period 1 is given in Table 5.2.

$$r = \frac{\sum_{i=1}^{n}(c_{xi} - \bar{c}_x).(c_{yi} - \bar{c}_y)}{\sqrt{\left[\sum_{i=1}^{n}(c_{xi} - \bar{c}_x)^2\right]\left[\sum_{i=1}^{n}(c_{yi} - \bar{c}_y)^2\right]}} \qquad 5.4$$

n = number of pairs of hourly observed hydrocarbon concentrations

c_{xi}, c_{yi} = concentration of hydrocarbons x and y, respectively, for the ith hour

$\bar{c}_x$ and $\bar{c}_y$ = average concentration of x and y, respectively between hours i to n

The correlation between most hydrocarbons is very strong. The main exceptions are ethane and propane which display a weaker correlation with other compounds but a stronger correlation with each other. This is due to natural gas leakage being the predominant source of these compounds (see Section 5.1.4), while vehicle emissions are dominant for other compounds. 1-butene also exhibits a weak correlation with the other hydrocarbons, but this is a reflection of the very low measured concentrations, with many zero readings being reported, rather than a contribution from other sources. Other compounds which display some zero readings over the monitoring period, such as n-heptane and the pentenes also have a slightly lower r-value, though the correlation with most compounds is still strong. Most other compounds display strong or very strong correlations, with r-values between 0.80 and 0.99. The correlation between acetylene and other compounds is strong, and as acetylene is an accepted indicator of vehicle emissions, this indicates the dominant source of the majority of hydrocarbons. The correlation of toluene with other compounds is lower than average, between 0.6 and 0.8. This confirms the presence of another source of toluene in the vicinity of the monitoring site. This source is identified in Section 5.2.1.

The correlation matrix for Period 2 is given in Table 5.3. Again, ethane and propane display a weaker correlation compared to the other compounds. Propylene also displays a weaker correlation with the other compounds compared to Period 1, as do the methylpentanes. This may be due to non-vehicular sources of these compounds in the vicinity of the monitoring site, however no specific sources could be identified.

Table 5.2 Correlation matrix for Period 1

	Ethane	Ethylene	Propane	Propylene	Isobutane	n-Butane	Acetylene	Trans-2-butene	1-Butene	Cis-2-butene	Isopentane	n-Pentane	1,3-Butadiene	Trans-2-pentene	Cis-2-pentene	2-Methylpentane	3-Methylpentane	Isoprene	n-Hexane	Benzene	n-Heptane	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene	1,3,5-trimethylben	1,2,4-trimethylben
Ethane	1.00																										
Ethylene	0.57	1.00																									
Propane	0.69	0.52	1.00																								
Propylene	0.47	0.97	0.48	1.00																							
Isobutane	0.49	0.86	0.56	0.87	1.00																						
n-Butane	0.46	0.89	0.52	0.91	0.98	1.00																					
Acetylene	0.50	0.93	0.46	0.88	0.81	0.84	1.00																				
Trans-2-butene	0.42	0.94	0.45	0.96	0.94	0.96	0.86	1.00																			
1-Butene	0.13	0.47	0.12	0.49	0.30	0.44	0.45	0.40	1.00																		
Cis-2-butene	0.42	0.91	0.45	0.93	0.92	0.94	0.84	0.97	0.40	1.00																	
Isopentane	0.40	0.92	0.45	0.96	0.94	0.98	0.83	0.98	0.46	0.95	1.00																
n-Pentane	0.44	0.92	0.48	0.96	0.93	0.97	0.84	0.98	0.46	0.95	0.99	1.00															
1,3-Butadiene	0.47	0.97	0.47	0.98	0.88	0.90	0.90	0.96	0.38	0.93	0.93	0.94	1.00														
Trans-2-pentene	0.34	0.84	0.38	0.91	0.88	0.92	0.72	0.95	0.34	0.93	0.96	0.95	0.88	1.00													
Cis-2-pentene	0.41	0.83	0.49	0.84	0.82	0.83	0.79	0.85	0.37	0.83	0.84	0.84	0.85	0.78	1.00												
2-Methylpentane	0.40	0.86	0.41	0.83	0.77	0.81	0.90	0.83	0.56	0.80	0.81	0.83	0.84	0.69	0.79	1.00											
3-Methylpentane	0.42	0.94	0.44	0.96	0.90	0.93	0.88	0.97	0.39	0.95	0.96	0.96	0.96	0.92	0.84	0.84	1.00										
Isoprene	0.36	0.84	0.38	0.86	0.77	0.82	0.78	0.85	0.43	0.83	0.85	0.85	0.85	0.82	0.74	0.74	0.86	1.00									
n-Hexane	0.35	0.81	0.40	0.89	0.84	0.88	0.67	0.91	0.31	0.89	0.93	0.92	0.86	0.96	0.74	0.63	0.89	0.77	1.00								
Benzene	0.41	0.94	0.43	0.99	0.88	0.93	0.84	0.97	0.47	0.95	0.97	0.97	0.96	0.95	0.83	0.81	0.96	0.86	0.93	1.00							
n-Heptane	0.52	0.83	0.50	0.85	0.79	0.81	0.71	0.84	0.35	0.82	0.84	0.85	0.84	0.83	0.72	0.68	0.84	0.73	0.84	0.86	1.00						
Toluene	0.34	0.76	0.33	0.76	0.70	0.72	0.72	0.77	0.30	0.75	0.75	0.75	0.77	0.71	0.64	0.68	0.77	0.66	0.69	0.77	0.67	1.00					
Ethylbenzene	0.43	0.95	0.44	0.98	0.87	0.92	0.87	0.96	0.51	0.94	0.96	0.97	0.97	0.92	0.84	0.85	0.96	0.87	0.90	0.99	0.86	0.77	1.00				
m+p-Xylene	0.43	0.95	0.44	0.98	0.87	0.92	0.87	0.96	0.50	0.94	0.96	0.96	0.97	0.92	0.84	0.85	0.96	0.87	0.89	0.99	0.86	0.77	1.00	1.00			
o-Xylene	0.43	0.96	0.44	0.99	0.87	0.92	0.87	0.96	0.51	0.94	0.96	0.96	0.97	0.92	0.84	0.86	0.96	0.87	0.89	0.99	0.86	0.77	1.00	1.00	1.00		
1,3,5-trimethylbenz.	0.44	0.95	0.45	0.98	0.86	0.91	0.85	0.95	0.52	0.93	0.95	0.96	0.96	0.92	0.82	0.83	0.95	0.86	0.90	0.98	0.86	0.76	0.99	0.99	0.99	1.00	
1,2,4-trimethylbenz.	0.45	0.93	0.46	0.97	0.86	0.91	0.83	0.95	0.47	0.93	0.95	0.95	0.95	0.92	0.82	0.79	0.94	0.86	0.91	0.98	0.86	0.76	0.98	0.98	0.98	0.99	1.00

Table 5.3 Correlation matrix for Period 2

	Ethane	Ethylene	Propane	Propylene	iso-Butane	n-Butane	Acetylene	Trans-2-Butene	1-Butene	Cis-2-Butene	Isopentane	n-Pentane	1,3-Butadiene	Trans-2-Pentene	Cis-2-pentene	2-Methylpentane	3-Methylpentane	Isoprene
Ethane	1.00																	
Ethylene	0.57	1.00																
Propane	0.71	0.48	1.00															
Propylene	0.37	0.69	0.32	1.00														
iso-Butane	0.59	0.82	0.62	0.58	1.00													
n-Butane	0.58	0.85	0.61	0.57	0.98	1.00												
Acetylene	0.48	0.91	0.42	0.65	0.78	0.77	1.00											
Trans-2-Butene	0.47	0.93	0.46	0.63	0.90	0.92	0.87	1.00										
1-Butene	0.50	0.96	0.47	0.65	0.86	0.89	0.88	0.97	1.00									
Cis-2-Butene	0.47	0.92	0.47	0.62	0.89	0.92	0.86	0.98	0.97	1.00								
Isopentane	0.50	0.91	0.52	0.62	0.94	0.96	0.86	0.98	0.96	0.97	1.00							
n-Pentane	0.56	0.91	0.58	0.61	0.93	0.96	0.85	0.95	0.94	0.95	0.98	1.00						
1,3-Butadiene	0.51	0.96	0.47	0.70	0.83	0.86	0.89	0.94	0.96	0.93	0.93	0.92	1.00					
Trans-2-Pentene	0.44	0.77	0.48	0.35	0.79	0.85	0.69	0.84	0.83	0.85	0.86	0.87	0.76	1.00				
Cis-2-pentene	0.38	0.80	0.43	0.42	0.78	0.83	0.74	0.88	0.87	0.88	0.88	0.86	0.81	0.90	1.00			
2-Methylpentane	0.22	0.63	0.22	0.36	0.49	0.55	0.54	0.66	0.68	0.69	0.64	0.64	0.61	0.65	0.58	1.00		
3-Methylpentane	0.52	0.66	0.57	0.27	0.74	0.79	0.57	0.69	0.69	0.69	0.74	0.80	0.64	0.89	0.74	0.56	1.00	
Isoprene	0.37	0.79	0.34	0.46	0.64	0.70	0.70	0.79	0.81	0.81	0.77	0.77	0.76	0.76	0.69	0.83	0.60	1.00

5.1.4 Non-Typical Behaviour of Ethane and Propane

The average diurnal concentration patterns identified for ethane and propane (see Figure 5.18 and Figure 5.19) have also been observed in hydrocarbon data collected in the UK hydrocarbon monitoring network. In these studies, the major source of ethane and propane emissions has been identified as fugitive emissions from the natural gas network ((PORG, 1993; QUARG, 1993; Field *et al.*, 1994; Derwent *et al.*, 1995; PORG, 1997; Derwent *et al.*, 2000). There is no natural gas distribution system in Belfast, and hence the concentrations at the Belfast site are lower than those experienced in other cities. The concentrations measured at the Belfast monitoring site are around 2 ppb, which is the reported tropospheric background concentration (QUARG, 1993). The low reactivity of ethane implies a long atmospheric lifetime (see Section 2.5), so even measurements at remote monitoring stations can be in the region of 2 to 3 ppb.

Details of the constituents of natural gas used in Dublin are included in Table 5.4 (Barrett, 2000). After methane, the most abundant hydrocarbons are ethane and propane. In Table 5.2 and Table 5.3 the strongest correlation for ethane is with propane (r value of approximately 0.70) indicating a common source for these two compounds, which is not related to vehicle emissions.

Table 5.4 Composition of natural gas used in Dublin (Barrett, 2000)

Compound	Volume percentage
Ethane	7.0 %
Carbon dioxide	2.4 %
Propane	2.2 %
Nitrogen	0.76 %
n-Butane	0.39 %
Isobutane	0.20 %
n-Pentane	0.07 %
Isopentane	0.06 %
n-Hexane	0.02 %
Methane	86.9 %

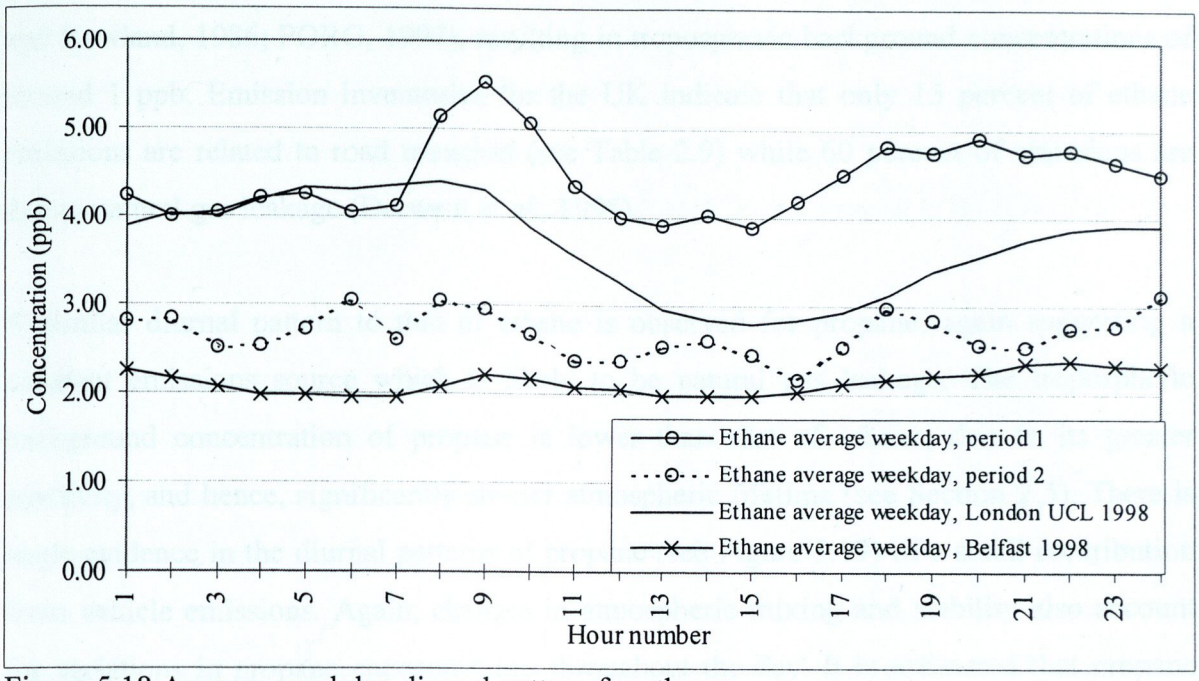


Figure 5.18 Average weekday diurnal pattern for ethane

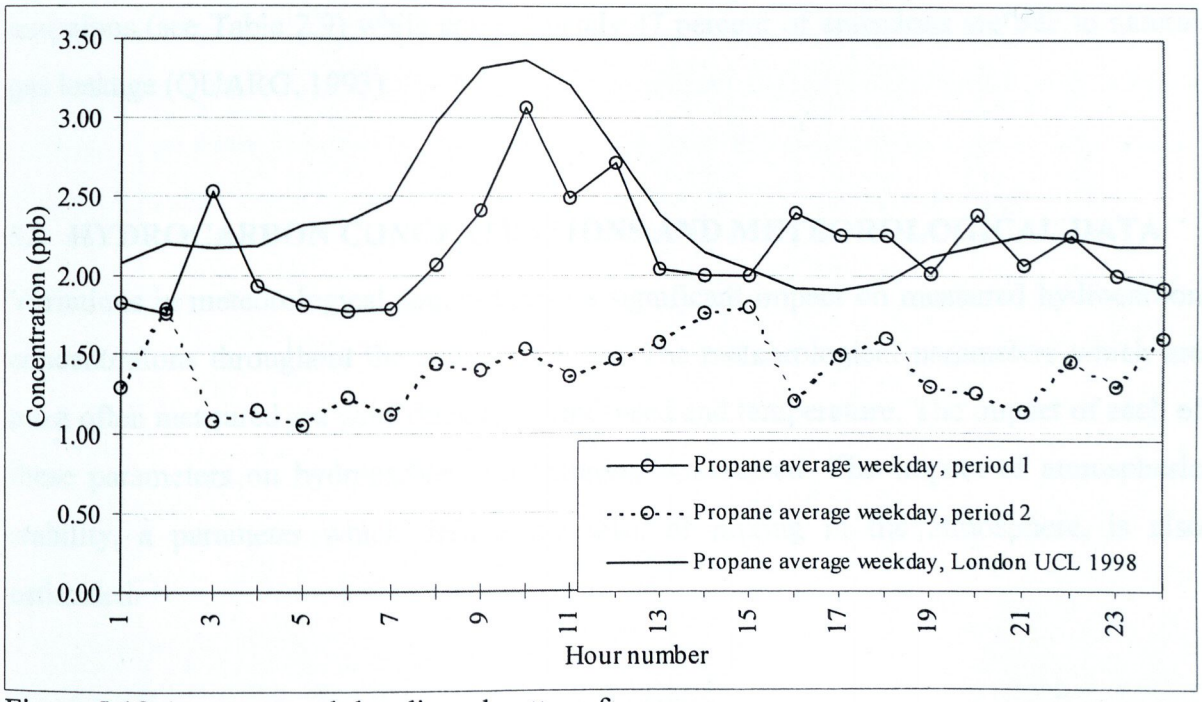


Figure 5.19 Average weekday diurnal pattern for propane

The diurnal pattern of ethane in Dublin during Period 1 indicates some contribution from vehicle exhaust emissions, although the variations in the ethane concentrations are also due to variations in atmospheric stability and mixing during the day, with improved atmospheric mixing during the afternoon being responsible for the day-time minimum concentration. Concentrations tend to be elevated during the night due to poorer mixing and more stable atmospheric conditions. Similarly, average concentrations are lower during the warmer summer months (as for Period 2) due to improved atmospheric mixing (Blake

and Rowland, 1986; PORG, 1997), resulting in tropospheric background concentrations of around 1 ppb. Emission inventories for the UK indicate that only 15 percent of ethane emissions are related to road transport (see Table 2.9) while 60 percent of emissions are due to natural gas leakage (Derwent *et al.*, 1995).

A similar diurnal pattern to that of ethane is observed for propane, again suggesting a constant emissions source which is likely to be natural gas leakage. The tropospheric background concentration of propane is lower than that of ethane, due to its greater reactivity, and hence, significantly shorter atmospheric lifetime (see Section 2.5). There is some evidence in the diurnal patterns of propane (see Figure 5.19) of a small contribution from vehicle emissions. Again, changes in atmospheric mixing and stability also account for variations in propane concentrations throughout the day. It is estimated that propane emissions from road transport in the UK account for only 1.25 percent of total annual emissions (see Table 2.9) while approximately 47 percent of emissions are due to natural gas leakage (QUARG, 1993).

5.2 HYDROCARBON CONCENTRATIONS AND METEOROLOGICAL DATA

Variations in meteorological data can have a significant impact on measured hydrocarbon concentrations throughout the course of a day. The meteorological parameters which are most often measured are wind direction, windspeed and temperature. The impact of each of these parameters on hydrocarbon concentration is assessed. The impact of atmospheric stability, a parameter which defines the level of mixing in the atmosphere, is also estimated.

5.2.1 Pollution Roses for Measured Hydrocarbon Concentrations

Wind direction can have a significant impact on measured concentrations of air pollutants, even at an urban roadside location. However, a review of previous urban air quality studies by Croxford and Penn (1998) reported that most studies have neglected to consider various meteorological factors, particularly wind direction data, in the analysis of air quality data. Through comparison with local meteorological measurements, the effects of variations in local wind direction on hydrocarbon concentrations can be observed. Similarly, comparison of concentration data and regional wind direction allows possible local and regional

hydrocarbon sources to be identified. As shown in Section 4.4.1, major differences can exist between local wind direction measurements in the city centre and regional data obtained at a suburban meteorological monitoring station. Therefore, hydrocarbon concentrations are compared to both local and regional wind direction in this section.

The wind direction data were broken up into 30 degree sectors, to ensure a reasonable number of data points in each sector. However, because the local wind direction data cover only a very narrow range (see Figure 4.19 and Figure 4.20), some of these sectors still only have a small number of data points. Hence these data is of limited use in identifying local hydrocarbon sources.

Hourly data points with windspeeds less than 1 m/s are not considered, as wind direction data at lower windspeed may not be reliable. 'Pollution roses' giving selected average hydrocarbon concentrations in each 30 degree sector are presented in Figure 5.20 to Figure 5.25. The pollution roses for each of the measured compounds display very similar patterns. The discrepancy between regional and local wind direction data is observable. Typical pollution roses for Periods 1 and 2 are shown in Figure 5.20 and Figure 5.21.

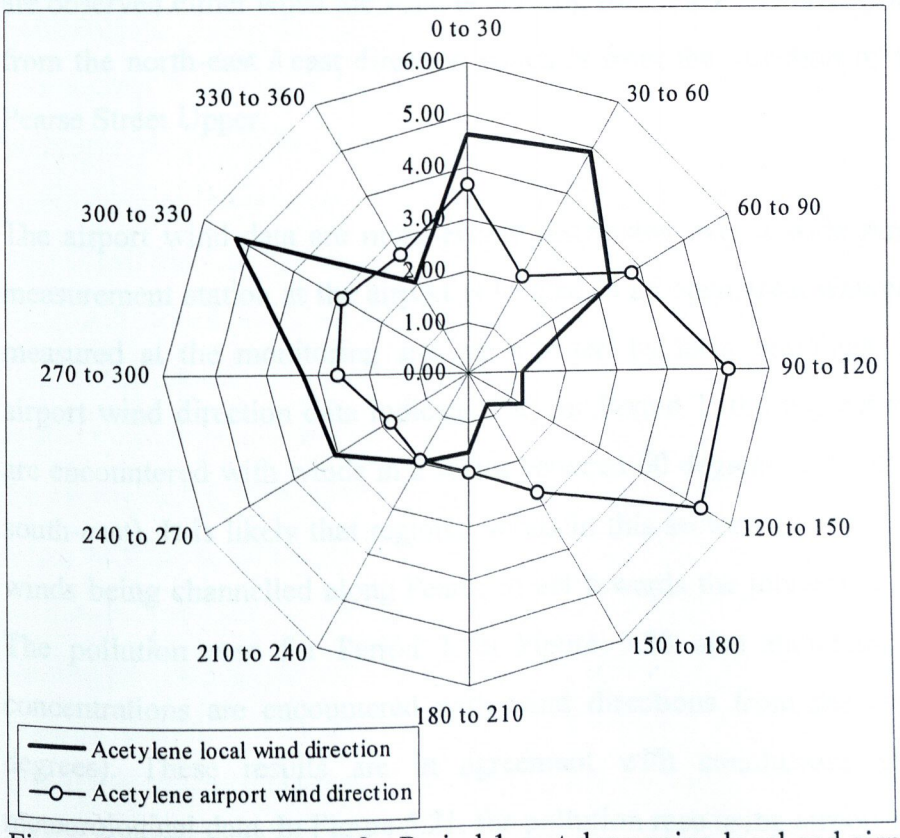


Figure 5.20 Pollution rose for Period 1 acetylene using local and airport wind data, ppb

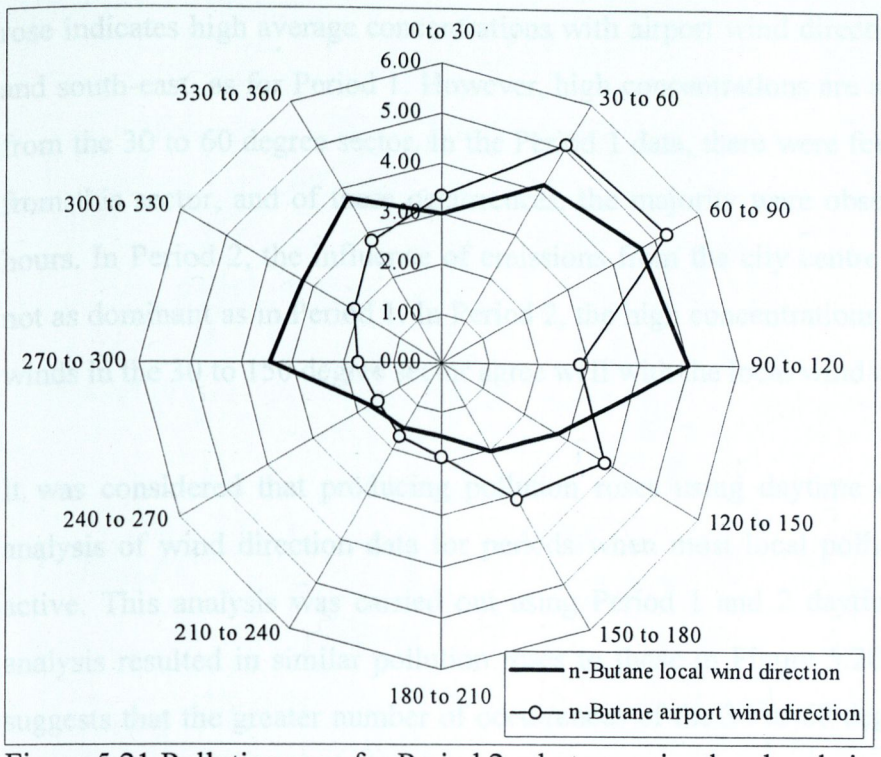


Figure 5.21 Pollution rose for Period 2 n-butane using local and airport wind data, ppb

As mentioned previously, interpretation of the pollution roses using local wind direction data is difficult due to the small number of observations in some sectors. However, the pollution roses for both monitoring periods indicate that the highest average concentrations are observed either when the wind is blowing from the north-west (city centre direction), or from the north-east / east direction which is from the direction of the junction and from Pearse Street Upper.

The airport wind data are more evenly distributed over a wide range of directions. The measurement station at the airport is located in an open area, whereas the wind directions measured at the monitoring site are affected by local buildings. Pollution roses using airport wind direction data indicate that, for Period 1, the highest average concentrations are encountered with winds in a sector between 60 degrees and 150 degrees (north-east to south-east). It is likely that regional winds in this sector would result, on a local scale, in winds being channelled along Pearse Street towards the junction, and the monitoring site. The pollution rose for Period 1 in Figure 5.20 also indicates that slightly elevated concentrations are encountered with wind directions from the city centre (270 to 360 degrees). These results are in agreement with conclusions drawn from the local meteorological data. In Figure 5.21, the pollution rose using airport meteorological data for Period 2 displays a slightly different pattern to that for Period 1. The Period 2 pollution

rose indicates high average concentrations with airport wind directions between north-east and south-east, as for Period 1. However, high concentrations are also observed for winds from the 30 to 60 degree sector. In the Period 1 data, there were few occurrences of winds from this sector, and of these occurrences, the majority were observed during night-time hours. In Period 2, the influence of emissions from the city centre (270 - 360 degrees) is not as dominant as in Period 1. In Period 2, the high concentrations observed with regional winds in the 30 to 150 degree sector agree well with the local wind direction data.

It was considered that producing pollution roses using daytime data only would allow analysis of wind direction data for periods when most local pollution sources would be active. This analysis was carried out using Period 1 and 2 daytime data. However, this analysis resulted in similar pollution roses to those in Figure 5.20 and Figure 5.21. This suggests that the greater number of occurrences of the 30 to 60 degree wind sector during the second period simply resulted in a higher number of elevated concentrations being measured, rather than any new hydrocarbon source in this direction during Period 2.

Pollution roses from both periods indicate that winds from anywhere between 0 and 150 degrees are likely to result in higher hydrocarbon concentrations. For ethane and propane, however, the pollution roses indicate different behaviour. The pollution roses for these compounds from Period 1 are shown in Figure 5.22 and Figure 5.23, respectively. Both pollution roses show similar average concentrations for each wind direction sector, particularly for the airport wind data. Some bias towards higher concentrations is observed with local wind directions from the city centre. Field (1995) reported a contribution from stationary combustion sources to measured concentrations of ethane and propane at a London roadside location. Similar effects in Dublin may account for the bias towards higher concentrations from the city centre for local meteorological data. The pollution rose for ethane concentrations in Period 2 (Figure 5.24) indicates constant concentrations for all wind directions using local wind direction data. This suggests lower emissions from stationary combustion during the warmer summer months, as would be expected, with natural gas leakage dominating during this period. These results indicate that ethane and propane concentrations are constant throughout the city, compared to other compounds, and again substantiates previous observations that the major source of ethane and propane concentrations in Dublin is natural gas leakage from the network in Dublin.

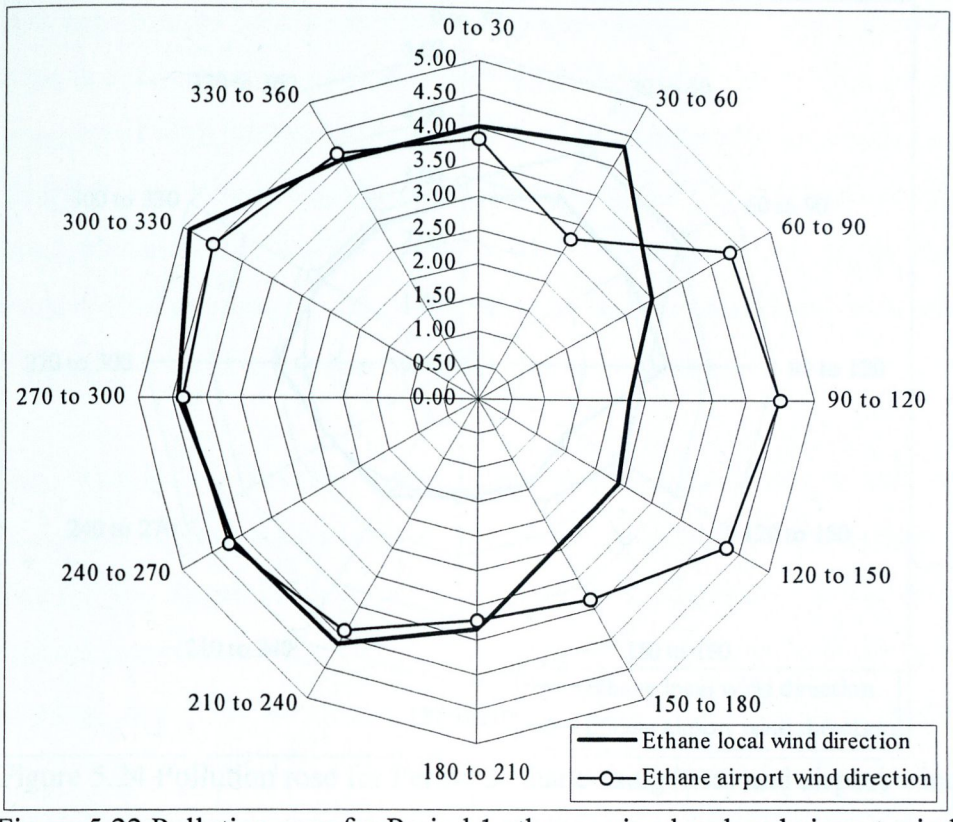


Figure 5.22 Pollution rose for Period 1 ethane using local and airport wind data, ppb

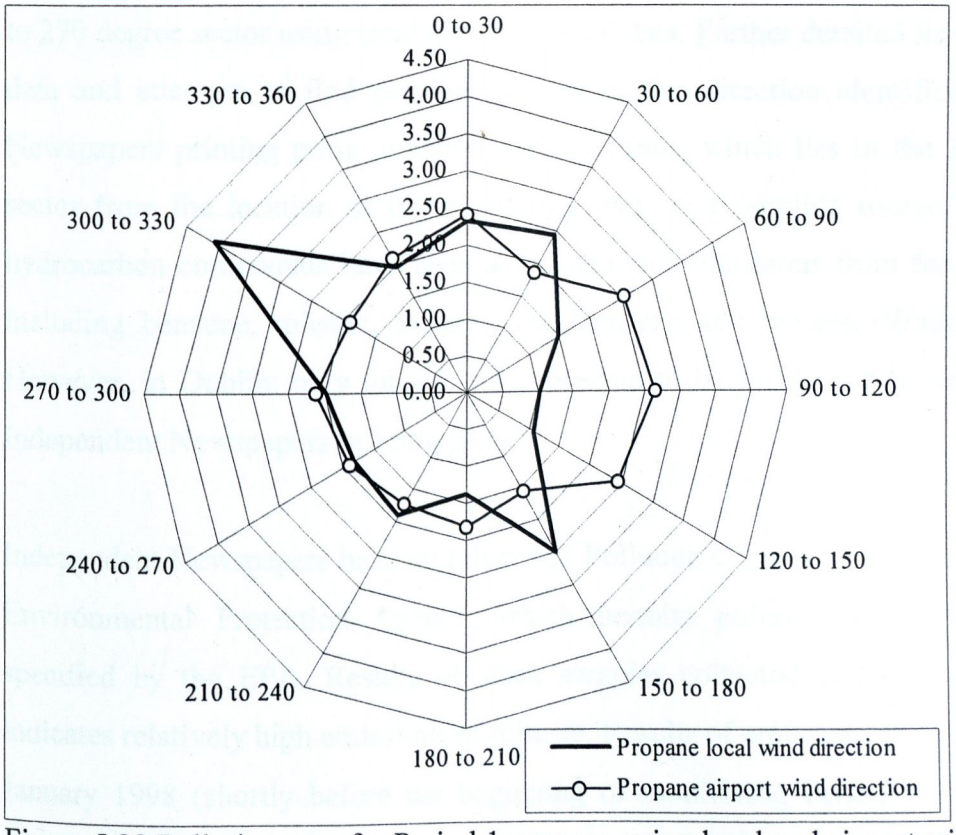


Figure 5.23 Pollution rose for Period 1 propane using local and airport wind data, ppb

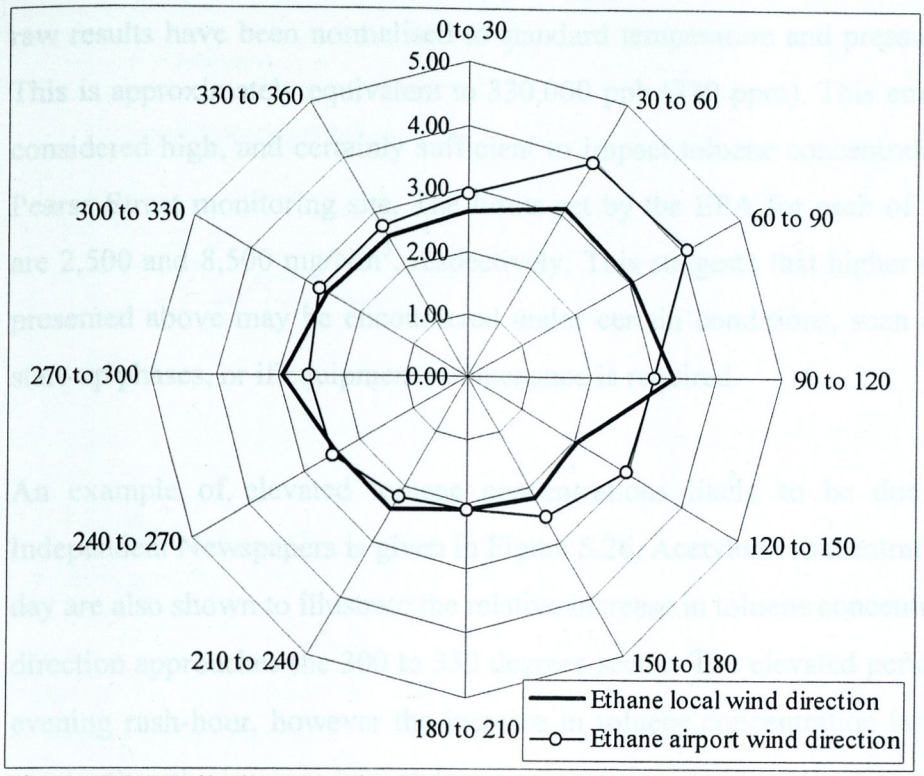


Figure 5.24 Pollution rose for Period 2 ethane using local and airport wind data, ppb

The only other compound which shows any deviation from the 'typical' pollution rose observed during the monitoring campaign is toluene (Figure 5.25). A significant peak in concentration is noted in the 300 to 330 degree sector using the airport data, or in the 240 to 270 degree sector using local meteorological data. Further detailed investigation of these data and attempts to find possible sources in this direction identified the Independent Newspapers printing press in Middle Abbey Street, which lies in the 300 to 330 degree sector from the location of the monitoring unit, as a possible source. A wide range of hydrocarbon compounds have been associated with emissions from the printing industry, including benzene, toluene, xylenes, ethylbenzene and hexane (Wadden *et al.,* 1995). However, in Dublin, only toluene was observed to be influenced by emissions from the Independent Newspapers printing press.

Independent Newspapers have an Integrated Pollution Control (IPC) licence granted by the Environmental Protection Agency, which permits pollutant emissions, within limits specified by the EPA. Results of stack samples collected at Independent Newspapers indicates relatively high emissions of toluene. Results of emissions tests carried out on 22nd January 1998 (shortly before the beginning of monitoring Period 1) revealed a toluene emission rate during normal operation of 836.67 mg/Nm^3 for one vent and 422.65 mg/Nm^3 for another (milligrammes per normal metre cubed, where normal (N) indicates that the

raw results have been normalised to standard temperature and pressure) (Buckley, 1998). This is approximately equivalent to 330,000 ppb (330 ppm). This emission rate would be considered high, and certainly sufficient to impact toluene concentrations measured at the Pearse Street monitoring site. The limits set by the EPA for each of the emissions points are 2,500 and 8,500 mg/Nm^3, respectively. This suggests that higher emissions than those presented above may be encountered under certain conditions, such as during equipment start-up phases, or if equipment maintenance is required.

An example of elevated toluene concentrations likely to be due to emissions from Independent Newspapers is given in Figure 5.26. Acetylene concentrations during the same day are also shown to illustrate the relative increase in toluene concentration when the wind direction approaches the 300 to 330 degrees sector. The elevated period occurs around the evening rush-hour, however the increase in toluene concentration is proportionally much greater than the increase in acetylene concentration, and the elevation occurs only while the wind direction remains between 300 and 330 degrees. Another example is shown in Figure 5.27, where several peaks occur during the course of a day, coincident with wind directions around the 300 to 330 degree wind sector. Peak concentration of more than 20 ppb were observed on this occasion, compared to the average concentration measured during Period 1 of 3.30 ppb, and the 98th percentile value of 13.78 ppb (see Table 4.6).

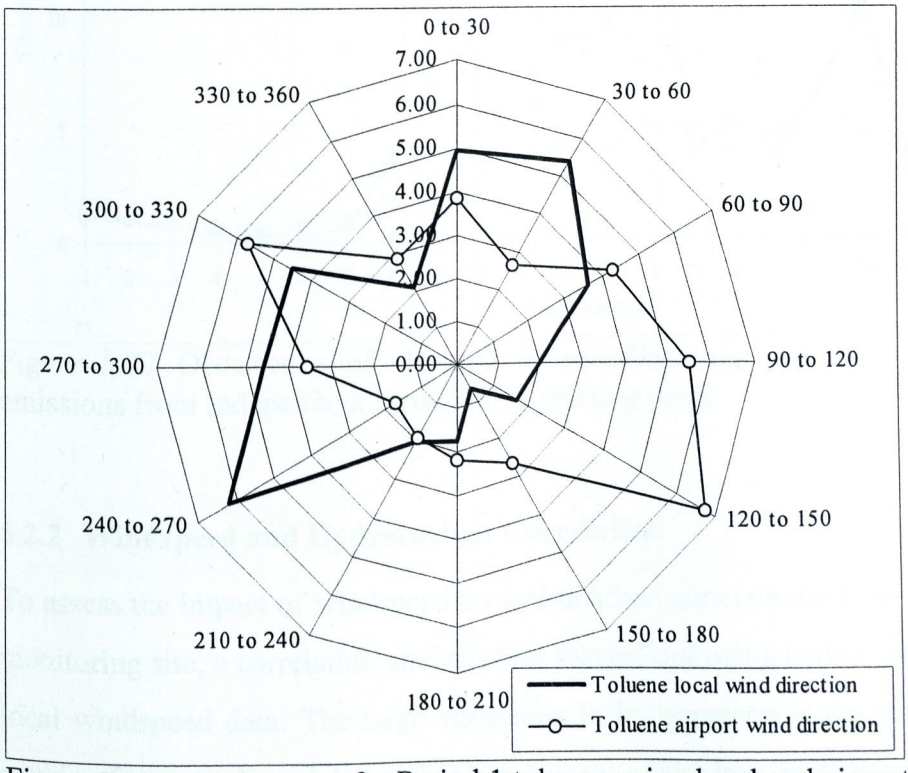


Figure 5.25 Pollution rose for Period 1 toluene using local and airport wind data, ppb

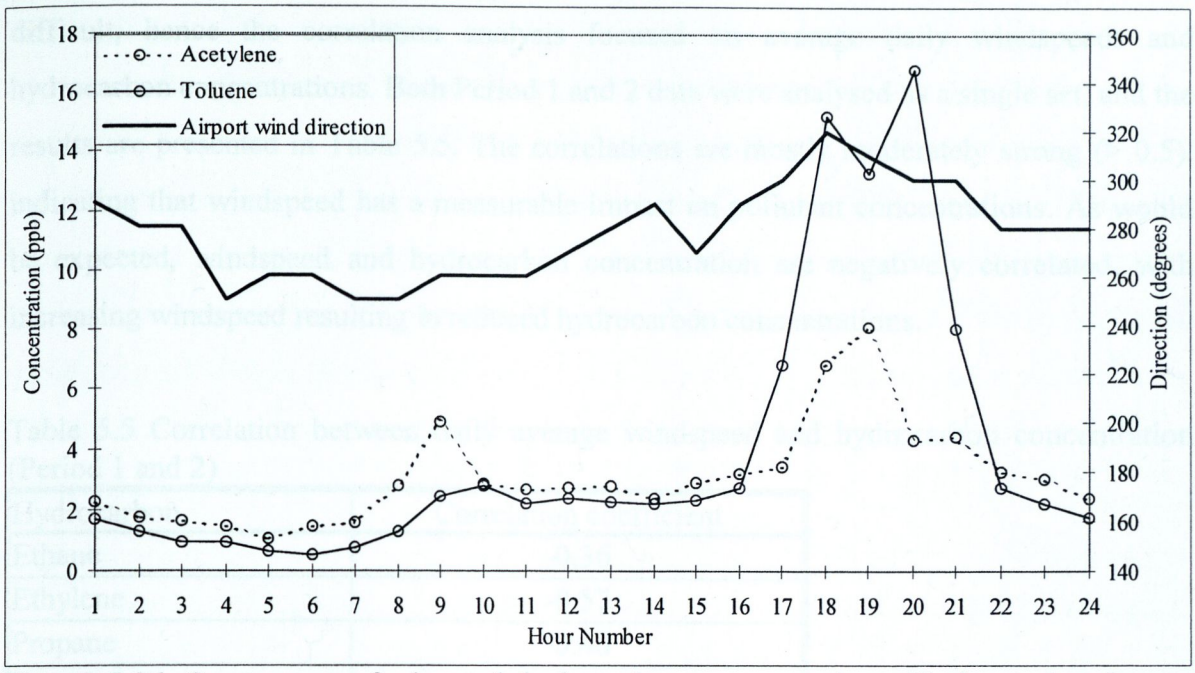


Figure 5.26 Occurrence of elevated hydrocarbon concentrations likely to be due to emissions from Independent Newspapers printing press

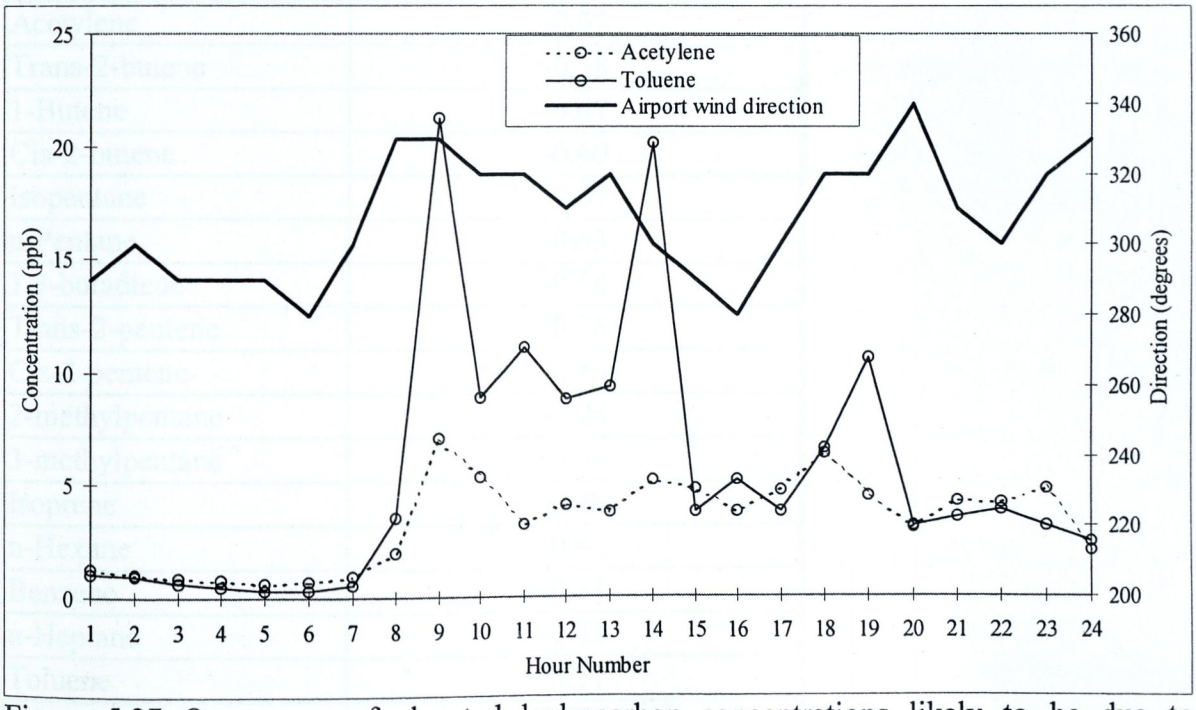


Figure 5.27 Occurrence of elevated hydrocarbon concentrations likely to be due to emissions from Independent Newspapers printing press

5.2.2 Windspeed and Hydrocarbon Correlation

To assess the impact of windspeed on hydrocarbon concentrations at the Dublin city centre monitoring site, a correlation analysis was carried out using hydrocarbon concentration and local windspeed data. The large variations in hydrocarbon concentrations throughout the course of a normal weekday makes assessment of the impact of windspeed on hourly data

difficult, hence the correlation analysis focused on average daily windspeeds and hydrocarbon concentrations. Both Period 1 and 2 data were analysed as a single set, and the results are presented in Table 5.5. The correlations are mostly moderately strong (> 0.5), indicating that windspeed has a measurable impact on pollutant concentrations. As would be expected, windspeed and hydrocarbon concentration are negatively correlated, with increasing windspeed resulting in reduced hydrocarbon concentrations.

Table 5.5 Correlation between daily average windspeed and hydrocarbon concentration (Period 1 and 2)

Hydrocarbon	Correlation coefficient
Ethane	-0.36
Ethylene	-0.57
Propane	-0.46
Propylene	-0.52
isobutane	-0.50
n-Butane	-0.59
Acetylene	-0.52
Trans-2-butene	-0.58
1-Butene	-0.47
Cis-2-butene	-0.60
Isopentane	-0.67
n-Pentane	-0.63
1,3-butadiene	-0.54
Trans-2-pentene	-0.36
Cis-2-pentene	-0.46
2-methylpentane	-0.28
3-methylpentane	-0.38
Isoprene	-0.49
n-Hexane	-0.42
Benzene	-0.44
n-Heptane	-0.43
Toluene	-0.31
Ethylbenzene	-0.50
m+p-Xylene	-0.51
o-Xylene	-0.50
1,3,5-trimethylbenzene	-0.50
1,2,4-trimethylbenzene	-0.58

A scatter plot of the average daily windspeed against n-pentane concentration is given in Figure 5.28. The decreasing trend in concentration with increasing windspeed is obvious from this plot, although there is a significant amount of scatter, particularly at lower

windspeeds (< 1.5 m/s) where a wide variation in daily average concentrations are observed. This is because, at lower windspeeds, other factors have more influence on ambient hydrocarbon concentrations. At high daily average windspeeds, low concentrations can always be expected, hence the scatter is less around this end of the trend line. The trend line is forced upwards by the outliers (which are all at high concentrations), hence using a power law trendline ($y = cx^b$, where c and b are constants) actually provides an improved correlation coefficient (0.69 compared to 0.63). However, this improvement appears to be due to the greater scatter at low windspeeds rather than to a closer approximation at higher windspeeds.

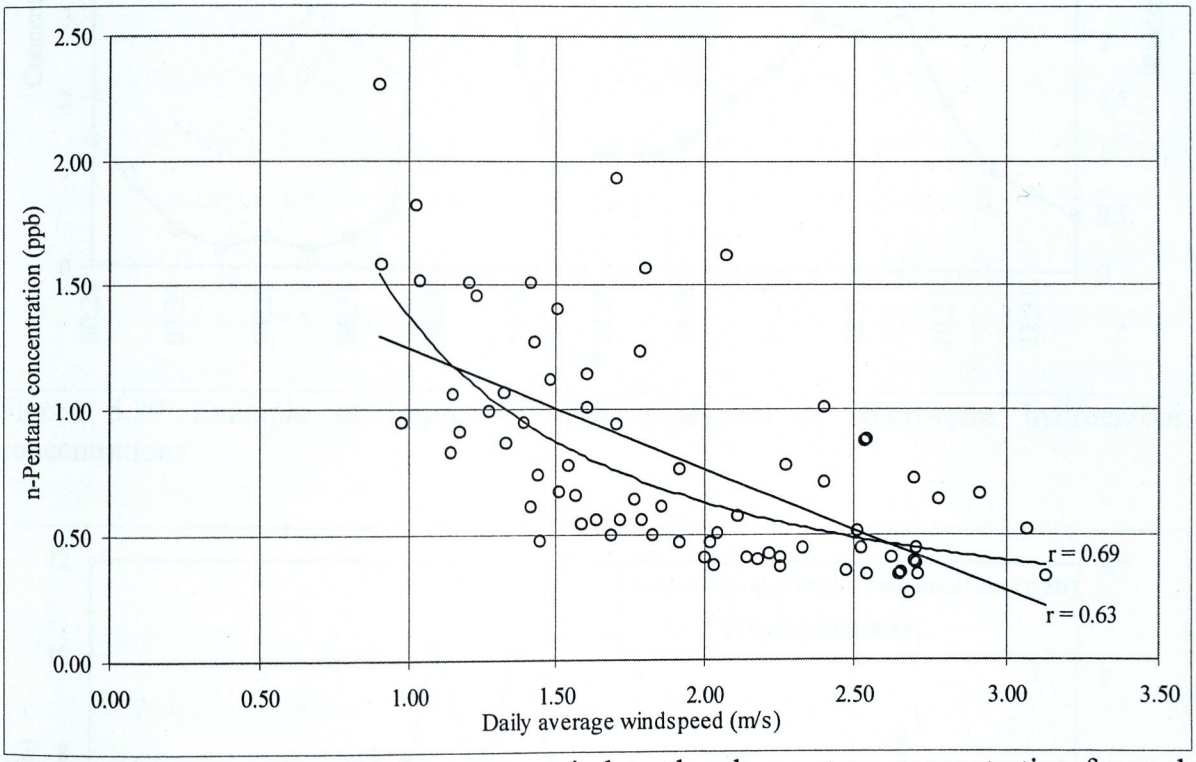


Figure 5.28 Scatter plot of daily average windspeed and n-pentane concentration for each weekday during Period 1 and 2

The above data indicate that high daily average windspeeds result in lower hydrocarbon concentrations. As mentioned previously, the impact of hourly windspeed variations on hourly hydrocarbon concentrations is generally hard to assess; however there are occasions where extremes of windspeed (very high or low) do produce noticeable impacts on short-term hydrocarbon concentrations. Examples of this behaviour are shown in Figure 5.29 and Figure 5.30. In Figure 5.29 average morning windspeeds result in a typical morning peak concentration, however, the increase in windspeed during the afternoon (to over 4 m/s) results in low mid-afternoon concentrations and a reduction in the magnitude of the typical evening peak concentration.

In Figure 5.30, low morning windspeed results in poor dispersion of the pollutants and an elevated morning peak concentration, while increased windspeed during the day results in an afternoon minimum concentration which is lower than the early morning minimum.

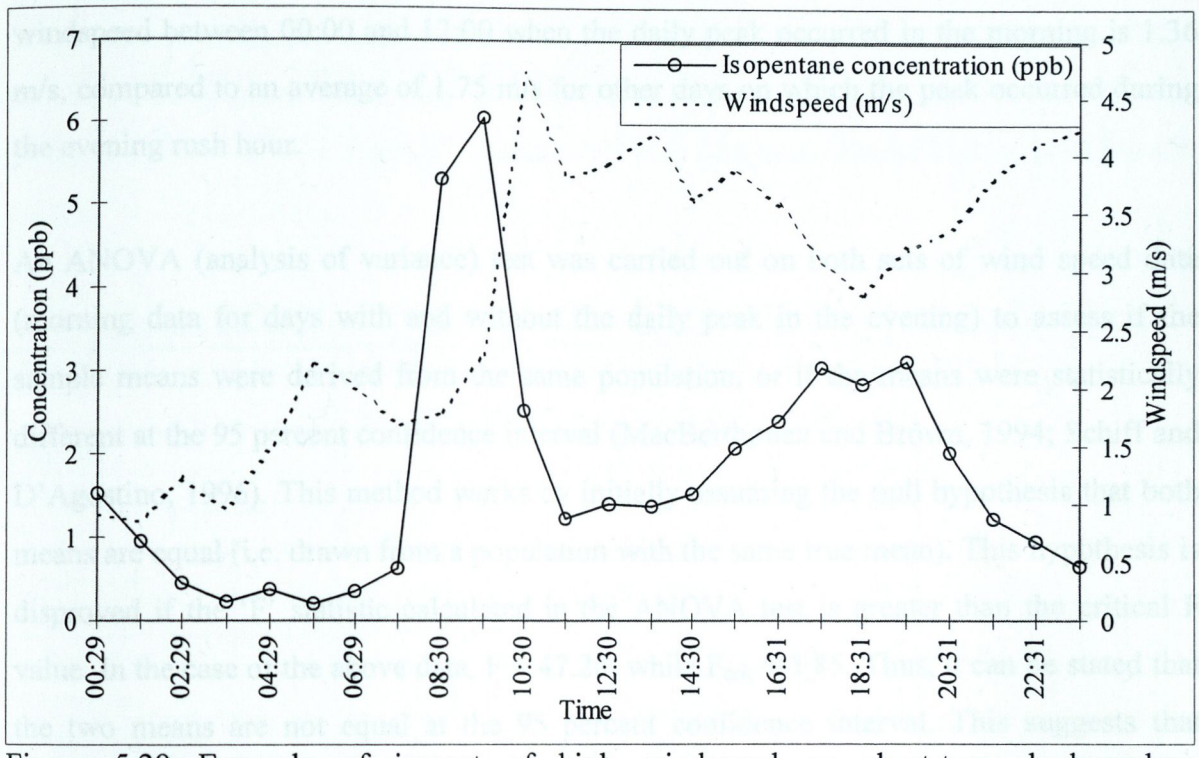


Figure 5.29 Example of impact of high windspeed on short-term hydrocarbon concentrations

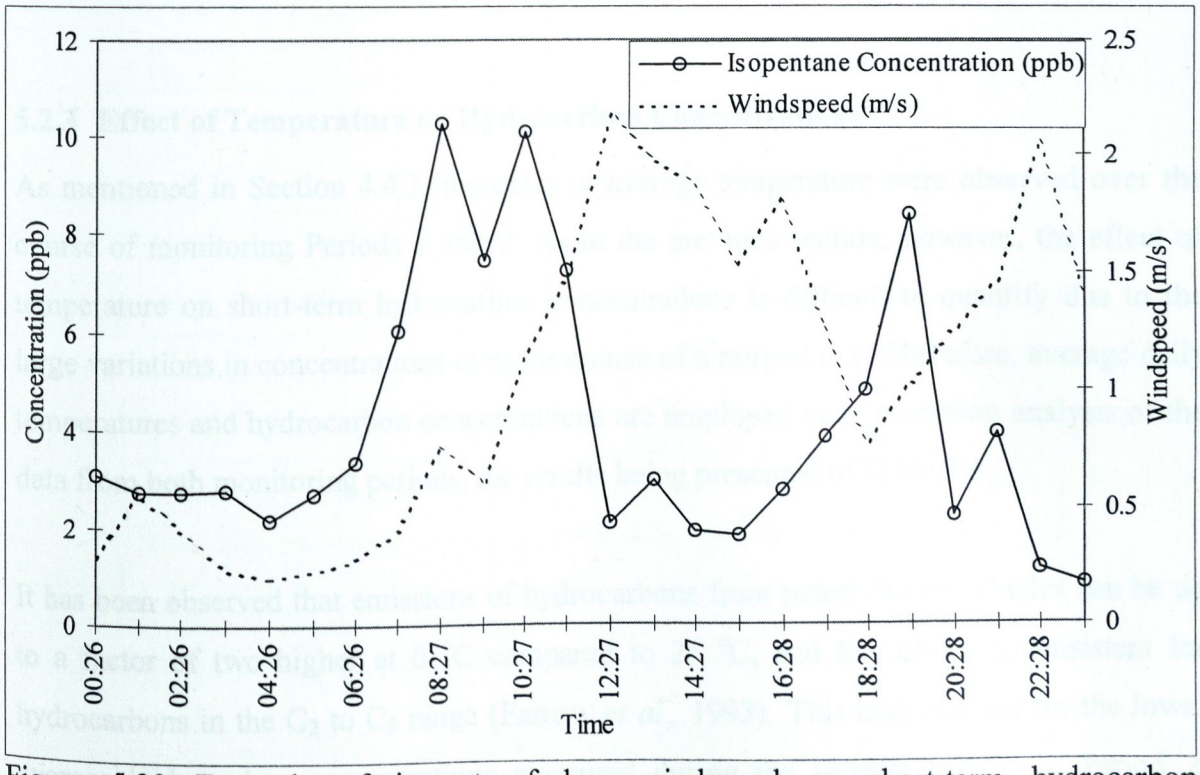


Figure 5.30 Example of impact of low windspeed on short-term hydrocarbon concentrations

As mentioned previously, the majority of daily peak concentrations occur during the evening rush hour (Section 5.1.1). Inspection of the data collected on days in which the morning peak is larger than the evening peak often reveals that low morning windspeeds contribute to high morning peak concentrations. Considering all measurements, the mean windspeed between 00:00 and 12:00 when the daily peak occurred in the morning is 1.36 m/s, compared to an average of 1.75 m/s for other days on which the peak occurred during the evening rush hour.

An ANOVA (analysis of variance) test was carried out on both sets of wind speed data (morning data for days with and without the daily peak in the evening) to assess if the sample means were derived from the same population, or if the means were statistically different at the 95 percent confidence interval (MacBerthouex and Brown, 1994; Schiff and D'Agostino, 1996). This method works by initially assuming the null hypothesis that both means are equal (i.e. drawn from a population with the same true mean). This hypothesis is disproved if the 'F' statistic calculated in the ANOVA test is greater than the critical F value. In the case of the above data, $F = 47.28$, while $F_{crit} = 3.85$. Thus, it can be stated that the two means are not equal at the 95 percent confidence interval. This suggests that windspeed has a significant impact on the diurnal pattern observed for hydrocarbon data at the monitoring site.

5.2.3 Effect of Temperature on Hydrocarbon Concentrations

As mentioned in Section 4.4.3, increases in average temperature were observed over the course of monitoring Periods 1 and 2. As in the previous section, however, the effect of temperature on short-term hydrocarbon concentrations is difficult to quantify due to the large variations in concentrations over the course of a normal day. Therefore, average daily temperatures and hydrocarbon concentrations are employed in a correlation analysis of the data from both monitoring periods, the results being presented in Table 5.6.

It has been observed that emissions of hydrocarbons from petrol driven vehicles can be up to a factor of two higher at 0 °C compared to 25 °C, and this effect is consistent for hydrocarbons in the C_2 to C_8 range (Farrow *et al.*, 1993). This may account for the lower average hydrocarbon concentrations measured during the warmer months of Period 2, along with the influence of other factors such as improved atmospheric mixing.

The correlation coefficients are weak for both periods, although the summer data produce a greater number of negative correlations. For Period 1, the strongest correlations are for n-hexane, 3-methylpentane, the butanes and the pentanes. These compounds are associated with evaporative emissions (see Table 2.9). Several of the aromatic compounds associated with evaporative emissions also have weak positive correlations with temperature, with the exception of toluene, which has no correlation whatsoever. This zero correlation for toluene is likely to be a result of interference from non-vehicular emissions (see Section 5.2.1).

Table 5.6 Correlation between daily average temperature and hydrocarbon concentration

Compound	Period 1 correlation coefficient	Period 2 correlation coefficient
Ethane	-0.12	-0.41
Ethylene	0.07	-0.37
Propane	0.16	-0.30
Propylene	0.12	-0.47
Isobutane	0.29	-0.21
n-Butane	0.32	-0.18
Acetylene	-0.12	-0.29
Trans-2-butene	0.10	-0.20
1-Butene	0.32	-0.24
Cis-2-butene	0.16	-0.17
Isopentane	0.33	-0.22
n-Pentane	0.33	-0.22
1,3-butadiene	-0.03	-0.30
Trans-2-pentene	0.29	0.23
Cis-2-pentene	0.04	0.15
2-methylpentane	-0.29	0.05
3-methylpentane	0.33	0.18
Isoprene	0.26	-0.08
n-Hexane	0.45	
Benzene	0.24	
n-Heptane	0.22	
Toluene	0.04	
Ethylbenzene	0.22	
m+p-Xylene	0.22	
o-Xylene	0.20	
1,3,5-trimethylbenzene	0.19	
1,2,4-trimethylbenzene	0.26	

For Period 2, the majority of hydrocarbons have a weak negative correlation with temperature. During this monitoring period, the daily average temperature was relatively constant, particularly towards the end of Period 2, as shown in Figure 4.29, thus making

correlation of variable hydrocarbon concentrations with a narrow range of temperatures difficult to detect. It is possible that improved mixing in the boundary layer, due to higher temperatures, resulted in lower average concentrations and produced the negative correlations seen in Table 5.6, masking any increased emissions due to fuel evaporation from vehicles. The data from Period 1, where a wider range of average temperatures is experienced, provide a clearer description of the impact of temperature changes on hydrocarbon concentrations. However, the correlation coefficients are still very weak.

A method was developed, during this study, to illustrate the impact of evaporative emissions on ambient measured hydrocarbon concentrations. This is presented in the following analysis using hydrocarbon data from Period 1, where a wide range of daily average temperatures were experienced.

Comparison of the ratio of the concentration of any hydrocarbon to that of acetylene over a range of ambient temperatures, should give an indication of the influence of temperature on evaporative emissions. Acetylene is accepted as a tracer for vehicle emissions. Due to its high vapour pressure, the majority of acetylene emissions are related to exhaust rather than evaporative emissions. Hence, for example, if evaporative emissions of n-butane increased relative to exhaust emissions of n-butane, the n-butane / acetylene concentration ratio should increase as the relative exhaust emissions of the two compounds would stay the same. The n-butane / acetylene ratio and temperature are plotted in Figure 5.31. Only days with more than 18 hourly values (75 percent of the day) were employed in calculating daily average concentrations, hence not all days in Period 1 are included.

During the early part of Period 1, the n-butane / acetylene ratio remains relatively constant despite some variations in temperature. Evaporative emissions are only significant at ambient temperatures above 10 °C (Field *et al.,* 1994), and such temperatures are generally not observed until later in the monitoring period, apart from two unusual days where the average temperature just exceeds 10 °C. From day 10 to 15, temperature remains just above 10 °C, and a small increase in the n-butane / acetylene ratio is noted. During the latter part of Period 1, large variations in temperature coincide with corresponding variations in the n-butane / acetylene ratio, which follow a very similar pattern to that displayed by the temperature plot. A similar plot for isopentane is given in Figure 5.32.

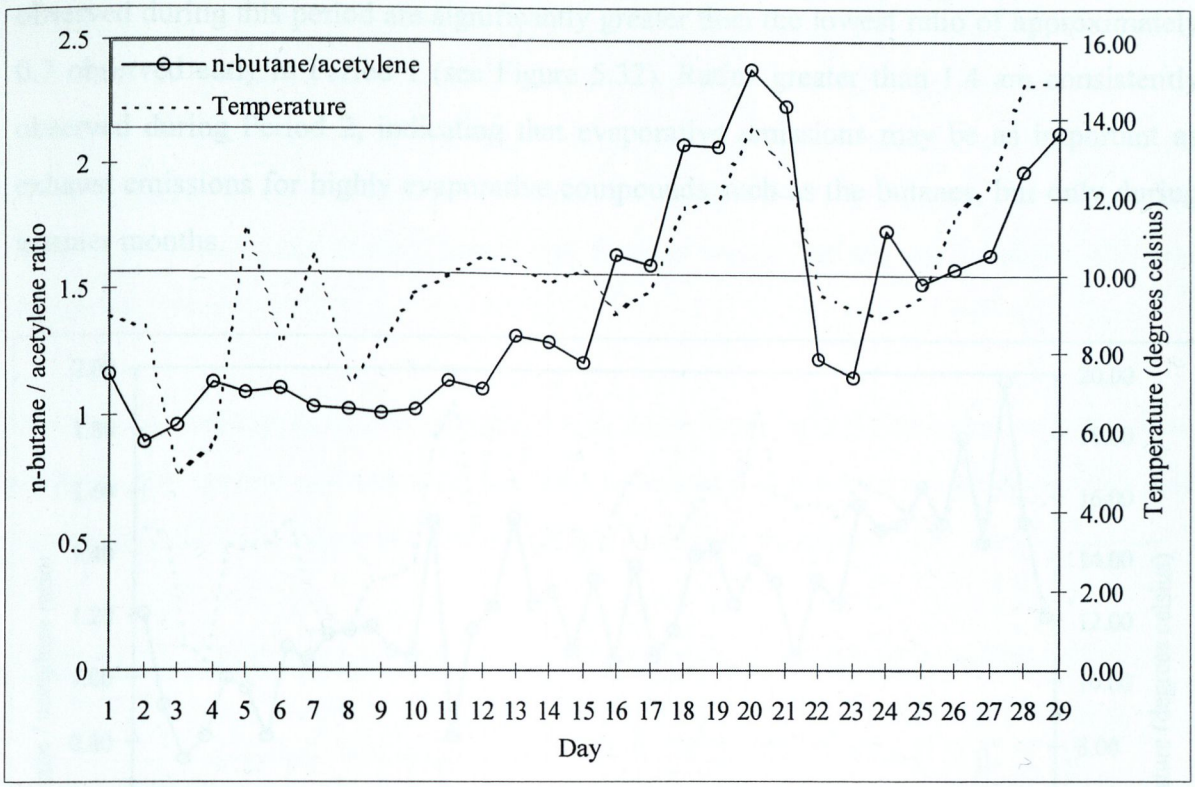


Figure 5.31 Daily average n-butane / acetylene ratio and temperature, Period 1

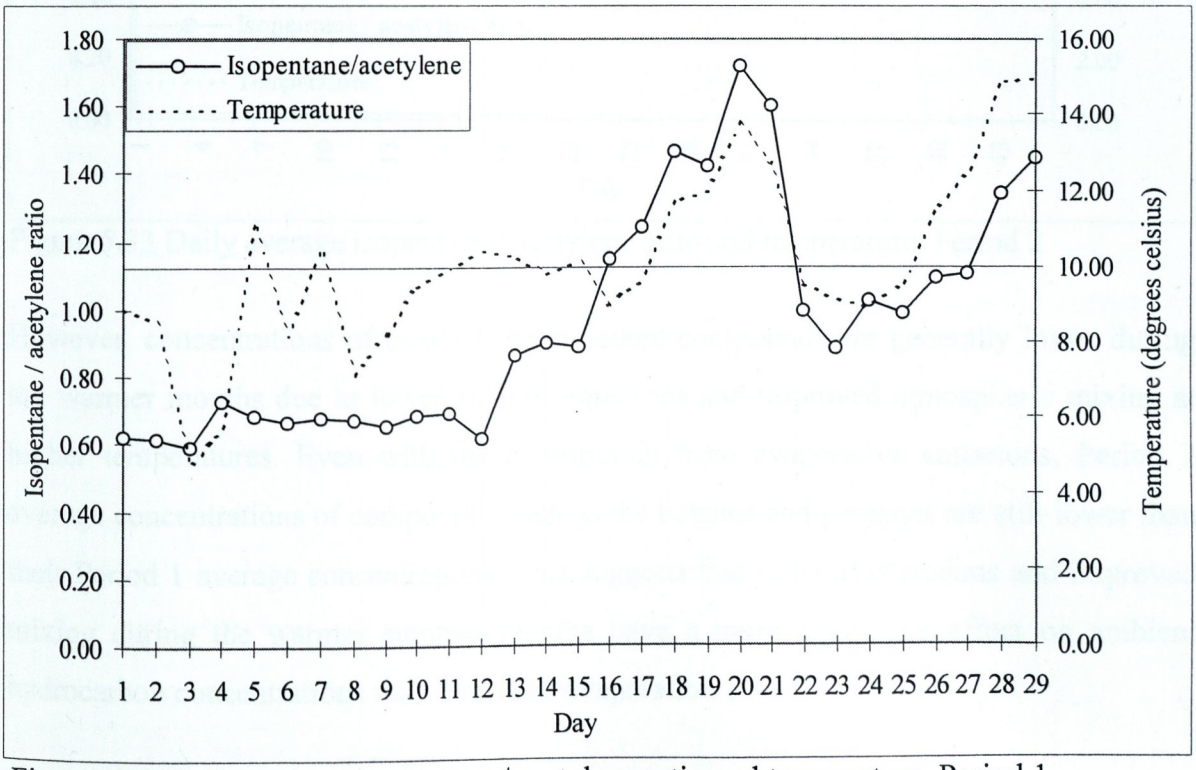


Figure 5.32 Daily average isopentane / acetylene ratio and temperature, Period 1

These results suggest that total evaporative emissions of some compounds can equal their exhaust emissions under certain circumstances. For example, the n-butane / acetylene ratio observed during hot weather is twice that observed during colder weather. The variation of the isopentane / acetylene ratio during Period 2 is shown in Figure 5.33. The ratios

observed during this period are significantly greater than the lowest ratio of approximately 0.7 observed early in Period 1 (see Figure 5.32). Ratios greater than 1.4 are consistently observed during Period 2, indicating that evaporative emissions may be as important as exhaust emissions for highly evaporative compounds such as the butanes, but only during warmer months.

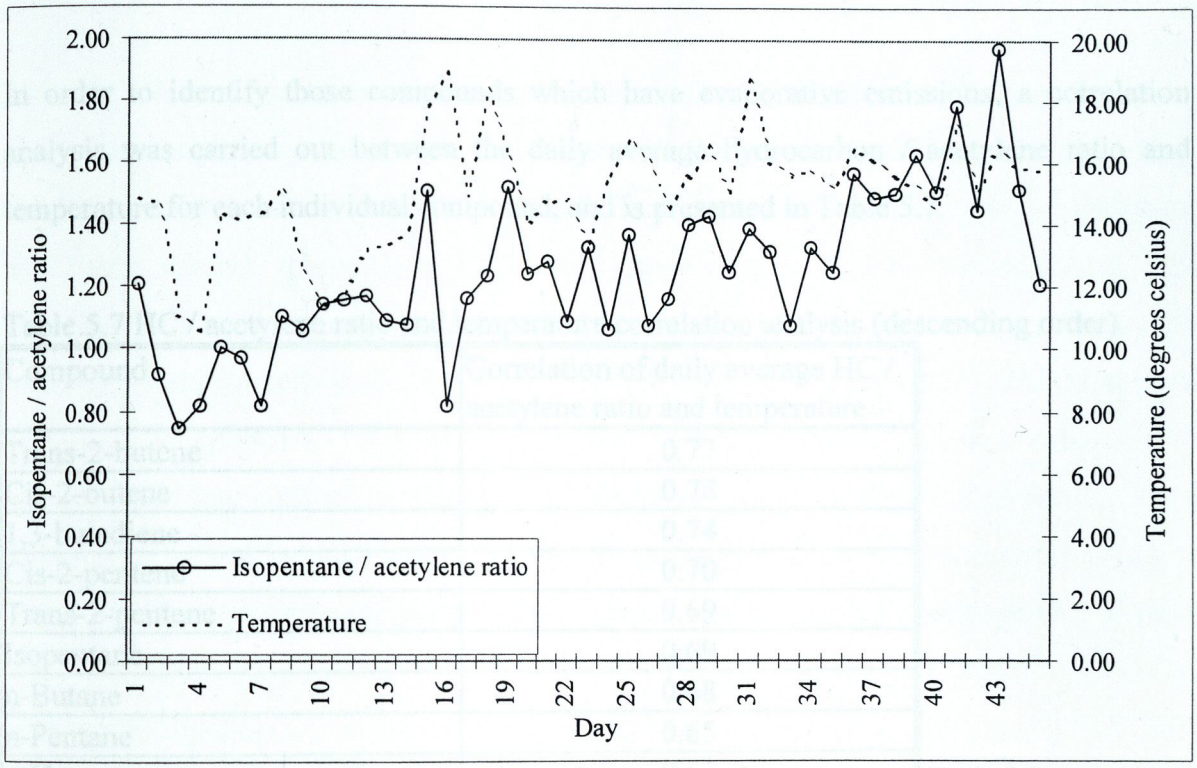


Figure 5.33 Daily average isopentane / acetylene ratio and temperature, Period 2

However, concentrations of most of the measured compounds are generally lower during the warmer months due to lower exhaust emissions and improved atmospheric mixing at higher temperatures. Even with the contribution from evaporative emissions, Period 2 average concentrations of compounds such as the butanes and pentanes are still lower than their Period 1 average concentrations. This suggests that reduced emissions and improved mixing during the warmer summer months have a more significant effect on ambient hydrocarbon concentrations than increased evaporation.

US research has reported that evaporative losses from spark ignition motor vehicles may constitute the majority of the total vehicles emissions over the course of a year (Pierson *et al.*, 1999), with estimates of evaporative contribution to total vehicle hydrocarbons emissions ranging between 20 and 70 percent. However, differences in the reported contribution from evaporative emissions between such studies can be large. For example,

Thijsse *et al.* (1999a) estimate a six percent contribution from vehicle evaporative emissions to hydrocarbons in Berlin, compared to 89 percent from the exhaust. The UK emissions inventory estimates that vehicle evaporative emissions contribute 17 percent, on average, to total emissions from petrol vehicles (DETR, 1998c). Differences in evaporative emissions between the United States and Europe would be expected due to climatic variations.

In order to identify those compounds which have evaporative emissions, a correlation analysis was carried out between the daily average hydrocarbon / acetylene ratio and temperature for each individual compound, and is presented in Table 5.7.

Table 5.7 HC / acetylene ratio and temperature correlation analysis (descending order)

Compound	Correlation of daily average HC / acetylene ratio and temperature
Trans-2-butene	0.77
Cis-2-butene	0.76
1,3-butadiene	0.74
Cis-2-pentene	0.70
Trans-2-pentene	0.69
Isopentane	0.69
n-Butane	0.68
n-Pentane	0.65
n-Hexane	0.63
1,2,4-trimethylbenzene	0.60
Isobutane	0.60
Benzene	0.59
Isoprene	0.59
1,3,5-trimethylbenzene	0.58
Ethylene	0.57
m+p-Xylene	0.55
Ethylbenzene	0.54
o-Xylene	0.54
Propylene	0.51
n-Heptane	0.42
3-methylpentane	0.40
Propane	0.30
Toluene	0.25
Ethane	0.23
1-Butene	-0.06
2-methylpentane	-0.14

A moderately strong correlation is observed for the majority of the hydrocarbons, indicating some contribution of evaporative emissions to ambient concentrations. However, the magnitude of this contribution is not considered in the correlation coefficient, hence some compounds may only have a small evaporative component. The actual amount of evaporative emissions of a given compound will depend on the quantity of that compound present in the fuel.

In Table 5.7, the highly reactive butenes have the highest correlation coefficients; however, the quantities of these compounds in the fuel are normally very small (see Section 5.3.3). Analysis of hydrocarbon data from the UK hydrocarbon monitoring network has also associated alkenes (particularly C_4 alkenes such as the butenes, pentenes and 1,3-butadiene) with evaporative emissions (Derwent *et al.*, 2000). These are the compounds with the strongest correlations in Table 5.7. The only C_4 alkene which exhibits a poor correlation is 1-butene. This is likely to be due to the large number of zero measurements observed for this compound. Compounds which are normally reported as having large evaporative emissions, such as the butanes and pentanes also show a strong correlation in Table 5.7. Butanes and pentanes have the highest mass evaporative emissions due to their large proportion in petrol (see Section 5.3.3), though they are not evaporated as easily as some of the alkenes.

It is generally difficult to distinguish evaporative emissions from exhaust emissions using only ambient measurements because, as noted in other studies, evaporative and exhaust emissions are so closely and consistently related that they behave as if they arose from a single motor traffic source (Derwent *et al.*, 2000). The above method is an effective way of assessing evaporative emissions, and can be applied to hourly as well as daily data. For example, Figure 5.34 shows the n-butane / acetylene ratio over the course of the average day for Period 1. The highest ratio is observed during the middle of the day, when temperatures are highest. The same pattern can be seen for other evaporative hydrocarbons including the alkenes.

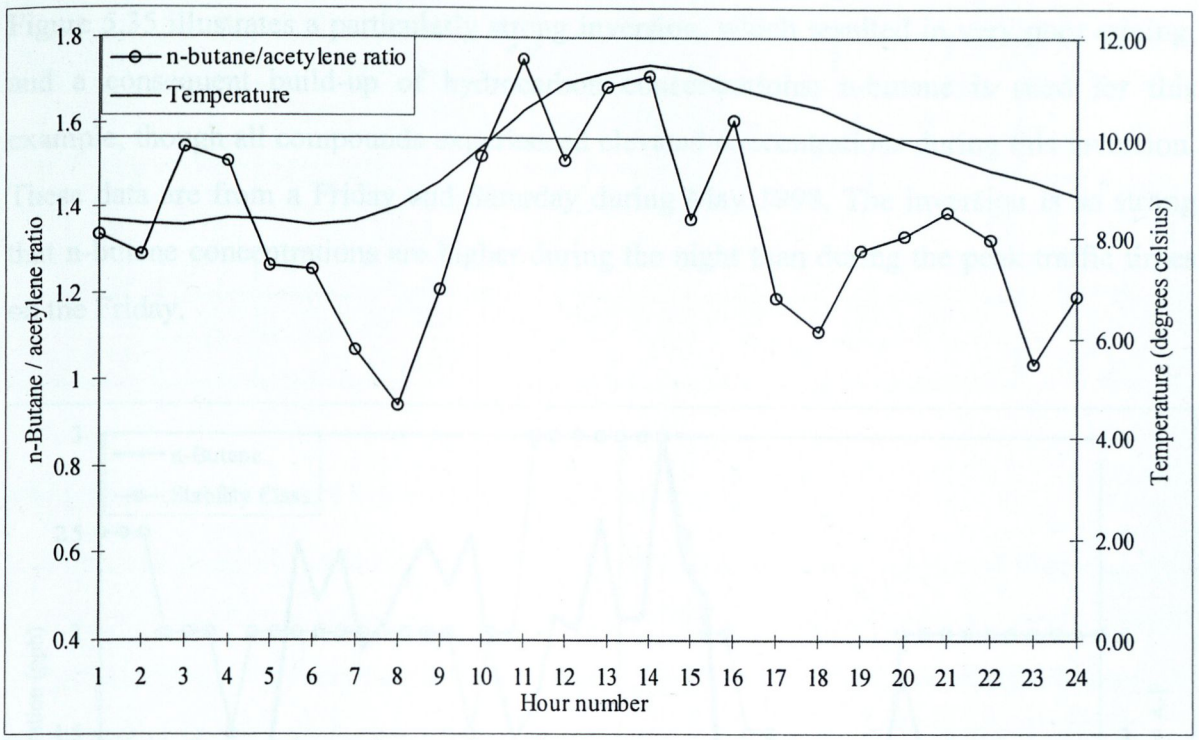


Figure 5.34 n-Butane / acetylene ratio and temperature over the course of the average day

5.2.4 Effect of Stability Class on Hydrocarbon Concentration

Atmospheric stability class defines the degree of upward motion of air due to thermal buoyancy, and depends upon the temperature gradient of the atmosphere (Carruthers *et al.*, 1996). During an inversion, the height of the mixing layer may be reduced to 100 m or less, compared to a typical height of 800 m in the UK and Ireland (Carruthers *et al.*, 1996). During the summer the depth of the mixing layer can be around 1500 m, leading to improved atmospheric mixing and pollutant dispersion. Inversions are most likely to occur during cool, still, clear winter nights.

The stability classification runs from A (very unstable) to F (very stable). The predominant stability class experienced in Ireland is class D, which represents conditions close to neutral stability. For example, available data for April to August 1998, indicate that 77 percent of the hourly observed stability classifications were class D, compared to 9.0 and 5.5 percent for classes E and F, respectively. These data were collected at the Dublin airport synoptic monitoring station run by Met Eireann, as stability class data were not measured on site. The monitoring site is close to the airport (approximately 10 miles), hence the data were expected to be applicable.

Figure 5.35 illustrates a particularly strong inversion, which resulted in very poor mixing, and a consequent build-up of hydrocarbon concentrations; n-butane is used for this example, though all compounds experienced elevated concentrations during this inversion. These data are from a Friday and Saturday during May 1998. The inversion is so strong that n-butane concentrations are higher during the night than during the peak traffic times on the Friday.

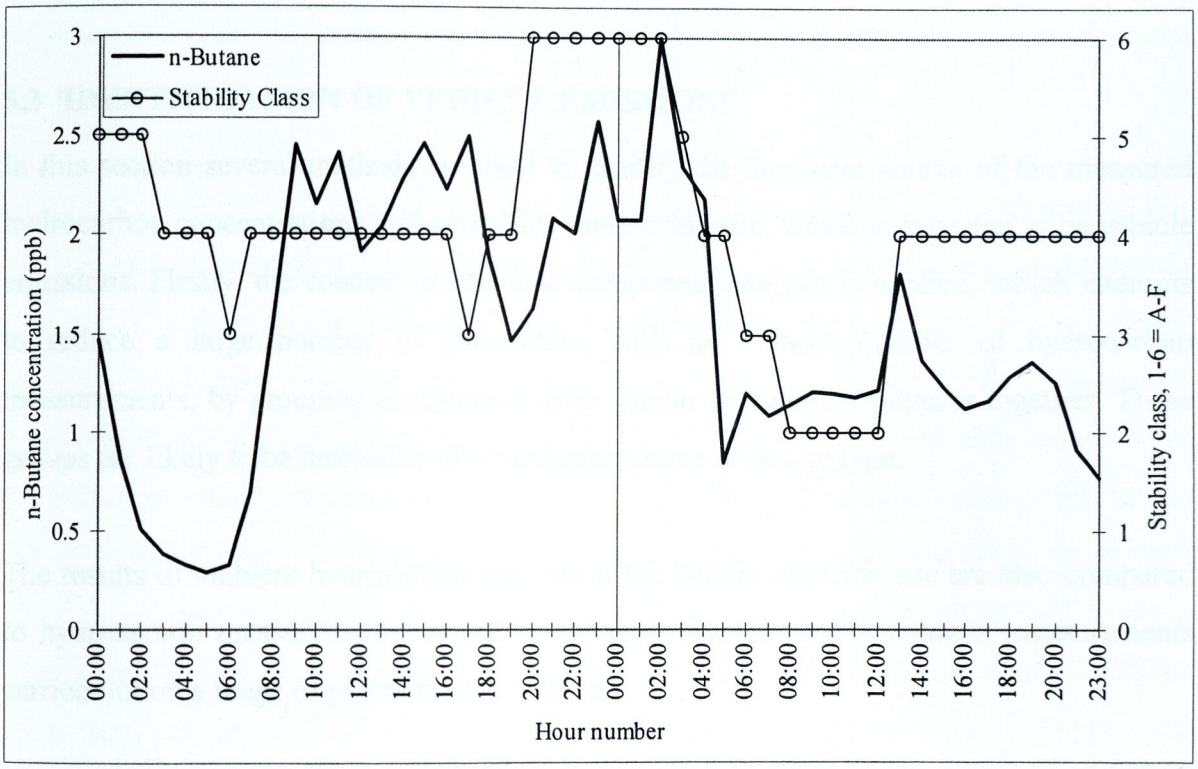


Figure 5.35 Stability class and n-butane concentration over a two day period

As stability classes E and F normally occur during night-time hours, the impact of stability class on night-time concentrations was analysed, the 12 hour off-peak period from 20:00 to 08:00 being employed. The average concentration measured during the occurrence of each stability class was calculated for all monitored data between April 1 and July 31 1998 (mostly Period 2). The results are presented in Table 5.8. The concentration data are presented as the sum of all the measured alkanes and alkenes (except n-hexane and n-heptane), as all these compounds were measured between April 1 and July 31 (covering part of monitoring Periods 1 and 2). The average concentration measured during periods where stability class F was observed is over 32 ppb, nearly twice that observed under more usual conditions (classes C, D and E). This suggests that stable atmospheric conditions can have a measurable effect on night-time hydrocarbon concentrations.

Table 5.8 Average off-peak concentration (sum of the concentration of all measured alkanes and alkenes) for each stability class

Stability class	Average concentration	Percentage of total hours for each stability class
B	too few data points	0.3
C	14.94	4.63
D	12.32	73.03
E	17.76	13.76
F	32.16	8.29

5.3 IDENTIFICATION OF VEHICLE EMISSIONS

In this section several methods are used to identify the dominant source of the measured hydrocarbon concentrations at the roadside monitoring site, which is expected to be vehicle emissions. Firstly, the concept of principal component analysis is applied, which attempts to reduce a large number of parameters, such as a large number of hydrocarbon measurements, by grouping components with similar behavioural patterns together. These groups are likely to be indicative of a particular source or source type.

The results of ambient hydrocarbon analysis at the Dublin roadside site are also compared to hydrocarbon measurements carried out in road tunnels, and to exhaust measurements carried out on a range of petrol-fuelled vehicles.

Results of detailed hydrocarbon analyses of a selection of Irish retail leaded and unleaded fuels are also presented. The proportion of each measured hydrocarbon in the fuels and in the ambient air is compared, to quantify the contributions of the raw fuel constituents to ambient concentrations.

5.3.1 Principal Component Analysis

Principal component analysis can assist in the objective determination of patterns of covariance between pollutants which are generally highly correlated (Derwent *et al.*, 1995), as is the case with the hydrocarbons in this study. This method has been used successfully in ambient air pollution studies (Thurston and Spengler, 1985; Wolff and Korsog, 1985; PORG, 1993; Derwent *et al.*, 1994; Derwent *et al.*, 1995; Pio *et al.*, 1996; Shi and Harrison, 1997; Main *et al.*, 1999), and in many cases has helped to identify sources of hydrocarbons, and the individual compounds associated with a particular source.

In principal component analysis, a large number of variables X_1, X_2, X_3, ..., X_n are represented by a smaller number of principal components Z_1, Z_2, ..., Z_p. Each component represents a pattern of association between a number of the original variables. Each principal component is assigned a factor loading for each of the original variables, indicating the extent to which each variable is associated with the particular factor. In principal component analysis carried out on air pollution data, it has often been found that different principal components can be associated with different sources, or different pollutant behaviour.

Principal component analysis carried out on the hydrocarbon data collected during this study reinforced the findings from previous data analyses, indicating that vehicle emissions were the dominant source of hydrocarbons at this site. The data were analysed on a week by week basis, with normally over 80 percent of the variance in concentrations being accounted for by a single factor, almost certainly vehicle emissions. The eigenvalues from the principal component analysis matrix indicate the proportion of the variance accounted for by a single factor. Although many factors are normally calculated, only those with eigenvalues greater than 1.0 are normally significant (Wolff and Korsog, 1985), while component loadings for the original variables are normally only considered if their absolute value is greater than about 0.2 (Pio *et al.*, 1996). The results from the principal component analysis of a sample week of data are presented in Table 5.9; only the components with the four highest eigenvalues are included. Results for other weeks revealed similar findings. The data analysis package 'DataDesk' was used to carry out the analysis.

The four principal components in Table 5.9 account for 94 percent of the variance observed in the hydrocarbon data. The first factor (principal component PC1) correlates well with all the measured hydrocarbons, although the factor loading for ethane, propane, isoprene, n-heptane and toluene are slightly weaker than the other compounds. This component is likely to represent the typical diurnal pattern followed by the majority of measured hydrocarbons, which is related to vehicle emissions and traffic flow variations during the day. The slightly weaker factor loadings for some compounds are due to deviations from this typical diurnal pattern caused by contributions from other, non vehicle-related sources.

Table 5.9 Results of principal component analysis for one week of hourly hydrocarbon data

Compound	PC1	PC2	PC3	PC4
Ethane	-0.346	-0.870	-0.089	0.162
Ethylene	-0.952	-0.139	0.004	0.148
Propane	-0.537	-0.767	0.084	-0.046
Propylene	-0.979	0.000	0.033	0.155
Isobutane	-0.934	-0.117	0.104	-0.279
n-Butane	-0.956	-0.083	0.094	-0.226
Acetylene	-0.962	0.028	0.002	0.044
Trans-2-butene	-0.981	0.093	0.071	-0.100
1-Butene	-0.801	0.116	-0.180	0.312
Cis-2-butene	-0.980	0.075	0.062	-0.123
Isopentane	-0.979	0.064	0.071	-0.155
n-Pentane	-0.987	0.004	0.052	-0.100
1,3-butadiene	-0.972	0.069	-0.005	0.101
Trans-2-pentene	-0.949	0.073	0.103	-0.052
Cis-2-pentene	-0.969	0.118	0.062	-0.093
2-methylpentane	-0.975	0.113	0.017	-0.110
3-methylpentane	-0.976	0.135	0.030	-0.069
Isoprene	-0.754	0.258	0.135	0.225
n-Hexane	-0.949	-0.078	-0.061	-0.105
Benzene	-0.988	0.091	0.024	0.068
n-Heptane	-0.760	-0.468	-0.141	-0.072
Toluene	-0.648	0.168	-0.694	-0.182
Ethylbenzene	-0.982	0.088	0.004	0.088
m+p-Xylene	-0.979	0.086	-0.006	0.098
o-Xylene	-0.981	0.090	0.004	0.102
1,3,5-trimethylbenzene	-0.965	-0.008	-0.029	0.148
1,2,4-trimethylbenzene	-0.955	-0.025	-0.032	0.165
Eigenvalue	22.339	1.825	0.627	0.580
Variance proportion	82.700	6.800	2.300	2.100

The second factor (PC2) has significant factor loadings for ethane and propane and also for n-heptane. Ethane and propane have already been identified as natural gas emissions; however, n-heptane is not a component of natural gas used in Dublin (see Table 5.4). This suggests another unknown but consistent source of n-heptane. The third factor only displays a significant factor loading for toluene, and is therefore likely to be related to the non-vehicle source of toluene identified in Section 5.2.1. The eigenvalue for this principal component is small, as it is associated with only one hydrocarbon. The fourth factor has weak factor loadings for all compounds. The higher factor loadings are assigned to the butanes, 1-butene and isoprene. The butanes are known to be important evaporative compounds, as are alkene compounds (including 1-butene) while isoprene emissions from natural sources are known to increase with increasing temperature. It is possible that this

factor is related to the effect of ambient temperature increases on hydrocarbon concentrations. However, the eigenvalue for this factor is small, accounting for only a very small proportion of the variance in the measured data.

By far the most important factor is PC1, which accounts for 82.7 percent of the observed variance. This emphasises the dominance of vehicle emissions at this monitoring site. The importance of natural gas leakage to the measured ethane and propane concentrations is also emphasised, as the eigenvalue for this factor is significant (> 1). The results from the principal component analysis corroborate earlier observations on the sources and behaviour of pollutants.

5.3.2 Comparison of Roadside, Tunnel and Exhaust Sampling Results

Many studies have been carried out in road tunnels in an attempt to identify the typical 'fingerprint' of road vehicle emissions, as the pollutants measured in the tunnel can be unequivocally assumed to be vehicle related. Other studies have measured the exhaust composition of vehicles under different operating conditions to identify typical vehicle emissions. Comparison of these tunnel and exhaust study results with roadside results will indicate the extent to which the ambient measurements from this study represent a 'fingerprint' of vehicle emissions in Dublin. Results from several different tunnel studies and vehicles exhaust emission tests are presented in Table 5.10. Most of the studies have been carried out in either the USA or Australia, however results from some European studies are included.

Overall average results from Monitoring Periods 1 and 2 and the average concentrations during weekday peak traffic hours, 08:00 to 09:00 and 17:00 to 18:00, for Period 1 and 2, respectively, are included in Table 5.10. The peak-hour measurements are most likely to represent the effects of the emissions from vehicles. Many of the tunnel and exhaust emissions studies report hydrocarbon data either as the mass of each hydrocarbon emitted per mile travelled or as a percentage of the total measured hydrocarbons. To overcome the differences in units between the studies, all results are given as the ratio of each hydrocarbon measurement relative to that of acetylene. Results from four of the studies present exhaust analysis results for both catalyst and non-catalyst vehicles (study numbers 11 / 12, 13 / 14, 15 / 16 and 20 / 21). Comparison of the Dublin hydrocarbon data with both

catalyst and non-catalyst studies should give an indication of the relative contributions of catalyst and non-catalyst emissions to roadside hydrocarbon concentrations in Dublin. Few of the studies measure all of the compounds monitored in Dublin, but most measure a reasonable range of compounds. The study by Leppard *et al.* (1992) (study number 18) presents emissions measurements for the major partial oxidation products from petrol combustion, i.e. compounds which are not present in the fuel but are present in the exhaust emissions. There is good agreement between the hydrocarbon / acetylene ratio observed for the Dublin measurements and those reported in several of the exhaust and tunnel studies. Poor agreement for ethane and propane is due to the contribution from natural gas to the concentrations of these compounds in Dublin.

Comparing the Dublin peak hour ratios to the Australian exhaust sample results (study no. 5) reveals good agreement for the majority of the measured compounds. The main exceptions are the butanes which have a much higher ratio to acetylene for the Dublin ambient data compared to the Australian exhaust measurements. The high butane ratios measured in Dublin are likely to be the result of contributions from evaporative emissions, which are not presented in exhaust measurement studies. The average Irish fuel butane content (5.5 percent on average, see Section 5.3.3) is also greater than the typical fuels used during the Australian study (4.1 percent) (Nelson *et al.*, 1983).

Study numbers 6, 7 and 8 present data from a number of tunnel studies carried out in the USA. The ratios to acetylene tend to be greater for the US studies compared to Dublin ambient roadside data. This indicates very efficient catalytic removal of acetylene. The main exceptions are the butanes, which exhibit lower ratios to acetylene compared to the Dublin data. This is likely to be due to the reformulated fuels used in the United States which have low butane content, and hence low butane exhaust and evaporative emissions.

Table 5.10 HC : acetylene ratio for this roadside study and for other tunnel and exhaust measurement studies

Study Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Ethane	1.55	1.53	1.02	0.73		0.72	0.43	0.83	0.17	0.16	0.15	0.67	0.10	2.10	0.14	0.40	0.30	0.17	0.16	0.11	1.12
Ethylene	1.82	1.93	1.54	1.62	1.05	2.93	2.53	3.31	1.56	1.30	1.27	1.50	1.07	3.01	0.85	1.46	0.94	1.48	1.29	1.23	2.27
Propane	0.76	0.77	0.44	0.34		0.05	0.15	0.00	0.04	0.05	0.05	0.17	0.03	0.34	0.02	0.05	0.66		0.01	0.01	0.04
Propylene	0.56	1.08	0.44	0.52	0.46	1.11	0.73	0.79	0.46	0.59	0.73	0.83	0.52	1.49	0.60	0.75	0.78	0.78	0.57	0.52	0.96
Isobutane	0.56	0.46	0.50	0.43	0.11	0.10			0.14	0.40	0.36	1.00			0.13	0.22	0.40		0.11	0.02	0.19
n-Butane	1.37	1.36	1.20	1.12	0.22	0.86	0.56	0.61	0.34	0.80	0.55	2.00			0.28	0.50	0.58		0.24	0.16	1.69
Acetylene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Trans-2-butene	0.07	0.07	0.06	0.07		0.17			0.04	0.24	0.15	0.20			0.06	0.08	0.10		0.07	0.06	0.12
1-Butene	0.03	0.11	0.02	0.02					0.06	0.10	0.07	0.03							0.10	0.10	0.15
Cis-2-butene	0.07	0.07	0.06	0.06		0.12			0.03	0.05	0.04	0.07			0.04	0.06	0.09		0.06	0.02	0.23
Isopentane	0.93	1.11	0.78	0.89	0.54	4.26	1.17	1.73	0.75	1.04	0.91	2.50			0.84	1.63	0.96		0.55	0.45	1.62
n-Pentane	0.32	0.39	0.25	0.29	0.33	1.29	0.41	0.62	0.07	0.36	0.36	0.83			0.50	0.88	0.37		0.34	0.23	0.69
1,3-butadiene	0.14	0.13	0.11	0.12		0.23					0.11	0.13	0.01	0.01	0.11	0.15	0.16	0.17	0.00	0.14	0.08
Trans-2-pentene	0.09	0.07	0.08	0.10		0.28			0.03										0.03		
Cis-2-pentene	0.06	0.05	0.04	0.05		0.17			0.01										0.03		
2-methylpentane	0.14	0.18	0.12	0.14	0.24	1.38	0.39	0.48	0.12						0.30	0.63	0.39		0.26	0.16	0.81
3-methylpentane	0.13	0.14	0.11	0.14	0.17	0.78	0.23	0.29	0.06						0.26	0.46	0.25		0.18	0.13	0.50
Isoprene	0.05	0.09	0.03	0.04		0.14									0.01	0.03					
n-Hexane	0.17		0.12	0.17	0.20	0.63	0.22	0.24	0.02						0.23	0.42	0.24		0.22	0.10	0.38
Benzene	0.64		0.49	0.62	0.55	1.97	0.67	0.80		1.20	0.91	2.00	0.74	2.63	0.94	1.75	0.78	0.45	0.57	0.43	1.42
n-Heptane	0.06		0.04	0.05		0.33	0.08								0.08	0.15	0.10		0.09	0.07	0.12
Toluene	1.18		1.10	1.17	1.13	3.81	0.94	1.23		2.79	2.09	3.33	1.61	4.96	1.63	2.58	1.39	0.31	1.17	0.70	3.42
Ethylbenzene	0.17		0.12	0.16	0.21	0.94	0.14	0.28		0.83	0.45	0.67			0.22	0.38	0.19		0.22	0.14	0.50
m+p-Xylene	0.56		0.40	0.53	0.74	3.19	0.57	0.97		2.63	1.82	3.00			0.79	1.46	0.73		0.75	0.51	1.35
o-Xylene	0.21		0.15	0.20	0.28	1.17	0.24	0.34		1.06	in total	in total			0.29	0.50	0.27		0.29	0.19	0.50
1,3,5-trimethylbenzene	0.15		0.10	0.13		0.54		0.14							0.06	0.13	0.06		0.08	0.07	0.50
1,2,4-trimethylbenzene	0.26		0.18	0.23	0.23	2.01	0.19	0.57							0.14	0.18	0.16		0.22	0.22	0.73

1: Average for monitoring Period 1
2: Average for monitoring Period 2
3: Average for 08:00 to 09:00, Period 1
4: Average for 17:00 to 18:00, Period 2
5: Australia, exhaust (1970s); Nelson and Quigley, 1984
6: USA, tunnel (1992); Sagebiel *et al.*, 1996
7: USA, tunnel (1991); Zielinska and Fung, 1994
8:USA, tunnel (1992); Zielinska *et al.*, 1996
9: France, tunnel (1996); Touaty and Bonsang, 2000
10: UK exhaust study (1987); Bailey *et al.*, 1990
11: Germany, exhaust (1995), non-catalyst; Friedrich and Obermeier, 1999
12: Germany exhaust (1995), catalyst; Friedrich and Obermeier, 1999
13: USA, exhaust (1970s), non-catalyst; Hoekman, 1992
14: USA, exhaust (1980s), catalyst; Hoekman, 1992
15: Australia, exhaust ('80 - '85), non-catalyst; Duffy *et al.*, 1999
16: Australia, exhaust ('86 - '91), catalyst; Duffy *et al.*, 1999
17: Australia, tunnel (1995); Duffy *et al.*, 1999
18: USA, exhaust (1990); Leppard *et al.*, 1992
19: Australia, exhaust (1970s); Nelson *et al.*, 1983
20: USA, exhaust (1988), non-catalyst; Harley *et al.*, 1992
21: USA, exhaust (1988), catalyst; Harley *et al.*, 1992

Several European studies are presented in Table 5.10 (study numbers 9, 10, 11 and 12). Agreement of the Dublin data with the French tunnel study (number 9) is reasonable for most of the measured compounds, and excellent for a few. However, the results from this tunnel study were averaged over six discrete grab samples, hence the representativity of this average may be called into question. Agreement with the UK exhaust measurements (study number 10) is particularly good for the alkanes and alkenes, but not good for aromatic compounds. The lack of agreement for the aromatic compounds is unexpected, as the vehicle fleet in the UK consists of the same vehicle types found in Ireland. However, the UK study was carried out in the 1980s, when fuel composition was likely to be different to the mixture of leaded and unleaded fuels used in the late 1990s. Comparison of the Dublin roadside data with the two more recent German studies (studies number 11 and 12, with and without catalyst) indicates better agreement for the non-catalyst data. This would be expected, as a large percentage of the Irish vehicle fleet is still non-catalyst (over 40 percent at the time of monitoring, see Section 4.1), and emissions from these vehicles are likely to dominate vehicle-related ambient hydrocarbon concentrations, particularly when it is considered that an efficient catalyst can remove many compounds completely (99 percent) from the exhaust (Shore and Tonkin, 1991).

Another exhaust measurement study using catalyst and non-catalyst vehicles was carried out in the USA by Hoekman (1992; studies 13 and 14). Although the dataset is limited, good agreement is found for the non-catalyst data, but not for the catalyst data. This agrees with the previous German studies (studies 11 and 12) and again confirms the dominance of emissions from non-catalyst vehicles at the time of monitoring. The exhaust study by Duffy *et al.* (1999; study numbers 15 and 16) present results for catalyst and non-catalyst vehicles commonly used in Australia. Catalysts were fitted to all Australian vehicles from model year 1986, hence cars from before and after this period were used in the study. The non-catalyst Australian results are in good agreement with the Dublin ambient results, and as in the previous Australian study (number 5), there is some discrepancy for the butanes. As with the previous catalyst / non-catalyst studies, agreement is poorer with the catalyst equipped emissions results.

The results from the catalyst studies also indicate the likely changes that can be expected in the characterisation of the Dublin ambient hydrocarbon content, as catalyst vehicles begin to dominate hydrocarbon emissions in the city centre. Catalysts do not have the same

removal efficiency for all hydrocarbons (Shore and Tonkin, 1991), and hence the relative concentrations of hydrocarbons in the exhaust is altered as are the relative ambient concentrations. It can also be expected that average hydrocarbon concentrations measured in Dublin will decrease as catalyst equipped vehicles become dominant in the Irish vehicle fleet, resulting in lower mass hydrocarbon emissions per vehicle.

The results from an Australian tunnel study (study number 17) are in good agreement with the ambient measured data from Dublin. Many of the hydrocarbon / acetylene ratios are slightly higher than those for the Dublin data. This suggests that catalyst equipped vehicles are more dominant in Australia compared to Ireland, as other studies which present both catalyst and non-catalyst data indicate that the hydrocarbon / acetylene ratio for catalyst equipped vehicles is generally higher compared to non-catalyst vehicles (see study numbers 11 / 12, 13 / 14, 15 / 16 and 20 / 21).

The study carried out by Leppard *et al.* (1992; study number 18) presents data on the exhaust emissions of compounds which are partial oxidation products, i.e. compounds formed by oxidation of other hydrocarbons. Agreement is good for all of the measured compounds, with the exception of toluene, which may be influenced by non-vehicle emissions at the Dublin monitoring site. This indicates that the concentrations of these compounds measured in Dublin are vehicle related, even though, as will be seen in Section 5.3.3, these compounds are not present in typical Irish fuels.

Results from another Australian exhaust measurement study carried out in the 1970s on non-catalyst vehicles are presented by Nelson *et al.* (1983, study number 19). Agreement with the Dublin hydrocarbon data is very close, with the exception of the butanes (as with the other Australian exhaust studies).

Finally, another US exhaust study carried out by Harley *et al.* (1992; study numbers 20 and 21) on 1980s US model vehicles, with and without catalysts, indicates similar results to other such studies. Compared to the Dublin results, better agreement is observed with non-catalyst equipped vehicles, while the catalyst equipped vehicles show higher hydrocarbon / acetylene ratios for most compounds. For the non-catalyst equipped vehicles, some discrepancy is noted for the butanes, for the reasons outlined earlier. The UK hydrocarbon emission inventory reports that the evaporative contribution to total butane emissions from

vehicles is likely to exceed that due to exhaust emissions (see Table 2.9), hence the exhaust butane / acetylene ratio can be expected to be lower than the ambient air ratio.

Overall, the ambient hydrocarbon data from the Dublin site demonstrate good agreement with analysis of vehicle hydrocarbon exhaust emissions and ambient tunnel hydrocarbon concentrations from other studies, although some differences are to be expected between results from different monitoring studies, as was noted for several recent exhaust and tunnel measurement studies carried out in the United States (Conner *et al.,* 1995). Some discrepancy has been noted for the major evaporative compounds (butanes), but agreement for other hydrocarbons is good. Better agreement is observed in studies on non-catalyst vehicles, suggesting that ambient hydrocarbon concentrations in Dublin are more influenced by such emissions than by emissions from catalyst equipped vehicles. Moreover, it is known that catalysts do not always operate at full efficiency, especially after a vehicle cold-start. In this context, it is interesting to note that the pattern of higher hydrocarbon / acetylene ratios observed in studies on catalyst equipped vehicles, is also observed when the evening and morning peak roadside results are compared, with a higher hydrocarbon / acetylene ratio being observed for the evening compared to the morning peak concentrations for most hydrocarbons. In the following section, the important relationship between hydrocarbon content in petrol and ambient air will further explain the association between vehicle emissions and urban ambient hydrocarbon concentrations.

5.3.3 Comparison of Irish Fuels and Roadside Monitoring Results

In urban areas, motor vehicles represent one of the main sources of hydrocarbon emissions. These emissions tend to be either unburned or partially-oxidised fuel components, and many, such as benzene and 1,3-butadiene, are known carcinogens. It has been estimated by the United States Environmental Protection Agency (USEPA) that over half of cancers caused by toxic chemicals in the air are attributable to vehicle fuels (Mirabella, 1997). Recent studies, in both the US and Europe, have sought to relate fuel hydrocarbon content with exhaust emissions, to better understand many of the complex reactions which take place during fuel combustion. The main group of studies are those within the Auto Oil programme - the tripartite co-operative initiative by the European automobile and oil industries and the European Commission (with the federal government in the US) - the results from which are used to develop the latest vehicle emission and fuel quality

standards. The work carried out during the Auto Oil programme has helped to increase understanding of the relationship between fuel content and exhaust emissions.

Although vehicle emissions are diluted by at least a factor of 1000 within a few seconds of leaving the exhaust pipe (Ye *et al.,* 1997), no significant atmospheric reactions occur within this time. The main chemical transformation processes for hydrocarbons in ambient air are reactions with the hydroxyl radical (OH), photolytic processes, reactions with nitrate radicals (NO_3), and reactions with O_3 (see Section 2.5). However, if an air sample is collected near a roadway, the hydrocarbon concentrations are high enough to suppress the ambient O_3 and OH chemistry, and the reactive hydrocarbons will remain preserved in the air sample (Ye *et al.,* 1997). This implies that the proportion of each hydrocarbon in an ambient sample should be similar to that measured in an exhaust sample, except for contributions from non-traffic sources.

To assess the relationship between fuel and ambient hydrocarbon components, a selection of ten leaded and unleaded petrol samples were collected and analysed. In this context, petrol fuels are taken as those used in the operation of positive ignition engines, rather than diesel-fuelled compression ignition engines. Analysis was carried out at the CE-CERT laboratory at the University of California, Riverside, where much research in the field of transport related emissions is performed (Parraguez *et al.,* 1998). During analysis, over 400 compounds were identified in most of the fuel samples. A comparison of these fuels is presented below, and an average Irish fuel composition derived. This average fuel is employed in a comparison of the relative magnitudes of measured ambient hydrocarbon concentrations from a roadside site, and their corresponding fuel content. This comparison facilitates assessment of the extent to which the research carried out during the Auto Oil programme, relating fuel and exhaust composition, can be applied to fuel and ambient air composition. The properties of the measured fuels are also compared to the latest fuel specifications which were to come into force from January 1st 2000. The impact of the changes in fuel properties on ambient hydrocarbon concentrations is predicted.

Analysis of Fuel Samples

Samples of ten different petrol products were collected from four different supply companies (Shell, Statoil, Maxol and Esso) in accordance with the sampling procedure

specified in the California Code of Regulations (State of California, 1992). Samples were collected in amber bottles to provide protection against direct exposure to light, and the bottles were sealed using a plastic screw cap with a Teflon liner. The samples were insulated after collection and during transportation to the laboratory. Two litres of each sample fuel were collected, the ten samples consisting of six unleaded and four leaded fuels. The samples were collected from filling stations, in Dublin city and suburbs, which were known to be busy. Fuel composition can change over time if the fuel remains in the underground storage tanks for extended periods, hence collecting samples from busy stations ensured that this had not occurred. Fuel types are identified as UL and L denoting unleaded and leaded fuels, respectively, and the suffix S refers to a special product (a higher octane fuel). The Shell Pura fuel is marketed on the basis that emissions from the use of this fuel are less damaging to the environment.

The detailed hydrocarbon analysis of the fuels was carried out using Auto/Oil test method number 930144: 'Co-operative study to evaluate a standard test method for the speciation of gasoline by capillary gas chromatography'.

Figure 5.36 details the volume percent by carbon number in each of the analysed fuels; only the $C_4 - C_{11}$ range is shown, all others contributing less than 1 percent each. All fuels display similar distributions, with the C_6 and C_7 contributions being the most consistent. On average, the C_8 component in leaded fuels is 30 percent lower than in unleaded fuels. Compared with all other fuels, Maxol ULS exhibits relatively higher C_4 and lower C_5 content, while the C_4 content of Shell Pura ULS is much lower. Compounds in the C_3 - C_{13} range comprise nearly 100 percent of each fuel. The ambient hydrocarbon results include compounds in the C_2 - C_9 range, which constitutes a large proportion of the identified fuel content. Indeed, the C_5 - C_8 compounds constitute over 80 percent (by volume) of the majority of the fuels analysed.

The percentage of each hydrocarbon group (by volume) in each fuel is given in Figure 5.37. The alkanes constitute the largest contribution to fuel content, followed by the aromatics and the alkenes (olefins). Very few oxygenated compounds are present. Comparing the average content of the leaded and unleaded fuels reveals only small differences: the total alkane content is similar, while the unleaded fuels have slightly higher aromatic content and lower alkene content. Shell Pura unleaded has a very low alkene content and high

alkane and aromatic content, while Statoil unleaded has the lowest aromatic content but the highest alkene content. Comparison with a typical Californian reformulated gasoline (aromatics 21 percent, alkenes 5.5 percent) reveals higher aromatic (32 percent) and alkene (16 percent) content in the Irish fuels (California data from Parraguez *et al.*, 1998).

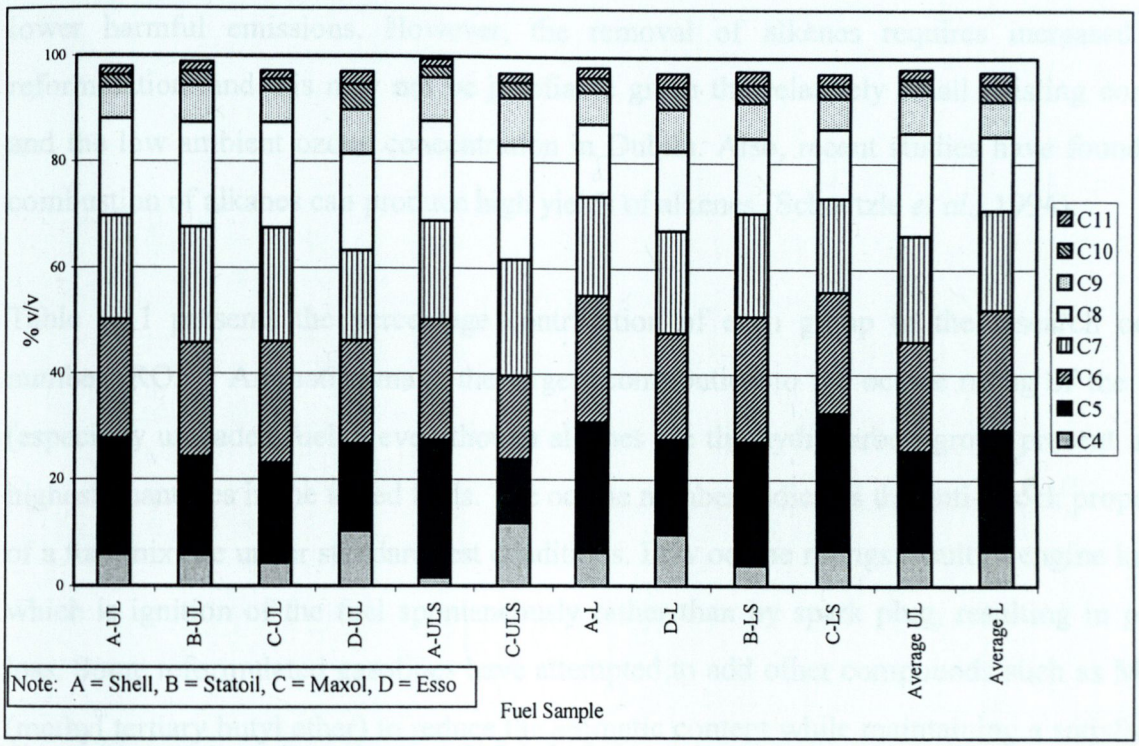


Figure 5.36 Hydrocarbon content of Irish fuels by carbon number (% volume)

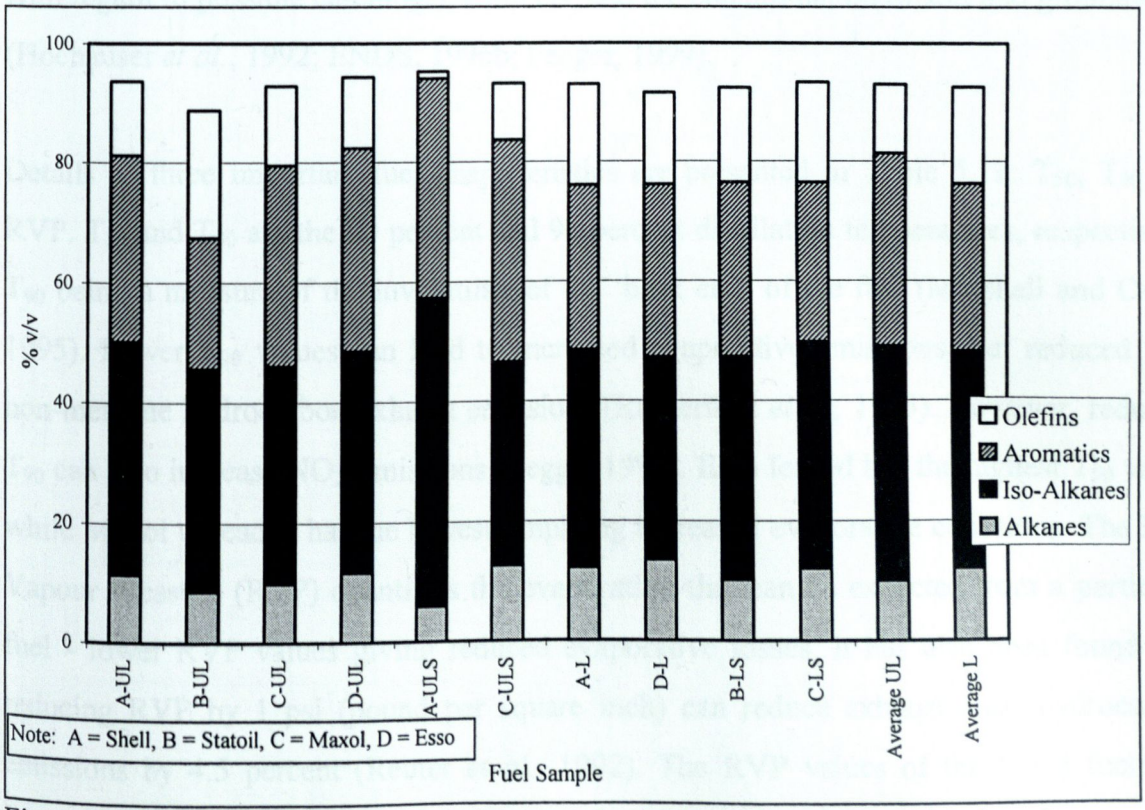


Figure 5.37 Contribution to total fuel content by hydrocarbon group (% volume)

Aromatics and alkenes are generally the more important compounds in fuel content analyses. Many aromatics are toxic compounds and of medium reactivity, contributing to ozone production. Alkenes are highly reactive compounds with high ozone creating potential, and some alkenes are toxic. In contrast, alkanes are unreactive compounds and are generally less toxic than aromatics; suggesting that alkane-based fuels may lead to lower harmful emissions. However, the removal of alkenes requires increased fuel reformulation, and this may not be justifiable given the relatively small existing content, and the low ambient ozone concentration in Dublin. Also, recent studies have found that combustion of alkanes can produce high yields of alkenes (Schuetzle *et al.*, 1994).

Table 5.11 presents the percentage contribution of each group to the research octane number (RON). Aromatics make the largest contribution to the octane rating of the fuels (especially unleaded fuels), even though alkanes are the hydrocarbon group present in the highest quantities in the tested fuels. The octane number indicates the anti-knock properties of a fuel mixture under standard test conditions. Low octane ratings result in engine knock, which is ignition of the fuel spontaneously rather than by spark plug, resulting in power loss. Some reformulated gasolines have attempted to add other compounds such as MTBE (methyl tertiary butyl ether) to reduce the aromatic content while maintaining a satisfactory RON. However, results from testing of such fuels have provided mixed results, particularly with regard to possible carcinogenic effects, and the contamination of soil and groundwater (Hochauser *et al.*, 1992; ENDS, 1996b; Fenger, 1999).

Details of three important fuel characteristics are presented in Table 5.12: T_{50}, T_{90} and RVP. T_{50} and T_{90} are the 50 percent and 90 percent distillation temperatures, respectively; T_{90} being a measure of the involatility of the 'back end' of the fuel (Marshall and Owen, 1995). Lower T_{90} values can lead to increased evaporative emissions, but reduced total non-methane hydrocarbon exhaust emissions (Rutherford *et al.*, 1995). However, reducing T_{90} can also increase NO_X emissions (Legge, 1997). Esso leaded has the highest T_{90} value, while Maxol unleaded has the lowest, implying increased evaporative emissions. The Reid Vapour Pressure (RVP) quantifies the evaporation that can be expected from a particular fuel - lower RVP values giving reduced evaporative losses. It has also been found that reducing RVP by 1 psi (pound per square inch) can reduce exhaust mass hydrocarbon emissions by 4.5 percent (Reuter *et al.*, 1992). The RVP values of the tested fuels are reasonably consistent, with the exception of that of Shell Pura, which is easily the lowest.

Table 5.11 Contribution of each group to RON of tested fuels

	Shell UL	Shell Pura ULS	Shell L	Statoil UL	Statoil LS	Maxol UL	Maxol ULS	Maxol LS	Esso UL	Esso L	Average UL	Average L
Alkanes	6.23	2.50	7.21	5.53	5.47	5.14	8.12	7.57	6.45	7.98	5.66	7.06
Iso-alkanes	30.94	40.50	28.54	28.97	28.61	28.35	26.31	29.93	28.76	26.12	30.64	28.30
Aromatics	43.87	51.53	38.89	29.86	40.29	46.68	50.90	37.66	46.70	38.96	44.92	38.95
Cyclo-alkanes	4.29	3.97	5.12	8.43	5.26	4.13	3.80	4.09	4.33	5.81	4.83	5.07
Alkenes	10.72	0.99	14.79	18.67	13.79	11.31	8.18	14.41	10.22	13.39	10.02	14.10
Total RON	97.43	99.76	95.68	93.14	94.98	97.79	99.49	95.68	96.97	94.04	97.43	95.10

Table 5.12 T_{50}, T_{90} and RVP values for Irish fuels

Fuel	T_{50} (°C)	T_{90} (°C)	RVP (psi)
Shell UL	82	139	11.3
Shell Pura ULS	83	147	9.7
Shell L	82	154	11.0
Statoil UL	92	171	13.6
Statoil LS	79	151	11.1
Maxol UL	86	138	11.6
Maxol ULS	98	162	12.3
Maxol LS	80	154	11.4
Esso UL	89	149	12.5
Esso L	92	170	13.6

Comparison of 1998 Fuel Parameters to EU Limit Values

As a result of the EU Auto Oil programme, new limit values were recently set for fuel quality in directive 98/70/EC relating to the quality of petrol and diesel fuels. This amends the previous limit values as defined in directive 93/12/EC. There has been some criticism of the new limit values for not being strict enough (Mirabella, 1997), as many EU countries already have fuel parameters lower than those proposed in the new directive. The limit values are certainly less stringent than those specified in the US (Mirabella, 1997). Table 5.13 details the limit values which were required to be implemented by January 2000, along with the specifications of the Irish fuels which were collected in February 1998. The current limit values for petrol sold in California are also included in Table 5.13 (Parraguez *et al.*, 1998). The aromatic content of fuels must be reduced to 35 percent by volume by January 2005. Due to upgrading work required at the Whitegate refinery in Cork (which supplies 20 percent of Irish petrol), not all of the specifications in directive 98/70/EC were implemented by January 1 2000. However, recent legislation has now brought fuel specifications fully into line with the standards in directive 98/70/EC. The new regulations are entitled Air Pollution Act, 1987 (Environmental Specifications for Petrol and Diesel Fuels) Regulations, 2000 (S.I. no. 72 of 2000). The full standards were required to be implemented by March 31st 2000.

Table 5.13 indicates that the analysed 1998 fuels do not meet all of the specifications defined in the directive, particularly the vapour pressure specifications. Only Statoil unleaded is below the minimum RON limit value, probably due to its low aromatic content, with all others having RONs close to 100. All of the fuels are below the limit value specified for maximum aromatic content, and only one of the fuels exceeds the maximum alkene content limit value. Indeed, several of the fuels already comply with the 2005 aromatic limit value, with the remainder being only slightly above. Several of the fuels have a relatively high benzene content, with only two fuels complying with the January 2000 limit value. Generally, the fuels show reasonable compliance with the limit values.

Table 5.13 Selected specifications for market fuels to be used for vehicles equipped with positive-ignition engines (CEC, 1998b)

Parameter	Limit				Irish fuel specifications					
	Unit	Minimum	Maximum	Californian limits	Shell UL	Maxol ULS	Maxol UL	Shell Pura ULS	Statoil UL	Esso UL
Research octane number (RON)		95.00	-		97.43	99.49	97.79	99.76	93.14	96.97
Reid vapour pressure (summer only)	kPa	-	60.00	48.23 (7 psi)	77.91	84.80	79.98	66.88	93.77	86.18
Distillation										
Evaporated at 100°C	% v/v	46.00	-		60.00	50.00	55.00	55.00	56.00	55.00
Evaporated at 150 °C	% v/v	75.00	-		90.00	85.00	87.50	86.00	85.00	87.50
Hydrocarbon analysis										
Olefins (alkenes)	% v/v	-	18.0	10.0	12.34	9.59	13.28	1.20	21.32	12.00
Aromatics	% v/v	-	42.0	30.0	30.99	37.06	33.4	36.71	21.77	33.83
Benzene	% v/v	-	1.00	1.20	3.15	2.76	3.89	0.70	0.77	4.07
Oxygen content	% m/m	-	2.70	2.70	0.16	0.00	0.00	0.01	0.00	0.00

The data in Table 5.13 suggest that the main parameter requiring reduction is the RVP. Reducing the RVP should result in a reduction in both evaporative and mass exhaust emissions, resulting in reduced ambient hydrocarbon concentrations. As mentioned previously, it was found that reducing the RVP by 1 psi (~ 6.8 kPa) can reduce exhaust hydrocarbon emissions by 4.5 percent. Therefore, the reductions required by the majority of the analysed fuels should have a significant effect on mass emissions and hence ambient concentrations. This is likely to particularly affect emissions of alkenes (olefins) and aromatics, rather than alkanes, and so some alteration of the present alkane / alkene / aromatic ratio in the vicinity of busy roads may be expected. However, the RVP specification applies only during the summer months, the minimum period of which is specified as May 1st to September 30th. Hence, some seasonal variation in hydrocarbon ratios may be noted if fuels are blended differently for summer and winter periods. The main difference between winter and summer grade fuels under the new regulations will be a reduction in the butane content of fuels marketed in Ireland during the summer months (Wallace, 2000).

The reduction in benzene content of the fuel to 1.0 percent by volume is likely to lead to some decrease in benzene emissions, and hence in ambient concentrations. However, as benzene is a partial oxidation product of other aromatic hydrocarbons, the reduction in benzene emissions will not be proportional to the reduction in fuel benzene content, particularly as the current aromatic content of the majority of unleaded fuels is already below that specified in the new limit values (42 percent v/v).

Comparison of Fuel and Ambient Hydrocarbons

The fuel hydrocarbon composition is compared to the measured hydrocarbon concentrations from Period 1, as the fuel samples were collected in late February (about the same time as Period 1). Results from Monitoring Period 2 are not compared, as this monitoring was carried out between May and August, and it is likely that some changes may have been made to the marketed fuel composition to keep evaporative emissions low.

As most vehicle exhaust hydrocarbon emissions are composed of unburned- or partially-burned fuel (partial oxidation) components, a good correlation between fuel and exhaust constituents is generally observed (Hochhauser *et al.*, 1992; Leppard *et al.*, 1992).

However, the introduction of catalysts has reduced the strength of this correlation, as catalytic efficiency is greater for certain hydrocarbons (McCabe *et al.,* 1991; Shore and Tonkin, 1991). Comparison of fuel content and ambient hydrocarbon concentrations has been carried out before (e.g. Smith *et al.,* 1978) but most of the more recent studies have used tunnel hydrocarbon measurements to give an approximation of the average vehicle exhaust content, ruling out any impact from non-traffic sources (Duffy and Nelson, 1996; Zielinska *et al.,* 1996; Staehelin *et al.,* 1998; Touaty and Bonsang, 2000).

To compare the ambient measured hydrocarbon concentrations and the fuel volume percentages, an average fuel was determined from all of the analysed fuels. The calculation of this average fuel included a weighting based on the sales of leaded and unleaded fuels at the time of monitoring (85 percent unleaded, 15 percent leaded), and only those compounds measured by the on-line monitoring system are included. As the fuel compositions are very similar, this weighted average fuel composition is similar to a simple average of all analysed fuels. The correlation matrix presented in Table 5.14 compares the variation in percentage content of each compound between pairs of fuels – coefficients close to 1.0 indicating similar compositions. It is clear that most of the fuels are very similar, the only exception being Statoil unleaded, implying that the concept of an 'average' fuel is valid.

For each measured compound, the average ambient concentration and the percentage volume present in the average fuel are compared in Table 5.15. A wide variation is observed. Of the twenty-seven compounds monitored, seven are absent or virtually absent in the average fuel. These include the two compounds with the highest average ambient concentration: ethane and ethylene, as well as acetylene, which has the fifth highest ambient concentration. In fact, these seven compounds contribute 44 percent of the total measured ambient hydrocarbons. For ethane and propane, other sources are likely to be responsible for the majority of the measured concentrations, with a small partial oxidation component. Acetylene, ethylene and 1,3-butadiene are also important partial-oxidation products, which are not present in the original fuel.

Table 5.14 Correlation matrix of fuel hydrocarbon compositions

	Esso UL	Maxol UL	Statoil UL	Maxol ULS	Shell Pura	Shell UL	Maxol LS	Statoil LS	Shell L	Esso L
Esso UL	1.00									
Maxol UL	0.99	1.00								
Statoil UL	0.67	0.64	1.00							
Maxol ULS	0.92	0.90	0.75	1.00						
Shell Pura	0.86	0.88	0.72	0.71	1.00					
Shell UL	0.98	0.98	0.69	0.86	0.92	1.00				
Maxol SL	0.96	0.96	0.68	0.95	0.82	0.93	1.00			
Statoil SL	0.98	0.98	0.66	0.93	0.85	0.96	0.99	1.00		
Shell L	0.98	0.97	0.70	0.94	0.85	0.95	1.00	0.99	1.00	
Esso L	0.91	0.90	0.79	0.85	0.88	0.90	0.92	0.91	0.94	1.00

Table 5.15 Comparison of fuel and ambient hydrocarbon composition

Description	% content of average fuel - all compounds	% content of average fuel - 27 measured compounds only (A)	Average ambient weekday concentration (ppb)	% of 27 measured compounds in ambient air (B)	Fuel: Ambient Ratio A/B	% of 20 measured compounds in ambient air (C)	Fuel: Ambient Ratio A/C
Isopentane	12.24	20.33	2.86	7.26	2.80	13.01	1.56
Toluene	11.65	19.35	3.76	9.54	2.03	17.11	1.13
M+p-Xylene	6.58	10.93	1.67	4.24	2.58	7.60	1.44
n-Butane	4.15	6.90	4.16	10.56	0.65	18.93	0.36
Benzene	2.94	4.88	1.92	4.87	1.00	8.74	0.56
n-Pentane	3.04	5.05	0.97	2.46	2.05	4.41	1.14
2-methylpentane	4.53	7.52	0.45	1.14	6.58	2.05	3.67
o-Xylene	2.44	4.05	0.63	1.60	2.53	2.87	1.41
3-methylpentane	2.62	4.35	0.42	1.07	4.08	1.91	2.28
1,2,4-trimethylb.	1.89	3.14	0.79	2.01	1.57	3.59	0.87
Ethyl Benzene	1.83	3.04	0.51	1.29	2.35	2.32	1.31
n-Hexane	1.61	2.67	0.53	1.35	1.98	2.41	1.11
Trans-2-pentene	0.82	1.36	0.29	0.74	1.85	1.32	1.03
Isobutane	1.21	2.02	1.72	4.37	0.46	7.83	0.26
n-Heptane	0.92	1.54	0.18	0.46	3.37	0.82	1.88
Cis-2-pentene	0.45	0.75	0.17	0.43	1.74	0.77	0.97
1,3,5-trimethylb.	0.62	1.03	0.45	1.14	0.90	2.05	0.50
Trans-2-butene	0.23	0.38	0.23	0.58	0.65	1.05	0.36
Cis-2-butene	0.20	0.34	0.20	0.51	0.67	0.91	0.37
1-Butene	0.13	0.22	0.07	0.18	1.24	0.32	0.69
Isoprene	0.03	0.06	0.14	0.36	0.17		
Propane	0.05	0.08	2.18	5.53	0.01		
Propylene	0.01	0.01	1.66	4.21	0.00		
Ethane	0.00	0.00	4.51	11.45	0.00		
Ethylene	0.00	0.00	5.44	13.81	0.00		
Acetylene	0.00	0.00	3.09	7.84	0.00		
1,3-butadiene	0.00	0.00	0.40	1.02	0.00		

If these seven compounds are excluded, the average ratio between the ambient and fuel content of the remaining twenty compounds is 1.09; eleven compounds making a greater contribution to the average fuel, and nine contributing more to the total ambient concentration. Clearly, for these hydrocarbons, there is a strong relationship between their presence in the average fuel and their average ambient concentration.

Table 5.16 compares the fuel and ambient air content of the measured compounds by hydrocarbon group. Previous studies have found that relative to the fuel composition, exhaust composition is depleted, or at a similar level, for alkanes and aromatics but is enriched in alkenes (Nelson and Quigley, 1984; Hoekman, 1992; Hochhauser *et al.*, 1992). Table 5.16 clearly indicates that the ambient alkene content is higher than the fuel alkene content, whereas the aromatic content in the ambient samples was less than that in the

average fuel. One possible reason for this increased alkene content is the fact that alkenes are partial oxidation products of alkanes. Hence, it can be expected that any increase in fuel alkane content will lead to exhaust emissions with a high alkene content (Jemma *et al.*, 1992; McGinty and Dent, 1995), implying a greater abundance of more reactive compounds. As each of the three hydrocarbon groups behaves in a different manner, each is discussed separately below.

Table 5.16 Fuel and ambient air composition by hydrocarbon group

	% of total fuel content	Average ambient weekday concentration (ppb)	% of ambient measured compounds in fuel	% of ambient measured compounds in roadside air
Total aromatics	27.95	9.73	47.93	28.75
Total alkanes	30.38	17.98	52.09	53.13
Total alkenes	1.88	8.61	3.22	25.44

Aromatics: The percentages of each of the measured aromatics in the fuel and the air are compared in Table 5.17, and are generally in good agreement. Comparison of the hydrocarbon content of exhaust emissions from European vehicles and the hydrocarbon composition of European fuels, also reported good agreement for aromatic compounds (Montells *et al.*, 2000). A close agreement between the fuel and exhaust aromatic constituents should be expected, as aromatic compounds emitted from the exhaust are largely made up of unburned aromatic fuel components (approximately 72 percent, Siegl *et al.*, 1992). Exhaust emissions of unburned fuel components are expected to be lower for non-aromatic compounds. However, the benzene content in the air is significantly higher than its fuel percentage; this is because benzene is also a partial oxidation product of the other aromatic compounds (Hoekman, 1992; Leppard *et al.*, 1992; McGinty and Dent, 1995). Sampling of European vehicle emissions and fuels also reported an increase in benzene content in vehicle exhausts to eight percent (of aromatics) compared to four percent in unleaded fuel (Montells *et al.*, 2000).

Most previous studies have found that reduction of the fuel aromatic content will lead to an overall reduction in mass hydrocarbon emissions (Schuetzle *et al.*, 1994). For example, results from the Auto Oil programme in the US, demonstrated that reducing fuel aromatics from 45 to 20 percent resulted in a 12 percent reduction in total hydrocarbon emissions, and a 42 percent reduction in benzene emissions, again indicating the importance of all

aromatic compounds in the production of benzene. However the same tests showed that emissions of other toxic compounds (e.g. 1,3-butadiene and formaldehyde) increased due to the increased content of aliphatic hydrocarbons in the fuel, required to replace the aromatics (Schuetzle *et al.*, 1994).

Table 5.17 Aromatic content of fuel and ambient air

Description	% of total fuel content	Ambient average weekday concentration (ppb)	% of measured compounds in fuel	% of measured compounds in ambient air
Toluene	11.65	3.76	45.34	42.35
m+p-Xylene	6.58	1.67	25.61	18.84
Benzene	2.94	1.92	11.45	21.59
o-Xylene	2.44	0.63	9.48	7.09
1,2,4-trimethylb.	1.89	0.79	7.35	8.86
Ethylbenzene	1.83	0.51	7.13	5.77
1,3,5-trimethylb.	0.62	0.45	2.42	5.01

Alkanes: Agreement between the alkanes in Table 5.18 is not as good as that displayed by the aromatic compounds, particularly for ethane and propane, as ambient concentrations of these compounds are dominated by natural gas emissions. Ethane also has a significant tropospheric background concentration due to its low reactivity and prolonged atmospheric lifetime. When these two compounds are removed from both the fuel and ambient alkane content, better agreement is observed between the two datasets, as shown in Figure 5.38.

In Figure 5.38 the relative percentage of each compound in the fuel and ambient air is similar for most compounds, with the notable exception of the butanes. Previous studies have found that the proportion of a compound in the exhaust to that in the fuel can be greater for butanes than other alkanes (Leppard *et al.*, 1992). Butanes are thought to derive from both unburned fuel and from partial oxidation processes, whereas most other alkanes are derived largely from unburned fuel components (Nelson and Quigley, 1984). The butanes are also the compounds which are expected to make the largest contributions to evaporative emissions from vehicles (see Table 2.9). The butanes have also been identified as minor components of natural gas; however, their contribution is very small (see Table 5.4). Another factor may be that the catalytic efficiency for the butanes has been found to be significantly lower than for other alkanes (Nelson and Quigley, 1984). A combination of these elements is likely to be responsible for the high atmospheric butane concentrations.

Table 5.18 Alkane content of fuel and ambient air

Description	% of total fuel content	Ambient average weekday concentration (ppb)	% of measured compounds in fuel	% of measured compounds in ambient air
Isopentane	12.24	2.86	40.29	16.95
n-Butane	4.15	4.16	13.66	24.66
n-Pentane	3.04	0.97	10.01	5.77
2-methylpentane	4.53	0.45	14.90	2.65
3-methylpentane	2.62	0.42	8.63	2.49
n-Hexane	1.61	0.53	5.30	3.15
Isobutane	1.21	1.72	3.99	10.19
n-Heptane	0.92	0.18	3.04	1.09
Propane	0.05	2.18	0.15	12.96
Ethane	0.00	4.51	0.00	26.75

Although alkanes are often used to replace aromatics and alkenes in reformulated fuels (particularly in the US), it is important to note that alkanes in the fuel can lead to increased exhaust alkene emissions (Schuetzle *et al.,* 1994). The efficiency of catalytic converters is also poorest for the alkanes (Shore and Tonkin, 1991), hence increased fuel alkane content may lead to increased mass hydrocarbon emissions from catalyst equipped vehicles.

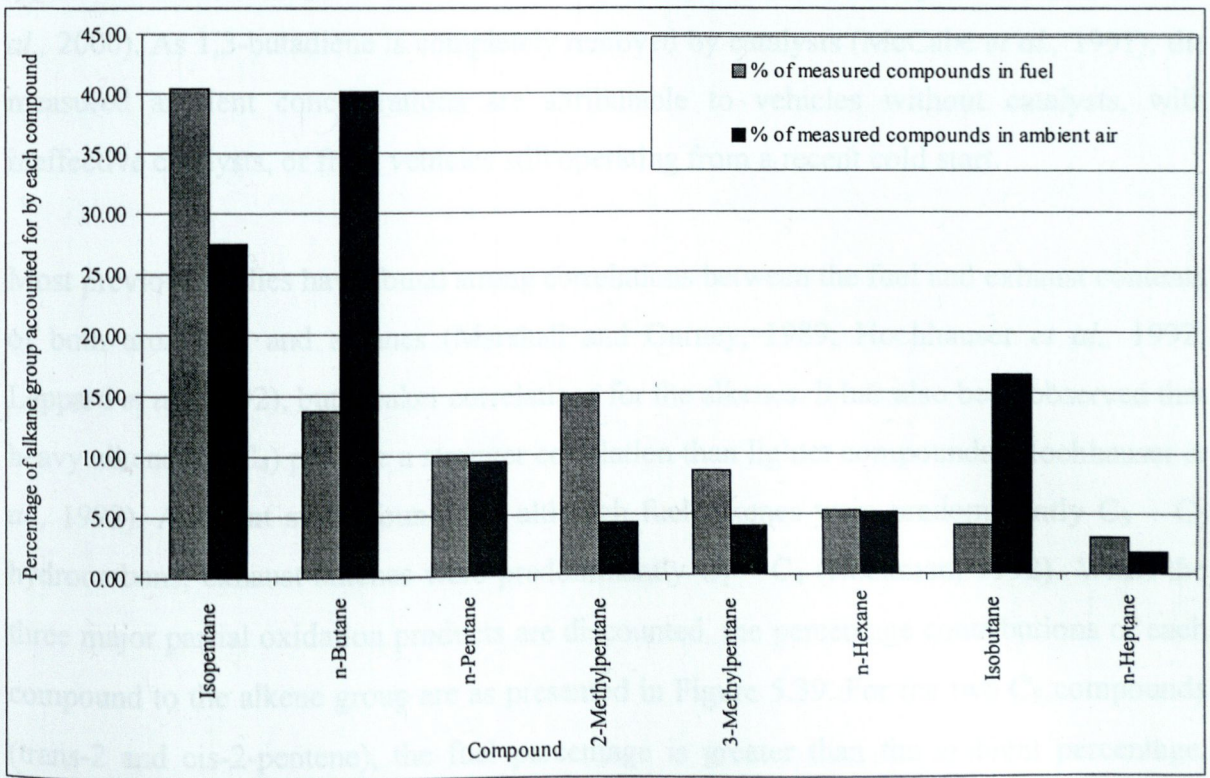


Figure 5.38 Alkane content of fuel and ambient air (propane, ethane removed)

Alkenes: The percentage contributions of each of the measured alkenes to the sum of measured alkenes in the fuel and the ambient air are presented in Table 5.19.

Table 5.19 Alkene content of fuel and ambient air

Description	% of total fuel content	Ambient average weekday concentration (ppb)	% of measured compounds in fuel	% of measured compounds in ambient air
Trans-2-pentene	0.82	0.29	36.34	3.59
Cis-2-pentene	0.45	0.17	20.05	2.14
Trans-2-butene	0.23	0.23	10.21	2.82
Cis-2-butene	0.20	0.20	8.94	2.51
1-Butene	0.13	0.07	5.91	0.89
Isoprene	0.03	0.14	1.47	1.72
Propylene	0.01	1.66	0.28	20.57
Ethylene	0.00	5.44	0.00	67.24
1,3-butadiene	0.00	0.40	0.00	4.99

The volume percentage contribution of each measured alkene to the total fuel volume is small, as is the average measured ambient concentration of each of the alkenes. Three compounds - propylene, ethylene and 1,3-butadiene - have a negligible presence in the fuel but are present in the ambient samples as partial oxidation products (Nelson and Quigley, 1984; Leppard *et al.,* 1992). European studies also noted an increased fraction of total alkenes in the exhaust of European vehicles to nine percent, compared to four percent in a typical fuel, due mainly to emissions of alkenes as partial oxidation products (Montells *et al.,* 2000). As 1,3-butadiene is completely removed by catalysts (McCabe *et al.,* 1991), the measured ambient concentrations are attributable to vehicles without catalysts, with ineffective catalysts, or from vehicles still operating from a recent cold start.

Most previous studies have found strong correlations between the fuel and exhaust contents of both aromatics and alkanes (Marshall and Gurney, 1989; Hochhauser *et al.,* 1992; Leppard *et al.,* 1992), but weaker correlations for the alkenes. It has also been observed that heavy alkenes (> C_4) provide a stronger correlation than lighter compounds (Hochhauser *et al.,* 1992). A recent study found that although fuel alkenes were predominantly $C_5 - C_7$ hydrocarbons, exhaust alkenes were predominantly $C_2 - C_4$ (Hoekman, 1992). When the three major partial oxidation products are discounted, the percentage contributions of each compound to the alkene group are as presented in Figure 5.39. For the two C_5 compounds (trans-2 and cis-2-pentene), the fuel percentage is greater than the ambient percentage, while for the C_4 compounds (trans-2, cis-2, and 1-butene), the fuel percentages are lower than the ambient air percentages. These findings are in broad agreement with those of the above studies. The only compound which does not agree is isoprene (a C_4 compound), possibly due to the contribution from natural emissions to ambient concentrations.

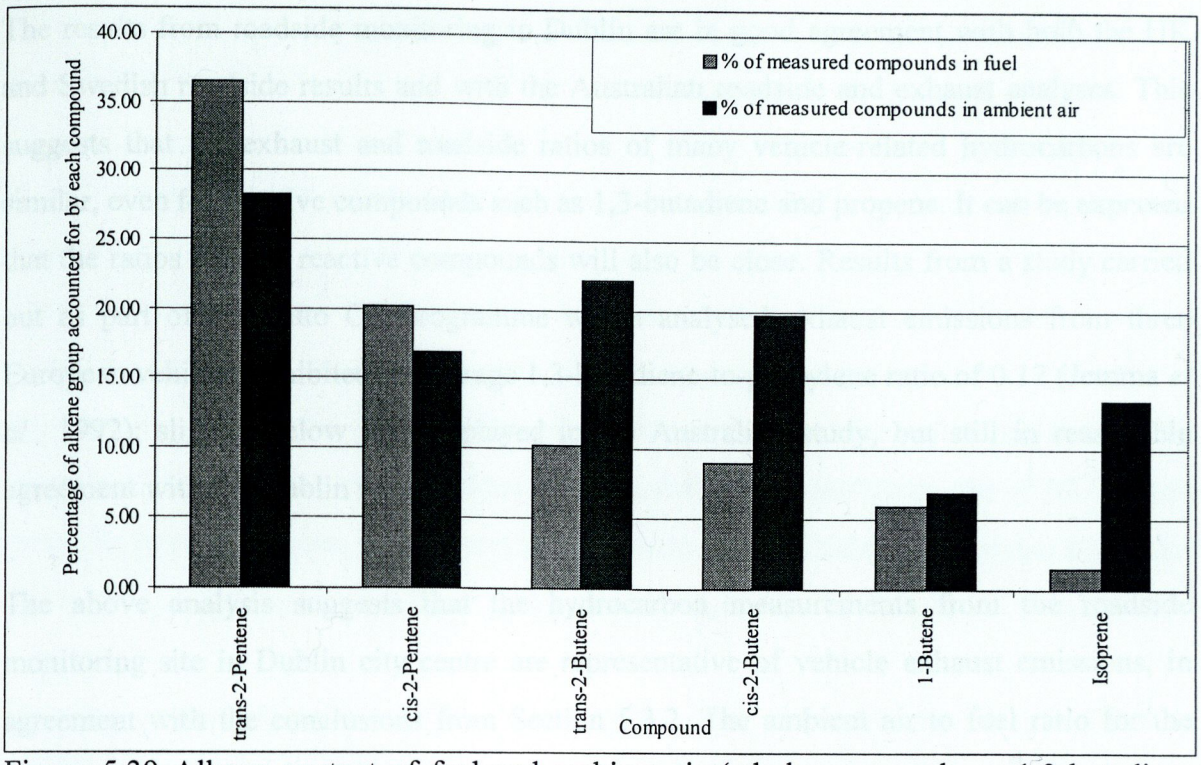


Figure 5.39 Alkene content of fuel and ambient air (ethylene, propylene, 1,3-butadiene removed)

Reduction of alkene fuel content has been found to result in increased hydrocarbon emissions, particularly in catalyst equipped vehicles as the catalytic removal efficiency for alkenes is very high. Reduction of alkene content also results in reduced emissions of the carcinogenic compound 1,3-butadiene (Schuetzle *et al.,* 1994), and interestingly, reduced exhaust emissions of oxides of nitrogen.

A comparison of the exhaust and roadside concentrations of 1,3-butadiene was carried out by Ye *et al.* (1997), who examined the ratio of 1,3-butadiene to propylene in exhaust and roadside samples. Both of these compounds originate solely from engine combustion processes and are removed with similar efficiencies by the catalytic converter. Hence, their relative emissions from catalyst and non-catalyst vehicles should be similar. Table 5.20 compares the 1,3-butadiene to propylene concentration ratio in roadside and tunnel studies from several countries, as well as the exhaust ratio measured by Ye *et al.* (1997).

Table 5.20 Ratios of 1,3-butadiene to propylene in roadside air and exhaust samples

Study city	Goteborg (Sweden)	London	Sydney	Melbourne	California	Dublin (this study)
Sample type	Roadside air	Roadside air	Tunnel air	Exhaust sample	Exhaust sample	Roadside air
Ratio	0.24	0.20	0.21	0.25	0.026	0.24

The results from roadside monitoring in Dublin are in good agreement with both the UK and Swedish roadside results and with the Australian roadside and exhaust analyses. This suggests that the exhaust and roadside ratios of many vehicle-related hydrocarbons are similar, even for reactive compounds such as 1,3-butadiene and propene. It can be expected that the ratios for less reactive compounds will also be close. Results from a study carried out as part of the Auto Oil programme which analysed exhaust emissions from three European vehicles exhibited an average 1,3-butadiene-to-propylene ratio of 0.17 (Jemma *et al.*, 1992); slightly below that displayed in the Australian study, but still in reasonable agreement with the Dublin results.

The above analysis suggests that the hydrocarbon measurements from the roadside monitoring site in Dublin city centre are representative of vehicle exhaust emissions, in agreement with the conclusions from Section 5.3.2. The ambient air to fuel ratio for the butanes suggests a significant contribution from fuel evaporation. It is not possible to conclude the representativeness of ambient compounds which are solely partial oxidation products (i.e. not present in the fuel), however the good agreement between compounds found in the fuel and the air, and the strong correlation between the ambient hydrocarbon concentrations suggests that the measured concentrations of partial oxidation products are representative of vehicle emissions. The good agreement between the exhaust partial oxidation study carried out by Leppard *et al.* (see Study 18 in Table 5.10) and the ambient results from monitoring in Dublin also suggests that these compounds are vehicle related.

5.4 SUMMARY

Detailed analysis of the roadside hydrocarbon concentrations measured in Dublin city centre was described in this chapter. Firstly, the detailed short-term (hourly) hydrocarbon concentrations were investigated using a number of methods. The typical diurnal concentration pattern followed by each of the hydrocarbons was identified and found to be similar for most compounds. The pattern indicated that vehicle emissions are likely to be the dominant hydrocarbon source at this location. The utility of the representative day methodology to assess the most and least representative days for a given dataset was also investigated, and found to be particularly useful for the identification of days with non-typical diurnal patterns, due to unusual meteorological or traffic conditions. The correlation between the hourly hydrocarbon concentrations was calculated and found to be very strong

for most compounds, with the exception of ethane and propane, which were identified as natural gas components.

An observable impact of variations in meteorological conditions was noted for wind direction, windspeed and temperature. Most compounds exhibited similar variations in concentration with wind direction; however a peak in measured toluene concentrations was identified for winds from the direction of a nearby toluene point source. Extremes of windspeeds, either very low or high, were observed to have a measurable effect on measured hydrocarbon concentrations. Average ambient temperatures above 10 °C were noted to have an impact on evaporative emissions from vehicles. Atmospheric stability class was also noted to have a significant impact on night-time hydrocarbon concentrations.

Principal component analysis of the hourly hydrocarbon concentrations identified vehicle emissions as the major source of hydrocarbon emissions in the area of the monitoring site. The impact of natural gas leakage and of a local toluene point source were also identified using this method. A small impact due to temperature variations was also observed. Comparison of Dublin roadside hydrocarbon measurements with world-wide tunnel and exhaust measurement studies indicated good agreement with most studies, and best agreement with non-catalyst exhaust studies. Results of analysis of 1998 Irish fuels indicated that these fuels were already close to meeting the latest EU fuel specifications. Comparison of the fuel and ambient hydrocarbon components indicated good agreement, particularly for those components which have been reported as being unburned fuel components.

6. PHASE 2 MONITORING RESULTS

6.1 INTRODUCTION

The second phase of monitoring addressed the impacts of emissions from point sources. This work constituted the Environmental Protection Agency (EPA) funded project "Optimal monitoring of air quality in the vicinity of point sources" (Misstear *et al.*, 2001a, b, c). Monitoring was carried out at two locations: Rhode, Co. Offaly where the priority pollutants measured were sulphur dioxide and particulates from a nearby power station; and at Lynn Industrial Estate, just outside Mullingar town (Co. Westmeath), where hydrocarbon emissions from two manufacturing plants were the priority pollutants; therefore, the majority of this chapter is dedicated to a description of the latter, although hydrocarbon data from the rural monitoring site at Rhode are also briefly presented. At the Mullingar monitoring site, passive and pumped tube sampling methods were also employed to allow improved spatial monitoring of air pollution in the area of the two sources, and to compare the usefulness of the methods with that of on-line monitoring.

As both of the emitting facilities in Mullingar hold Integrated Pollution Control (IPC) licences, reliable data were available from emissions tests carried out at both sites. This allowed dispersion modelling to be undertaken for this location. Two different models were used and the results from both were compared to the measured concentrations.

Section 6.2 describes both monitoring locations, providing greater detail for the Mullingar monitoring site. Sections 6.3 and 6.4 detail the monitoring programme at Mullingar and Rhode, respectively. Section 6.5 presents summary hydrocarbon results from Rhode and Mullingar. Section 6.6 summarises the meteorological data collected at Mullingar, which are used in analysing the hydrocarbon data. Details of meteorological data collected at the Rhode monitoring site are not included, as these data are not extensively used in the analysis of the Rhode hydrocarbon data. Finally, Section 6.7 provides an introduction and background to dispersion modelling, and to the models used during this study. Details are also provided of the emissions characteristics of the two Mullingar sites, and the modelling studies carried out.

A number of specific objectives were defined for Phase 2 of the project:

- to assess the relative merits of fixed and mobile sampling units for ambient air quality monitoring;
- to make recommendations on the most appropriate sampling and measurement systems for such pollutants in the vicinity of point sources;
- to assess the utility of dispersion modelling in monitoring programmes, by investigating their accuracy in estimating ambient concentrations due to point source emissions.

Monitoring carried out at Lynn Industrial Estate was designed specifically to fulfil these objectives in terms of hydrocarbon compounds, while the monitoring programme at Rhode dealt with other pollutants including sulphur dioxide and particulate emissions from the nearby power station, though hydrocarbon concentrations were also measured at Rhode, as this provided an opportunity to assess the background concentrations which can be expected at a rural location, away from significant sources of hydrocarbon emissions.

6.2 SITE DESCRIPTION

6.2.1 Mullingar Monitoring Site

This monitoring location was chosen after consultation with regional inspectors from the EPA, who suggested possible sites of interest where significant hydrocarbon emissions were expected. One important tool used during site selection was the EPA database of emission measurements from IPC licensed facilities, which was supplied by the EPA laboratory in Cork (see Table 2.8 for details of IPC facilities in each county). Based on these data, a short-list of facilities was compiled for detailed consideration. This short-list is presented in Table 6.1. Factors which rendered individual sites unsuitable included:

1) complex local terrain (e.g. Schering Plough, surrounded by woodlands);
2) low or infrequent and poorly defined emissions (e.g. Swords Laboratories where batch processing meant that different compounds, at different emission rates, may be encountered from day to day, making dispersion modelling impossible);
3) difficulty in finding downwind monitoring location (considering prevailing winds);
4) proximity to major roadways which may overwhelm point source emissions;
5) travelling distance from Dublin.

The monitoring location at Lynn Industrial Estate, Mullingar (Penn Racquet Sports Company and Taconic International, hereafter referred to as Penn and Taconic) was eventually decided upon as the most suitable monitoring location, as it met a number of distinct criteria to fulfil the above objectives:

1) hydrocarbon emissions from two manufacturing facilities;
2) both facilities hold IPC licences, which meant that emissions were measured regularly;
3) emissions were reasonably constant and well defined, compared to other possible monitoring locations;
4) presented a more complex emissions environment compared to the Rhode location;
5) simple local topography;
6) the proximity of the site to Dublin;
7) availability of a power supply;
8) security of the mobile monitoring unit.

The area surrounding Lynn Industrial Estate is shown in Figure 6.1. The entire industrial estate covers a significant area just south of Mullingar town. However, the two facilities with licensed emissions are located by the main road through the industrial estate, close to the National Route N52 (black and white dashed road running north-easterly across Figure 6.1). The town centre of Mullingar is situated about one kilometre north of the industrial estate. The remainder of Lynn Industrial Estate is located to the west of the two IPC facilities, while small residential areas are located to the east. South of the industrial estate is predominantly open countryside, with some dwellings scattered along the main road.

A schematic of the immediate area surrounding the Penn and Taconic facilities is given in Figure 6.2. In relation to Figure 6.1, National Route N52 can be seen on the extreme right of Figure 6.2. Other facilities in this part of the industrial estate are identified, while those buildings with no identification are units occupied by a number of different companies. None of the other facilities has known hydrocarbon emissions, although emissions would be expected from the petrol stations opposite Taconic, and at the entrance to the industrial estate. The location of the monitoring unit, in the car park beside Penn, is indicated, as are the pumped and passive sampling locations (these will be referred to in later sections). Photographs of the monitoring area are presented in Figure 6.3, Figure 6.4 and Figure 6.5.

Table 6.1 Facilities short-listed for point source monitoring project

Plant Name	Location	IPC Register No.	Activity Class[1]	Substances emitted (those in italics are measurable using the on-line hydrocarbon monitoring system)	Notes
Irish Cement	Drogheda, Louth	30	10.1	Particulate matter, NO_X, SO_X	
Swords Laboratories	Swords, Fingal	14	5.6	Acetone, DCM[2], *heptane*, 2-propanol, THF[3]	
Schering Plough	Rathdrum, Wicklow	15	5.6	*Hexane, toluene, xylene*, 2-propanol, Ethyl acetate, THF, ethanol, acetone	Thermal oxidising unit planned
Merck, Sharp and Dohme	Clonmel, Tipperary	11 / 208	5.6	2-propanol, acetone, *toluene*, *cyclo-hexane*, THF, *benzene*	
Irotec Laboratories	Little Island, Cork	134	5.6	*Hexane, heptane, toluene*, 2-propanol, ethyl acetate, ethanol, acetone, DCM, THF, *cyclo-hexane*, MIBK[4]	Other chemical and pharmaceutical facilities nearby
Roche Ireland	Clarecastle, Clare	68	5.6 and 11.1	*Hexane, benzene, toluene*, ethyl acetate, THF, acetone, 2-propanol, DCM, *cyclo-hexane, heptane*	High emitter of hydrocarbons
Iropharm	Arklow, Wicklow	89	5.6	*Benzene, toluene*, 2-propanol, THF, MCB	
Helsinn Chemicals	Mulhuddart, Dublin 15	125	5.6	*Xylene*, 2-propanol, ethyl acetate, ethanol	Close to line source of M50 motorway
Taconic International	Mullingar, Westmeath	124	12.2	*Toluene, xylene*, 2-propanol, *hexane*	Close to Penn Racquet Sports Co. premises
Penn Racquet Sports Co.	Mullingar, Westmeath	104	12.2	*Hexane*	Different hydrocarbons emitted by Penn and Taconic
PPI Adhesives	Waterford	93	12.2	*Hexane, heptane, toluene, xylene*, 2-propanol, ethyl acetate, ethanol, acetone, DCM, THF, *cyclo-hexane*	

[1] Activity classes referenced:

Activity Class 5.6: The manufacture of pesticides, pharmaceutical or veterinary products and their intermediates;

Activity Class 10.1: The production of cement;

Activity Class 11.1: The incineration of hazardous waste;

Activity Class 12.2: The manufacture or use of coating materials in processes with a capacity to make or use at least 10 tonnes per year of organic solvents, and powder coating manufacture with a capacity to produce at least 50 tonnes per year.

[2] DCM = Dichloromethane; [3] THF = tetrahydrofuran; [4] MIBK = Methyl isobutyl ketone



Figure 6.1 Area surrounding Lynn Industrial Estate, Mullingar (scale 20 mm to 1 km)

Figure 6.2 Area immediately surrounding Penn and Taconic

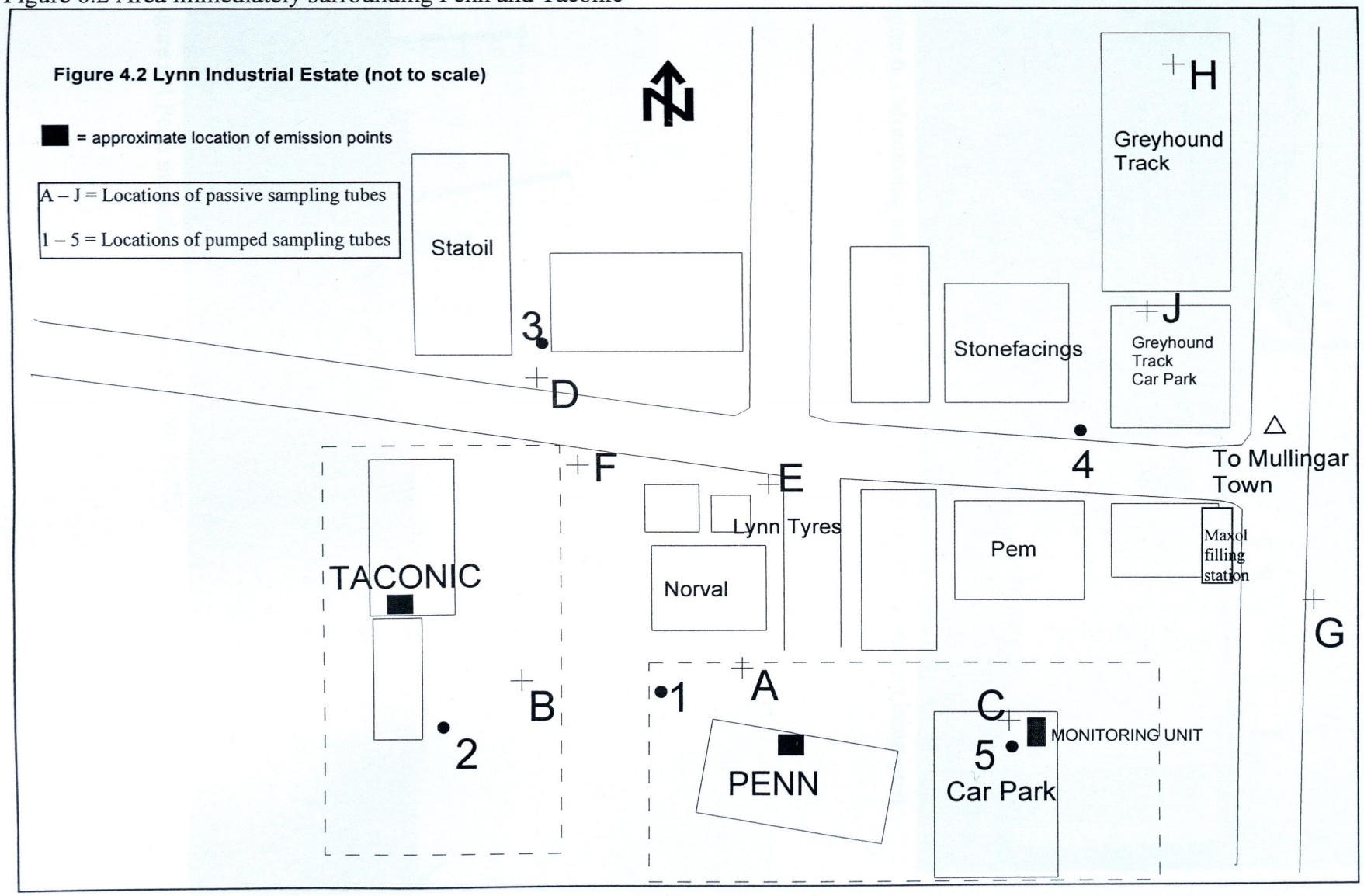




Figure 6.3 Monitoring unit on-site, and passive sampler deployment on lamp-post


Figure 6.4 Penn manufacturing facility (from north)



Figure 6.5 Taconic manufacturing facility (from north)

The Penn Racquet Sports Company manufacturing plant is shown in Figure 6.3 and Figure 6.4. This plant manufactures tennis balls (90,000 per day), and operates 24 hours / day from Monday morning to Saturday lunch-time, with the plant closing completely for the remainder of the weekend. The main emissions from this plant are n-hexane and cyclo-hexane. Large hexane storage tanks are located beside the plant. The emission points at Penn are five low level vents located on the roof. Details of emissions from each of these stacks are given in Section 6.7.5. The large stack in Figure 6.4 is for the plant boiler only, and, as such, has no defined hydrocarbon emissions. Under the terms of its IPC licence, Penn is required to sample all emissions on a quarterly basis, and forward the results to the EPA. The EPA also carries out its own sampling intermittently at the facility. The results from these emissions tests have mostly been in compliance with the limit values specified in their IPC licence. Shortly after monitoring was concluded in the industrial estate, Penn introduced a water-based adhesive during manufacture to reduce hexane consumption. It is estimated that this will reduce emissions to air by 60 percent. As operation is continuous at Penn, and only one product is manufactured, emissions are relatively constant, with little difference noted between results from quarterly emissions sampling.

The Taconic International facility manufactures PTFE (polytetrafluoroethylene) and silicone elastomer coated fabrics. The facility is shown in Figure 6.5. Production is carried

on for eight to ten hours each day, from Monday to Friday. The main hydrocarbons emitted from Taconic are toluene and the xylene isomers, plus a small amount of ethylbenzene. There are two hydrocarbon emission points at Taconic, which, as with Penn, are low level vents. There are no hydrocarbon emissions from the large stack shown in Figure 6.5. In January 2000, a thermal oxidising unit was fitted to each of the emissions points at Taconic. Results from initial tests indicate that emissions have been reduced to negligible levels. As part of its obligations under the IPC licence, both of the emissions points at Taconic are sampled monthly and the results are forwarded to the EPA. The EPA inspectors also carry out intermittent testing. All results from emissions measurements are available to the public through the EPA. Prior to the installation of the thermal oxidising units, the emissions limits set by the EPA in the Taconic IPC licence were frequently breached. Emissions parameters for Taconic are given in Section 6.7.5. Two production lines are operated at the Taconic facility (known as the sealcon adhesive line (A6) and the rubber coater (A7)), and emissions from each of these processes are discharged separately through one of the two emissions points. However, production is not continuous on these lines, particularly the rubber coater line, where several weeks may pass between successive operations. The sealcon adhesive line is normally operated on a daily basis, but the number of hours of production each day can vary from three to ten hours. The sealcon adhesive production line is responsible for both toluene and xylene emissions, with xylene emissions normally being greater. The rubber coater is responsible for high emissions of toluene (up to ten times greater than the sealcon line) but has practically no emissions of xylene. Therefore, any elevated ambient xylene concentrations are attributable to emissions from the sealcon adhesive production line.

There are several other possible sources of gaseous emissions in the vicinity of Penn and Taconic, including a number of other manufacturing and processing facilities in the industrial estate. None of these requires an IPC licence, indicating that none is likely to have significant hydrocarbon emissions. There are two petrol stations in and around the industrial estate and one oil storage facility, as well as the busy main road (N52), which passes by the Penn facility, and the main road through the industrial estate. Mullingar town, which is north of the industrial estate, represents another probable source of emissions due to combustion of fuels in open fires and central heating systems, and from vehicles passing through the town.

Selection of Monitoring Location in Lynn Industrial Estate

The ISC Gaussian dispersion model was employed to guide the selection of monitoring locations in Lynn Industrial Estate. Preliminary modelling, based on available source data, indicated that reasonably high hydrocarbon concentrations could be expected in the vicinity of the two licensed facilities. The highest concentrations occur relatively close to the source, owing to the low emission heights at both facilities. Initial model results indicated that peak concentrations would occur at approximately 80 to 100 m from the source with concentrations at 200 m being 60 to 75 percent lower. Meteorological data from the Met Eireann monitoring station, located north of Mullingar (see Figure 6.1, Met. Stn. marked in Irishtown, 1.5 km north of Mullingar town), were used in the dispersion model. The frequency of occurrence of each wind direction at the Mullingar meteorological station during 1998 is shown in Figure 6.6.

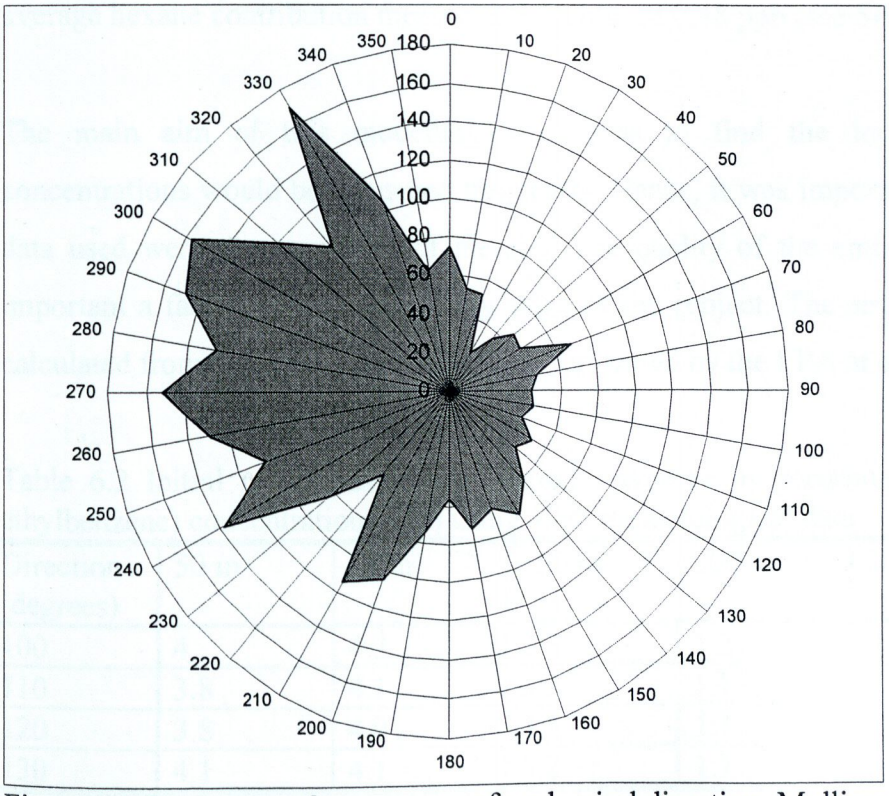


Figure 6.6 Frequency of occurrence of each wind direction, Mullingar (May to Aug. 1998)

Historic meteorological data indicated that the dominant wind direction was between 200 and 300 degrees, i.e. roughly from the west. The Penn car parking area, which can be seen in Figure 6.2, is located in a suitable position downwind of Penn and Taconic. The monitoring unit was positioned approximately 90 m east of the Penn factory building and 240 m east of the Taconic facility. The greyhound track car park nearby was considered as a potential location for the monitoring unit; however, security was an issue, as this area is

very open, while in the Penn car park the unit was hidden from view of the general public. Finding a power supply at the greyhound track car park also proved to be difficult.

Results of initial dispersion modelling are presented in Table 6.2 to Table 6.5. Peak ground-level concentrations occur at a distance of approximately 80 m from the stack for both Penn and Taconic. The approximate directions of the monitoring unit from the stacks were 120 degrees for Taconic and 80 degrees for Penn. The model results indicated significant concentrations of all hydrocarbons emitted from the stacks at the monitoring site. The model indicated that the average ambient concentration at the monitoring site, due to Taconic emissions, would be low, but that peak concentrations, when the wind was blowing from the direction of Taconic, would be elevated. Model results for emissions from Penn indicated that both the average and peak ambient hexane concentrations would be significant. In fact, the predicted average concentrations are much higher than the average hexane contribution measured in Dublin of 0.48 ppb (see Section 4.3).

The main aim of this modelling work was to find the location where elevated concentrations would be measured frequently. Hence, it was important that meteorological data used were representative of the site. The quality of the emissions data was not as important a factor at this preliminary stage of the project. The emissions data used were calculated from stack emissions sampling performed by the EPA at each of the facilities.

Table 6.2 Initial model results for Taconic, average hydrocarbon (toluene + xylene + ethylbenzene) concentration (ppb) using 1998 meteorological data

Direction (degrees)	50 m	75 m	100 m	200 m	300 m	500 m
100	4	4.3	3.3	1.2	0.6	0.3
110	3.8	4.1	3.2	1.1	0.5	0.3
120	3.8	4.0	3.2	1.1	0.5	0.3
130	4.1	4.1	3.2	1.1	0.5	0.3

Table 6.3 Initial model results for Taconic, highest 1-hour hydrocarbon concentration (ppb) using 1998 meteorological data

Direction (degrees)	50 m	75 m	100 m	200 m	300 m	500 m
100	126	163	148	61	31	12
110	166	167	148	61	31	12
120	166	167	167	78	40	16
130	152	164	167	78	40	16

Table 6.4 Initial model results for Penn, average hydrocarbon (n-hexane) concentration (ppb) using 1998 meteorological data

Direction (degrees)	30 m	50 m	80 m	100 m	150 m	200 m
70	61	234	234	192	115	75
80	63	239	238	193	113	73
90	66	256	255	208	123	80
100	70	276	279	228	137	89

Table 6.5 Initial model results for Penn, highest 1-hour hydrocarbon concentration (ppb) using 1998 meteorological data

Direction (degrees)	30 m	50 m	80 m	100 m	150 m	200 m
70	3250	5438	5404	5171	3538	2540
80	3250	5053	5404	5171	3538	2355
90	3250	5053	5404	5171	3538	2628
100	3250	5438	5404	5171	3538	2355

6.2.2 Rhode Monitoring Site

Monitoring was carried out at Rhode during April to June 1999, although hydrocarbon monitoring was only carried out for a short period during this time. The monitoring point was located approximately 4 km to the east of Rhode power station, as indicated in Figure 6.7. The monitoring unit was located at the rear of Ballybryan National School. A photograph of the unit in-situ is shown in Figure 6.8.

A small hill is indicated Figure 6.7 (Fahy Hill), lying between the monitoring location and the power station, which would be expected to have some impact on the plume from the station as it approaches the monitoring location. A view of the power station from this hill is shown in Figure 6.9. The remainder of the area surrounding the monitoring site is flat boggy terrain, with dwellings and farms sparsely located around the town centre of Rhode. There are no major roads in the vicinity of the monitoring location. The town of Rhode itself is very small, though the larger town of Edenderry is located at approximately 7 km east (at 113 degrees) of the monitoring location. There are no other towns in the vicinity of the monitoring site.

The power station is peat-fuelled, being supplied from the surrounding boglands. At the start of 1999 two generating units were in operation at the plant: Unit 1 (20 MW) and Unit 3 (40 MW). At the end of May, Unit 3 was shut down for overhaul, and did not return to

operation until the beginning of August, shortly after which unit 1 was decommissioned. When the units are operational, they are normally run at base load, i.e. they are run at a constant loading, and are not used for stop-start situations. When both units were operational, over 15,000 tonnes of milled peat was consumed each week.

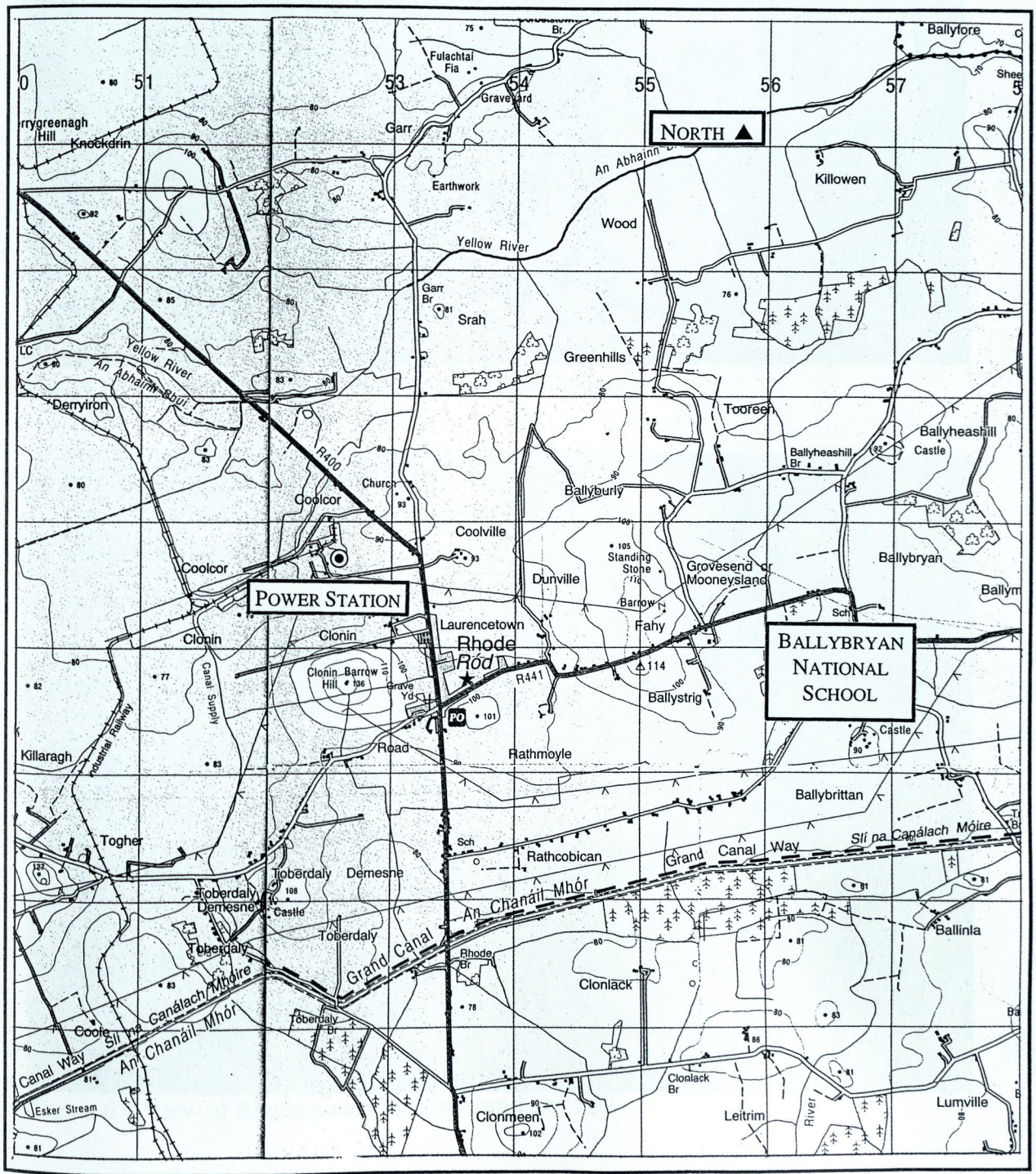


Figure 6.7 Rhode power station and surrounding area (scale 20 mm to 1 km)



Figure 6.8 Monitoring unit at Ballybryan National School

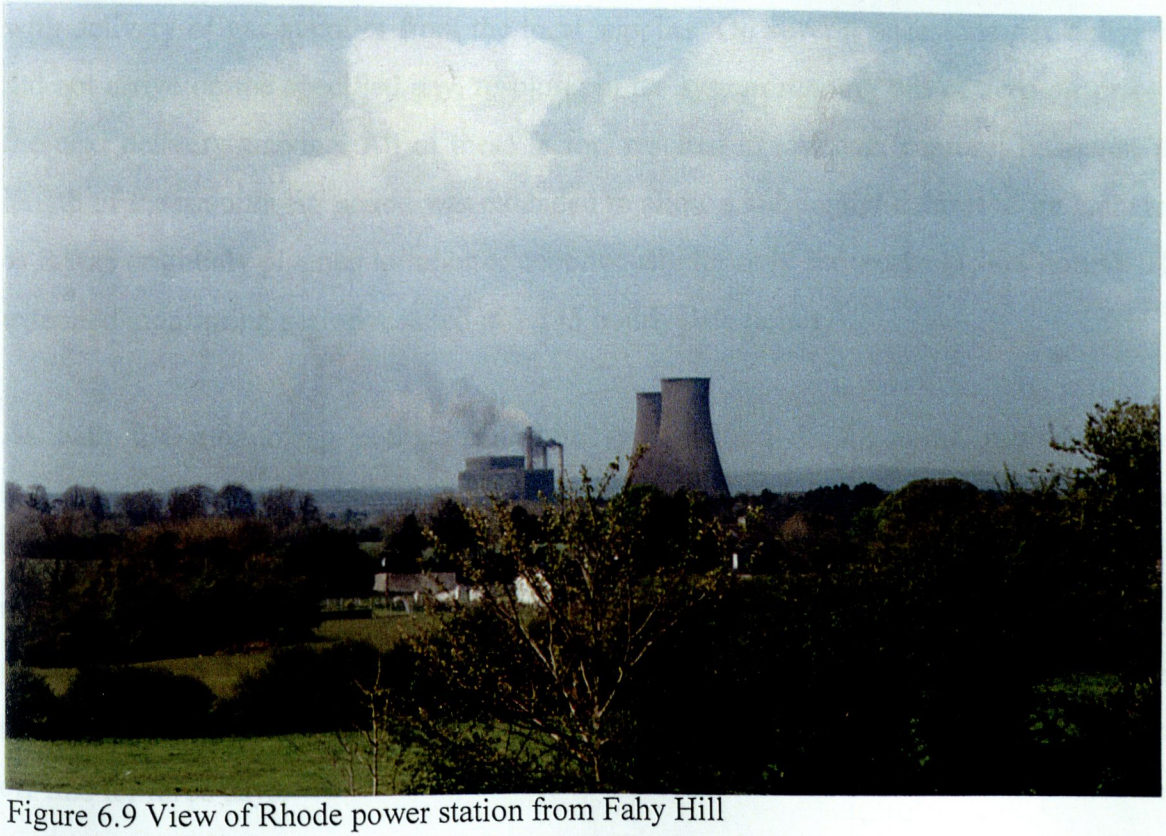


Figure 6.9 View of Rhode power station from Fahy Hill

6.3 MONITORING PROGRAMME AT MULLINGAR

Details of the monitoring programmes for each of the three monitoring methods (on-line, pumped tube and passive tube) used at Mullingar are presented below. The pumped and

passive tube samples were analysed at either the EPA laboratory in Cork, or the Enterprise Ireland laboratory in Dublin. Such tubes can be analysed using the on-line system located in the mobile monitoring unit; however, this would have resulted in a loss of a significant amount of continuous hourly data, hence it was decided to analyse the tubes elsewhere.

6.3.1 Continuous Hydrocarbon Monitoring System

Monitoring was carried out between 27 September and 9 December 1999. Details of the monitoring study are presented in Table 6.6. There were several breaks in monitoring during the study. The electricity supply at the monitoring location was interrupted on three occasions, resulting in the loss of nine days of monitoring results. When the electricity supply to the hydrocarbon monitoring system is broken, sampling and analysis do not resume once the electricity supply has been restored. This resulted in the loss of data until the monitoring unit had been visited to check the operation of the system, which was normally every four to five days. Other breaks in operation were also required for maintenance and repairs. Breaks in operation were also caused by problems encountered with delivery of gas supplies from the local supplier. On several occasions gas deliveries did not arrive on the specified day, resulting in the system running out of zero air prior to the next delivery arriving. All of these factors resulted in low data capture; however, the length of the monitoring period was extended to allow a substantial dataset to be gathered, as it was originally planned to monitor continuously for only six weeks (1,008 hours). The extended monitoring period resulted in 1,145 hourly data points.

As with the monitoring period in Dublin (see Section 4.2.2), some problems were experienced with the hydrocarbon monitoring system at Mullingar. Two main problems were encountered, one with the GC and the other with the ATD. Firstly, a solenoid valve in the ATD400 became stuck, resulting in the carrier gas (helium) being prevented from passing through the cold trap. This resulted in an error display from the ATD. This simply required the fitting of a new solenoid valve, and resulted in the monitoring system being off-line for three days.

The problem with the GC was slightly more difficult to detect than the ATD problem. The problem manifested itself in a very low zero air flow through the flame ionisation detectors (FIDs), which resulted in the FID flame being extinguished. This problem was initially

thought to be the result of a blocked filter in the air line. However, the problem was eventually traced to a worn o-ring in a valve in the zero air line connected to the FIDs, which allowed large air leaks from the system. This resulted in the system being off-line for four days while repairs were carried out. Short breaks (several hours) were also required for replacement of filters and system conditioning. Other items of general maintenance carried out during monitoring are detailed in Section 3.2.8.

Table 6.6 Details of hydrocarbon monitoring study at Mullingar

Start date	September 27th 1999
End date	December 9th 1999
Breaks in monitoring	9 days in total due to breaks in electricity; Breaks due to zero air supply running out (approximately 6 days); Breaks for regular maintenance and for repairs require due to equipment problems (approximately 8 days).
Total number of hours between start and end of monitoring period	1,748
Total number of samples collected and analysed	1,145
Percentage data capture	65.5 %

Calibration of the system was carried out on a two weekly basis, as described in Section 4.2.1. A new cylinder of calibration gas was used during this study as the previous cylinder was expended. The new cylinder of calibration gas had the advantage of having cyclo-hexane (which was an expected emission from Penn) as one of the components, which was not present in the original gas supply. Details of the constituents of the calibration gas are presented in Table 3.1. During monitoring at Mullingar a BP1 column was fitted which resolve the compounds detailed in Table 3.1. A sample chromatogram from monitoring at Lynn Industrial Estate is presented in Figure 6.10. The group of peaks which can be seen near the start of the chromatogram are the lower boiling point components which are not well resolved by the BP1 column. A PLOT column would be required for resolution of these compounds (see Section 3.2.4).

As for the Dublin hydrocarbon monitoring period, the qualitative and quantitative precision of the monitoring equipment was investigated during monitoring at Mullingar. For details of the calculations of these parameters, see Section 4.2.1, which provides greater detail of

the calibration and evaluation of the chromatographic performance of the system. Sample chromatograms produced by the system are also included in this section. The resolution of the method is not reported for the Mullingar data, as this can normally be checked visually without recourse to Equation 4.1. The suggested average qualitative and quantitative precision for a good chromatographic method is 0.05 and 1.00 percent, respectively. The qualitative and quantitative precision for the chromatographic system while in use at Mullingar were calculated from four consecutive calibration analyses, and are presented in Table 6.7.

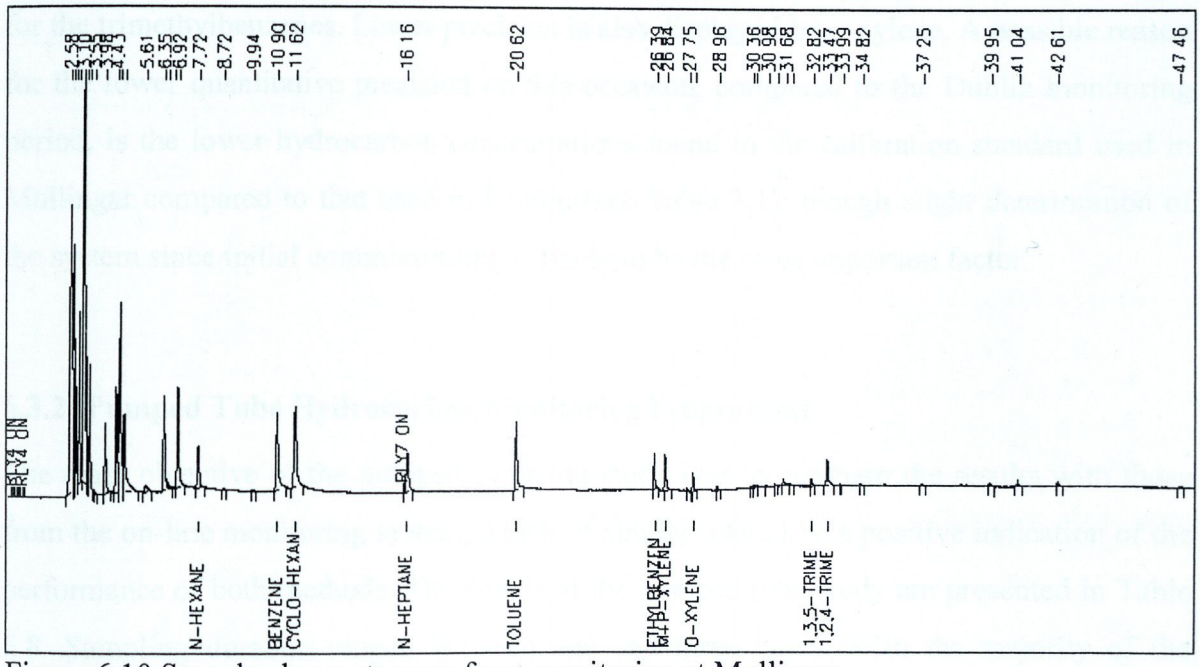


Figure 6.10 Sample chromatogram from monitoring at Mullingar

Table 6.7 Qualitative and quantitative precision of the chromatographic method for all of the measured compounds (%)

	Qualitative precision (%)	Quantitative precision (%)
n-Hexane	0.09	1.89
Benzene	0.14	1.53
Cyclo-hexane	0.13	0.38
n-Heptane	0.04	1.73
Toluene	0.30	0.81
Ethylbenzene	0.10	1.88
m+p-Xylene	0.08	0.76
o-Xylene	0.06	2.50
1,3,5-trimethylbenzene	0.04	3.42
1,2,4-trimethylbenzene	0.05	3.56

The performance of the system is satisfactory, although the qualitative and quantitative precision of the monitoring equipment has deteriorated somewhat, compared to the initial

values calculated during monitoring at Dublin. Some deterioration of the performance of the capillary columns and cold trap with time is to be expected. The qualitative precision, in particular, has reduced significantly for many of the compounds. This was noted during monitoring, as there was more drift in the retention times of the compounds compared to the system performance during monitoring in Dublin. However, all chromatograms were manually inspected to ensure correct identification of the chromatographic peaks, and when necessary, incorrectly identified peaks were manually identified using the Turbochrom software (see Section 3.2.1). The quantitative precision is acceptable for the measured compounds, though as for the Dublin monitoring data, the quantitative precision is lowest for the trimethylbenzenes. Lower precision is also displayed by o-xylene. A possible reason for the lower quantitative precision on this occasion, compared to the Dublin monitoring period, is the lower hydrocarbon concentrations found in the calibration standard used in Mullingar compared to that used in Dublin (see Table 3.1), though slight deterioration of the system since initial commissioning is likely to be the most important factor.

6.3.2 Pumped Tube Hydrocarbon Monitoring Programme

The main objective of the pumped sampling study was to compare the results with those from the on-line monitoring system, which, if similar, would be a positive indication of the performance of both methods. The details of the pumped tube study are presented in Table 6.8. Sampling duration ranged between one and three hours, with the majority of the samples being taken at the mobile monitoring unit, and a few others being sampled around the industrial estate (see Figure 6.2). One tube was analysed at the Enterprise Ireland laboratory, while the remainder were analysed at the EPA laboratory in Cork. At the EPA laboratory the tubes were analysed for benzene, toluene, xylene and n-hexane, while only benzene, toluene and xylene were identified at the Enterprise Ireland laboratory. There were some concerns regarding the sensitivity of the analytical method used at the EPA laboratory, hence a high sampling rate was used to ensure that sufficient quantities of each compound were trapped on the tubes.

During sampling at the monitoring unit, the pumping unit was placed on the roof of the unit, as close as possible to the hydrocarbon intake point. The pumped sampling tubes were provided by the EPA laboratory in Cork and were supplied with Swagelok fittings to ensure that no contaminants could enter the tubes prior to sampling. Immediately after

sampling the fittings were replaced and the tubes were sent to the laboratory for analysis. Details of the tubes are given in Section 3.3. Because of the portability of the pumped sampling unit, all of the samples were collected downwind of either Penn or Taconic. This is the major advantage of this sampling method, as the continuous monitoring system must be considered as a fixed sampling location for the duration of the monitoring period. The only problem encountered with the pumped sampling system was related to the pump used to draw the sample through the system. The pump battery was old and tended to run down relatively quickly, hence not more than two consecutive samples could be taken before the battery needed to be recharged overnight.

Table 6.8 Summary details of pumped tube monitoring study

Tube no.	Start (date / time)	End (date / time)	Location (see map, Figure 6.2)	Analysed by
P1	22/10/99 09:40	22/10/99 12:40	Penn yard (1)	EPA Cork
P2	21/10/99 11:00	21/10/99 13:00	Taconic car park (2)	EPA Cork
P3	27/10/99 09:45	27/10/99 12:45	Statoil (3)	EPA Cork
P4	28/10/99 10:00	28/10/99 13:00	Stonefacings (4)	EPA Cork
P5	07/09/99 10:15	07/09/99 12:55	Monitoring unit (5)	EPA Cork
P6	07/09/99 15:15	07/09/99 16:15	Monitoring unit (5)	EPA Cork
P7	29/11/99 13:00	29/11/99 16:00	Monitoring unit (5)	EPA Cork
P8	01/12/99 08:37	01/12/99 11:02	Monitoring unit (5)	EPA Cork
P9	01/12/99 11:02	01/12/99 12:02	Monitoring unit (5)	EPA Cork
P10	07/12/99 09:50	07/12/99 10:50	Monitoring unit (5)	EI
P11	07/12/99 10:50	07/12/99 11:50	Monitoring unit (5)	EPA Cork
P12	07/12/99 11:50	07/12/99 12:50	Monitoring unit (5)	EPA Cork
P13	07/12/99 12:50	07/12/99 14:50	Monitoring unit (5)	EPA Cork
P14	09/12/99 09:30	09/12/99 11:30	Monitoring unit (5)	EPA Cork
P15	09/12/99 11:30	09/12/99 13:30	Monitoring unit (5)	EPA Cork

6.3.3 Passive Tube Hydrocarbon Monitoring Programme

The passive sampling tubes which were used during this study are a new design of radial passive sampling tubes (see Section 3.4), rather than the more traditional axial passive samplers which have a very low sampling rate. Several of these tubes were located beside the monitoring unit to assess their performance relative to the on-line monitoring system. The tubes were attached to lamp posts (permission being received from Westmeath County Council), at a height of three metres from ground level, inside purpose-built shelters which protect the tubes from adverse weather conditions. Details of the sampling duration and location (see Figure 6.2) for each of the tubes are presented in Table 6.9. Twenty passive

tubes were deployed during the monitoring period, with a much wider spatial distribution in and around the industrial estate, than was achieved in the pumped sampling tube study (see Figure 6.2). The recommended exposure period for these tubes is approximately one week. However, due to initial reservations about the sensitivity of the analytical equipment at the EPA laboratory in Cork, it was decided to increase the exposure time to trap a greater amount of contaminant on each tube. Exposure times of at least two weeks were therefore employed. Pairs of tubes were deployed at several locations to allow the analyses carried out at both laboratories to be compared, and to assess the repeatability of pollutant uptake between two tubes sampled at the same location for the same duration. Owing to the simplicity of this sampling method, no problems were encountered during the sampling period. The main advantages of the passive sampling method were portability, ease of use, and the low capital cost of the samplers.

Table 6.9 Summary details of passive tube monitoring study

Tube no.	Start Time	End Time	Location (see Figure 6.2)	Analysed by	Notes
R1	20/10/99 12:00	03/11/99 12:00	Penn yard (A)	EPA Cork	
R2	20/10/99 12:00	10/11/99 12:25	Penn yard (A)	EPA Cork	
R3	10/11/99 12:25	01/12/99 11:25	Penn yard (A)	EPA Cork	
R4	20/10/99 15:00	03/11/99 12:00	Taconic car park (B)	EPA Cork	
R5	20/10/99 15:00	10/11/99 13:00	Taconic car park (B)	EPA Cork	
R6	10/11/99 12:40	01/12/99 12:25	Taconic car park (B)	EPA Cork	
R7A	22/10/99 13:00	10/11/99 13:00	Monitoring unit (C)	EPA Cork	Pair
R7B	22/10/99 13:00	10/11/99 13:00	Monitoring unit (C)	EI	Pair
R8A	10/11/99 13:10	01/12/99 13:00	Monitoring unit (C)	EPA Cork	Pair
R8B	10/11/99 13:10	01/12/99 13:00	Monitoring unit (C)	EI	Pair
R9	10/11/99 12:50	01/12/99 12:35	Statoil (D)	EI	
R10A	22/10/99 13:10	10/11/99 12:15	Tyre shop (E)	EPA Cork	Pair
R10B	22/10/99 13:10	10/11/99 12:15	Tyre shop (E)	EPA Cork	Pair
R11	10/11/99 12:15	01/12/99 11:20	Tyre shop (E)	EI	
R12	10/11/99 13:00	01/12/99 12:30	Jones Oil (F)	EI	
R13	10/11/99 12:00	01/12/99 12:10	Road outside Penn (G)	EPA Cork	
R14A	22/10/99 14:10	25/11/99 12:00	In greyhound track (H)	EPA Cork	Pair
R14B	22/10/99 14:10	25/11/99 12:00	In greyhound track (H)	EPA Cork	Pair
R15A	22/10/99 14:00	25/11/99 12:10	In track car park (J)	EI	Pair
R15B	22/10/99 14:00	25/11/99 12:10	In track car park (J)	EPA Cork	Pair

6.4 MONITORING PROGRAMME AT RHODE

Hydrocarbon monitoring at Rhode was carried out from June 30th to July 14th 1999. Monitoring was carried out using only the on-line monitoring system. Data capture was

good (93 percent) with only short breaks due to calibration and a break in electricity, which fortunately occurred just prior to a site visit, hence only approximately 12 hours of data were lost. The monitoring system was operated using the zero air generator, rather than cylinders of zero air. Meteorological data were also collected at this site.

6.5 HYDROCARBON MONITORING RESULTS

6.5.1 Results from Mullingar Monitoring Period

Hydrocarbon concentrations using three different methods (on-line measurement, pumped tube sampling and passive tube sampling) were measured at Lynn Industrial Estate. The average results from all continuous measurements are presented in Table 6.10.

Table 6.10 Summary statistics for continuous HC monitoring at Mullingar, ppb

				Percentile				
	Average	Maximum	Median	90th	95th	98th	$D_{avg,1}$ [a]	$D_{max,1}$ [b]
n-Hexane	58.94	764.28	2.46	221.4	399.2	476.5	0.48	4.85
Benzene	0.48	80.07	0.15	0.8	1.6	3.1	1.80	16.97
Cyclo-Hexane [c]	3.17	67.18	0.00	10.4	21.0	31.2		
n-Heptane	0.07	1.93	0.00	0.2	0.3	0.8	0.17	1.54
Toluene	1.89	72.48	0.38	5.1	8.8	15.6	3.30	30.87
Ethylbenzene	0.39	7.20	0.16	1.0	1.4	2.3	0.48	3.93
m+p-Xylene	1.18	23.90	0.53	2.4	3.7	6.3	1.56	12.49
o-Xylene	0.50	8.20	0.25	1.2	1.7	2.3	0.59	4.82
1,3,5-trimethylbenzene	0.75	6.56	0.49	1.7	2.2	3.0	0.42	3.30
1,2,4-trimethylbenzene	1.18	5.10	1.12	1.6	2.5	3.1	0.74	5.94

[a] Davg,1 = average concentration during monitoring Period 1 in Dublin
[b] Dmax,1 = maximum concentration during monitoring Period 1 in Dublin
[c] Cyclo-hexane not present in calibration gas used during Dublin monitoring

The compounds which display the highest average concentrations are n-hexane, cyclo-hexane, toluene, and the sum of the xylene concentrations, in that order. These are the compounds which have known emissions in Lynn Industrial Estate. The n-hexane concentrations are particularly high. For comparison, the average and maximum concentration measured for each of the compounds during Phase 1 monitoring in Dublin is included in Table 6.10. For example, the average n-hexane concentration at the Mullingar monitoring site is 123 times higher, and the maximum concentration is 158 times higher. For toluene and total xylene, the Mullingar to Dublin ratios are 0.57 and 0.78, respectively, for the average concentration, and 2.35 and 1.85, respectively, for the maximum hourly

concentration. This indicates different behaviour for these compounds at Mullingar compared to Dublin, due to the impact of point source emissions at Lynn Industrial Estate. Average benzene concentrations measured at Lynn Industrial Estate are low compared to the Dublin Period 1 average of 1.8 ppb. However, as for toluene and xylene, the peak concentration is much greater than that measured in Dublin (16.97 ppb). This indicates the influence of emissions from a local source. The average measured concentrations for the trimethylbenzenes at Lynn Industrial Estate are also higher than the average Dublin roadside concentration (given in Table 4.6). The average concentration of ethylbenzene measured at Lynn Industrial Estate is slightly lower than that in Dublin, but the maximum measured concentration is nearly twice the maximum measured roadside concentration in Dublin. For n-heptane, the average measured concentration is low (as for the Dublin monitoring data), and the maximum measured concentration is similar to that measured in Dublin. The median values for cyclo-hexane and n-heptane are zero, indicating a large number of measured zero concentrations. Cyclo-hexane concentrations tended only to be elevated when n-hexane concentrations were very high.

The results from analysis of pumped tube samples are presented in Table 6.11. The mass of contaminant on each tube is presented, as is the average ambient concentration calculated from this mass. The average ambient concentration, C_{amb}, measured over the sampling period is given by:

$$C_{amb}\ (mg/m^3) = \frac{\text{mass of contaminant on tube } (\mu g)}{\text{volume of air sampled (litres)}} \qquad 6.1$$

For most of the tubes sampled at the mobile monitoring unit, simultaneous concentrations measured by the continuous monitoring equipment are available. Comparison can only be made between the continuous and pumped concentrations of n-hexane and benzene, as ambient concentrations of toluene and xylene at the monitoring site were very low, and no quantifiable trace of these compounds was found on the tubes. Benzene was measured on three of the tubes sampled at the monitoring unit; however agreement with the on-line data is poor. Agreement between the n-hexane concentrations is good, and is analysed further in Chapter 7. One of the pumped tubes was analysed at the Enterprise Ireland laboratory (Tube P10), hence hexane was not identified on this tube. The remaining tubes were analysed at the EPA laboratory. The sampling duration for each tube is given in Table 6.8.

Table 6.11 Results from analysis of pumped tube samples

Tube no.	Location (see Figure 6.2)	Mass of pollutant on tube (microgrammes)				Benzene average ppb	Hexane average ppb	Toluene average ppb	Xylene average ppb	Simultaneous average concentrations at on-line unit (ppb)				Analysed by
		Benzene	Hexane	Toluene	Xylene					Benzene	Hexane	Toluene	Xylene	
P1	Penn yard (1)	6.40	19.90	0.16	0.10	122.62	341.33	2.57	1.39					EPA Cork
P2	Taconic car park (2)	0.00	5.40	0.00	0.14	0.00	138.93	0.00	2.93					EPA Cork
P3	Statoil (3)	0.00	0.00	1.20	2.80	0.00	0.00	19.26	39.00					EPA Cork
P4	Stonefacings (4)	0.12	8.60	0.20	0.12	2.30	147.51	3.21	1.67					EPA Cork
P5	Monitoring unit (5)	0.00	11.50	0.00	0.00	0.00	221.91	0.00	0.00					EPA Cork
P6	Monitoring unit (5)	0.00	2.70	0.00	0.00	0.00	166.72	0.00	0.00					EPA Cork
P7	Monitoring unit (5)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					EPA Cork
P8	Monitoring unit (5)	0.60	30.40	0.00	0.00	14.27	647.28	0.00	0.00	1.73	527.96	0.67	1.32	EPA Cork
P9	Monitoring unit (5)	0.00	9.80	0.00	0.00	0.00	605.13	0.00	0.00	2.59	599.21	0.10	1.13	EPA Cork
P10	Monitoring unit (5)	0.011	NA	0.00	0.00	0.63	NA	0.00	0.00	0.10	45.09	0.12	0.40	EI
P11	Monitoring unit (5)	0.00	4.60	0.00	0.00	0.00	236.70	0.00	0.00	0.05	303.80	0.12	0.41	EPA Cork
P12	Monitoring unit (5)	0.00	5.40	0.00	0.00	0.00	277.86	0.00	0.00	0.20	325.62	0.10	0.30	EPA Cork
P13	Monitoring unit (5)	0.00	8.70	0.00	0.00	0.00	223.83	0.00	0.00	0.02	274.93	1.92	1.94	EPA Cork
P14	Monitoring unit (5)	0.70	19.50	0.00	0.00	20.12	501.70	0.00	0.00	0.20	601.39	0.16	0.50	EPA Cork
P15	Monitoring unit (5)	0.50	12.40	0.00	0.00	14.37	319.03	0.00	0.00					EPA Cork

Results of analyses of passive tube samples are presented in Table 6.12. Both the mass of contaminant collected on the tube and the equivalent average ambient concentration calculated from this mass are included. The equivalent ambient concentration depends on the uptake rate of each of the hydrocarbons by the adsorbent material. Each compound has a slightly different affinity for the adsorbent, and hence a different uptake rate. The uptake rate of the adsorbent for each compound is derived experimentally and is dependent on ambient temperature. The equivalent ambient concentration, C_{amb}, of a given hydrocarbon trapped on a Radiello tube is given by the equation:

$$C_{amb}\ (\mu g/m^3) = \frac{\text{mass of compound found on tube } (\mu g)\ .\ 1{,}000{,}000}{Q\ (cm^3 / \text{minute})\ .\ t\ (\text{minutes})} \qquad 6.2$$

Q = sampling rate; t = sampling duration

The equivalent sampling rates, Q, are quoted by the manufacturer for each compound, and are presented in Table 6.13 for each compound identified in this study. The uptake rate, Q, must be adjusted for ambient temperature, as follows:

$$Q_T = Q_{25}\left(\frac{273+T}{298}\right)^{1.5} \qquad 6.3$$

Q_{25} = Q value at 25 °C, as quoted in Table 6.13; T = average temperature during sampling

The ambient temperature measured at the monitoring unit was used to adjust the sampling rate in the results given in Table 6.12. The average concentrations measured by the Radiello tubes are generally low, particularly for n-hexane, where the high average concentrations measured by the on-line system were not captured by the passive samplers. The passive sample results for xylene and toluene at the monitoring unit location are in better agreement with the continuous analyser results, and several of the tubes located near Taconic, notably those located beside the Statoil garage (R9) and Jones Oil (R12), display high average toluene and xylene concentrations. These average concentrations are higher than the averages measured by the on-line system for the complete monitoring period. This reflects the proximity of the two tube locations to Taconic, compared to the monitoring unit location. All of the measured benzene concentrations are very low, reflecting the lack of a significant point source of benzene in the industrial estate.

Table 6.12 Results from analyses of passive tube samples

Tube no.	Location (see map)	Mass of pollutant on tube (microgrammes)				Benzene average ppb	Hexane average ppb	Toluene average ppb	Xylene average ppb	Simultaneous average concentrations at on-line unit (ppb)				Notes	Analysed by
		Benzene	Hexane	Toluene	Xylene					Benzene	Hexane	Toluene	Xylene		
R1	Penn yard (A)	0.1	3.7	0.68	0.42	0.07	2.80	0.43	0.28						EPA Cork
R2	Penn yard (A)	0.21	1.26	1.64	1.41	0.10	0.64	0.69	0.63						EPA Cork
R3	Penn yard (A)	0.5	1	5	6.8	0.24	0.51	2.15	3.07						EPA Cork
R4	Taconic car park (B)	0.1	0.1	0.43	0.42	0.07	0.08	0.27	0.28						EPA Cork
R5	Taconic car park (B)	0.19	0.66	1.48	0.9	0.09	0.34	0.63	0.40						EPA Cork
R6	Taconic car park (B)	0.5	0.2	6.5	6.4	0.24	0.10	2.78	2.89						EPA Cork
R7A	Monitoring unit (C)	0.2	1.14	1.54	0.94	0.10	0.64	0.72	0.46	0.28	23.23	1.74	1.4	PAIR	EPA Cork
R7B	Monitoring unit (C)	0.179	NA	1.973	1.457	0.09	NA	0.92	0.71	0.28	23.23	1.74	1.4	PAIR	EI
R8A	Monitoring unit (C)	0.4	21	3.5	4	0.19	10.78	1.50	1.80	0.55	72.75	3.6	3.05	PAIR	EPA Cork
R8B	Monitoring unit (C)	0.048	NA	1.564	2.04	0.02	NA	0.67	0.92	0.55	72.75	3.6	3.05	PAIR	EI
R9	Statoil (D)	0.086	NA	17.41	13.88	0.04	NA	7.46	6.26						EI
R10A	Tyre shop (E)	0.28	1.75	2.71	1.45	0.15	0.98	1.27	0.71					PAIR	EPA Cork
R10B	Tyre shop (E)	1	2.1	8.9	5.8	0.52	1.17	4.16	2.85					PAIR	EPA Cork
R11	Tyre shop (E)	0.062	NA	3.145	4.212	0.03	NA	1.35	1.90						EI
R12	Jones Oil (F)	0.118	NA	12.477	6.195	0.06	NA	5.35	2.80						EI
R13	Road outside Penn (G)	0.5	12.3	6.8	9.1	0.24	6.31	2.91	4.10						EPA Cork
R14A	In greyhound track (H)	0.7	3	7.4	6.6	0.21	0.95	1.95	1.83					PAIR	EPA Cork
R14B	In greyhound track (H)	0.7	3.3	7.8	6.6	0.21	1.04	2.05	1.83					PAIR	EPA Cork
R15A	In track car park (J)	0.263	NA	2.724	3.238	0.08	NA	0.72	0.90					PAIR	EI
R15B	In track car park (J)	1.1	11.3	7.6	7.7	0.32	3.56	2.00	2.13					PAIR	EPA Cork

Table 6.13 Radiello sampling rates for selected compounds, cm^3 / minute

Compound	Sampling rate at 25 °C
Benzene	23.6
Toluene	22.2
Xylene isomers	18.3
n-Hexane	19.8

6.5.2 Distribution of Hourly Hydrocarbon Concentrations at Mullingar

To assess the most likely frequency distribution of the hydrocarbon data collected at Lynn Industrial Estate, the Kolmogorov-Smirnov test was used to compare the frequency distribution of the measured data and the expected frequency distribution for lognormal, normal and gamma distributed data. The Kolmogorov-Smirnov test is explained in detail in Section 4.3.2. The analysis of hydrocarbon data from the Dublin roadside site showed that the gamma and lognormal distributions could both be applied to ambient hydrocarbon data, although air pollution measurements are generally accepted to have a lognormal frequency distribution. As the emission characteristics of many of the hydrocarbons measured at Mullingar were different to those in Dublin, it was expected that some differences in the observed frequency distribution may be apparent. For compounds such as hexane, toluene and the xylenes, because of the wide range of measured concentrations, it was expected that the right-hand tail of the distribution would be very long, i.e. the distribution would be highly skewed, as the mean concentration is much smaller than the highest measured concentrations. For other compounds the measured concentrations were very low or exhibited a large number of zero hourly concentrations (e.g. cyclo-hexane, n-heptane).

The Kolmogorov test was applied to hourly weekday data (Monday to Friday) from each week over the monitoring period at Mullingar, for each of the measured compounds. The results from this test are summarised in Table 6.14, and were carried out at a 95 percent confidence interval. They indicate that, for the majority of weeks, none of the above distributions is statistically similar to the distribution followed by the monitored data.

The frequency distribution of the measured hydrocarbons was not statistically different from lognormal behaviour on 28 out of 90 occasions, compared to 13 and 15 occasions for normal and gamma distributions, respectively. However, some compounds displayed a greater tendency towards lognormal behaviour, namely n-hexane, benzene and toluene, which exhibited lognormal behaviour on at least five of the ten weeks analysed. Although

few compounds are statistically defined as lognormal using the Kolmogorov-Smirnov test at the 95 percent confidence interval, it is clear that the frequency distribution of the majority of the compounds tends more towards lognormal behaviour, rather than gamma or normal distributions. The main exception is 1,2,4-trimethylbenzene, which tends towards normal behaviour on the majority of weeks.

Table 6.14 Results of Kolmogorov-Smirnov test for each week of weekday data at Mullingar

	Lognormal weeks	Normal weeks	Gamma weeks	None	More lognormal	More gamma
n-Hexane	5	1	1	4	9	0
Benzene	5	0	1	5	10	0
Cyclo-hexane	0	0	0	10	9	0
Toluene	7	0	3	3	9	1
Ethylbenzene	3	2	2	6	6	1
m+p-Xylene	2	3	3	6	5	1
o-Xylene	3	2	2	5	5	1
1,3,5-trimethylbenzene	2	4	2	6	4	3
1,2,4-trimethylbenzene	1	1	1	8	1	2
Total	28 (of 90)	13	15	53	58	9

The Kolmogorov-Smirnov test suggests that the Mullingar monitoring data tend towards lognormal behaviour, with the gamma distribution not being as important in this situation compared to the Dublin roadside monitoring data. It is likely that the larger number of zero and very low concentrations measured at this site resulted in poor agreement between the observed and the lognormal frequency distribution. The gamma distribution was not important for the compounds measured at this site, suggesting that this distribution may be more relevant for urban air quality measurements.

6.5.3 Results from Rhode Monitoring Period

Measured concentrations from hydrocarbon monitoring at the Rhode site were very low for most compounds. This was to be expected due to the remote location of the site, with very little local traffic. Summary results for this period are presented in Table 6.15. The magnitude of the higher concentrations shown are questionable. It is thought that these may have arisen due to malfunctions in the zero air generator used during this study (cylinders were used during monitoring at Mullingar). It is likely that the hydrocarbon removal mechanism in the zero air generator (a catalytic oxidation chamber) was not operating

efficiently, resulting in contaminated air being supplied to the FIDs in the GC. Therefore, the magnitude of the highest hourly hydrocarbon concentrations should be treated with caution, although the relative concentrations may be correct.

The compounds which exhibit the highest average concentration are isoprene and ethane. Isoprene is emitted from plants and trees, particularly during the warmer summer months, while ethane emissions may be high due to livestock farming and slurry spreading in the monitoring area. The ethane concentrations measured at this rural site agree very well with measurements at a rural monitoring site in the UK, where average concentrations of 7.45 ppb have been measured (Colbeck and Harrison, 1985a). Ethylene is another compound known to be emitted from the leaves of plants and trees (see Section 2.3.1), and natural sources are likely to have been partly responsible for the high average concentration of ethylene measured at this rural site. n-Pentane is the only other compound which displays an average concentration above 1 ppb. No source of this compound was identified in the vicinity of the monitoring site. Average acetylene concentrations are very low at this site, indicating the generally negligible impact of vehicle emissions at this location.

Table 6.15 Summary statistics for continuous HC monitoring at Rhode, ppb

	Average	Median	Maximum	Standard deviation	90th percentile	95th percentile	98th percentile
Ethane	7.21	7.04	15.71	1.95	9.44	9.83	11.04
Ethylene	2.02	0.00	20.78	3.97	5.66	9.59	16.70
Propane	0.20	0.16	2.79	0.31	0.34	0.49	0.75
Propylene	0.06	0.00	2.27	0.18	0.18	0.28	0.46
Isobutane	0.11	0.00	2.07	0.30	0.54	0.72	1.16
n-Butane	0.07	0.00	1.91	0.17	0.22	0.33	0.44
Acetylene	0.09	0.00	0.77	0.13	0.25	0.31	0.43
Trans-2-butene	0.01	0.00	1.27	0.10	0.00	0.00	0.17
1-Butene	0.02	0.00	0.65	0.07	0.07	0.10	0.21
Cis-2-butene	0.12	0.13	0.46	0.12	0.27	0.32	0.37
Isopentane	0.21	0.00	6.80	0.64	0.53	1.04	2.49
n-Pentane	1.64	1.60	19.40	1.75	3.20	4.00	5.60
1,3-butadiene	0.17	0.14	9.56	0.63	0.60	0.77	1.02
2-methylpent.	0.19	0.00	7.00	0.81	0.00	1.87	3.51
3-methylpent.	0.07	0.00	4.59	0.30	0.29	0.39	0.55
Isoprene	18.60	15.59	99.69	18.38	42.15	54.91	72.07

6.6 METEOROLOGICAL DATA

Meteorological data collected during monitoring at Mullingar are described in this section. Meteorological data collected at Rhode are not described, as the small amount of hydrocarbon data collected at this site do not merit detailed comparison with the meteorological data. At Mullingar, meteorological parameters (windspeed, wind direction and temperature) were measured at the monitoring unit. Met Eireann also supplied meteorological data from their regional monitoring station, located 1.5 km north of Mullingar town (in Irishtown, see Figure 6.1). Meteorological parameters from both locations are presented and compared in the following sections.

6.6.1 Wind Direction Data

The wind direction data collected at the monitoring unit are likely to be influenced by turbulent effects due to nearby buildings, even though the monitoring equipment was elevated approximately 10 metres above ground level. The Met Eireann monitoring location is free from such obstructions, as it is situated to provide a good indication of the regional meteorological conditions. Hence, there are likely to be differences between the readings at each site. The frequency of occurrence of each ten degree wind sector in both datasets are compared in Figure 6.11.

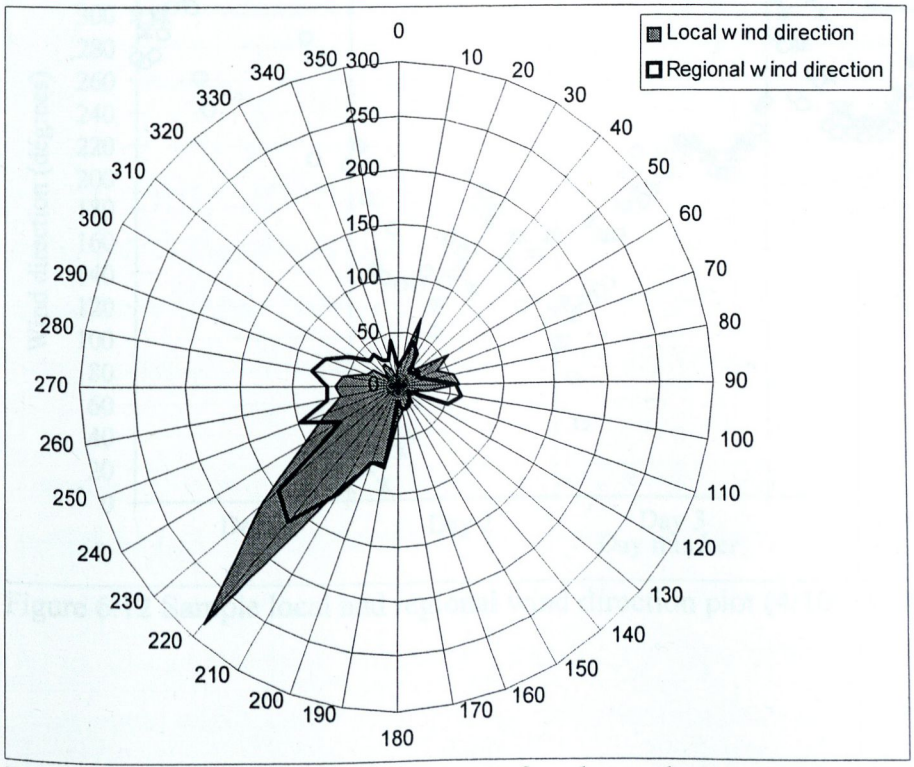


Figure 6.11 Frequency of occurrence of each ten degree wind sector during monitoring at Mullingar

It is worth noting that the wind directions experienced during monitoring cover a narrower range of directions than were noted at the regional Met Eireann station during May to August 1998 (see Figure 6.6), which were used in initial modelling to identify suitable monitoring locations.

The prevailing wind direction for local and regional data is similar, at approximately 220 to 240 degrees. The local data exhibits a greater frequency of winds from the 250 to 350 degrees direction, and a smaller number of occurrences in the 220 to 240 degree sector. However, the agreement between the two data sets is normally good, as can be seen from the time series plot in Figure 6.12. On four of the five days shown, agreement between local and regional wind direction is good. However, on day two, the regional wind directions of 0 to 80 degrees during the morning hours are not reflected in the local meteorological data. It is probable that trees located to the north and west of the monitoring site influenced the local wind direction measurements. However, the influence of local obstructions on wind direction is less than that observed during the Dublin monitoring period, where much more significant differences in wind direction were noted (see Figure 4.19 and Figure 4.20).

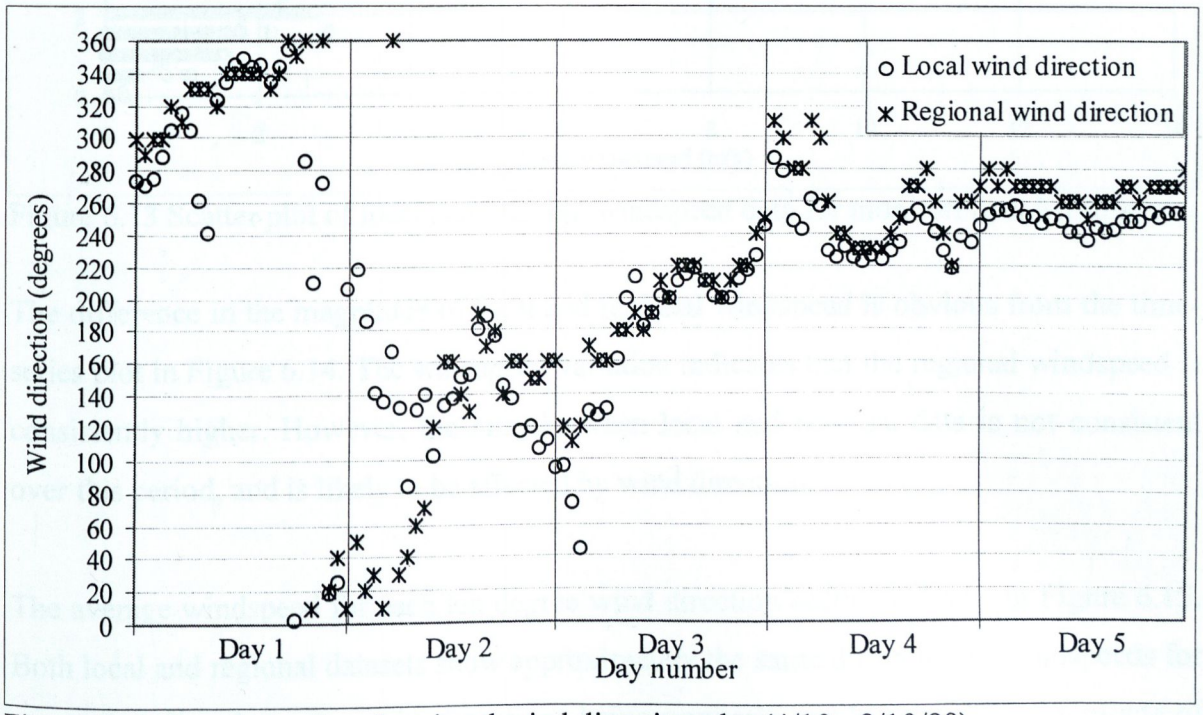


Figure 6.12 Sample local and regional wind direction plot (4/10 - 8/10/99)

6.6.2 Windspeed Data

The regional windspeed data are divided into discrete classes, while the local data are continuous. Some discrepancies are therefore likely to occur in comparisons of the two datasets. A scatter plot of the local and regional windspeed data for the complete monitoring period is given in Figure 6.13. A line with a slope of unity is included in Figure 6.13, indicating that the regional windspeed is normally higher than local data. This is to be expected, due to local obstructions reducing windspeed at the monitoring site. The same effects were observed with Dublin local and regional windspeed data (see Figure 4.22).

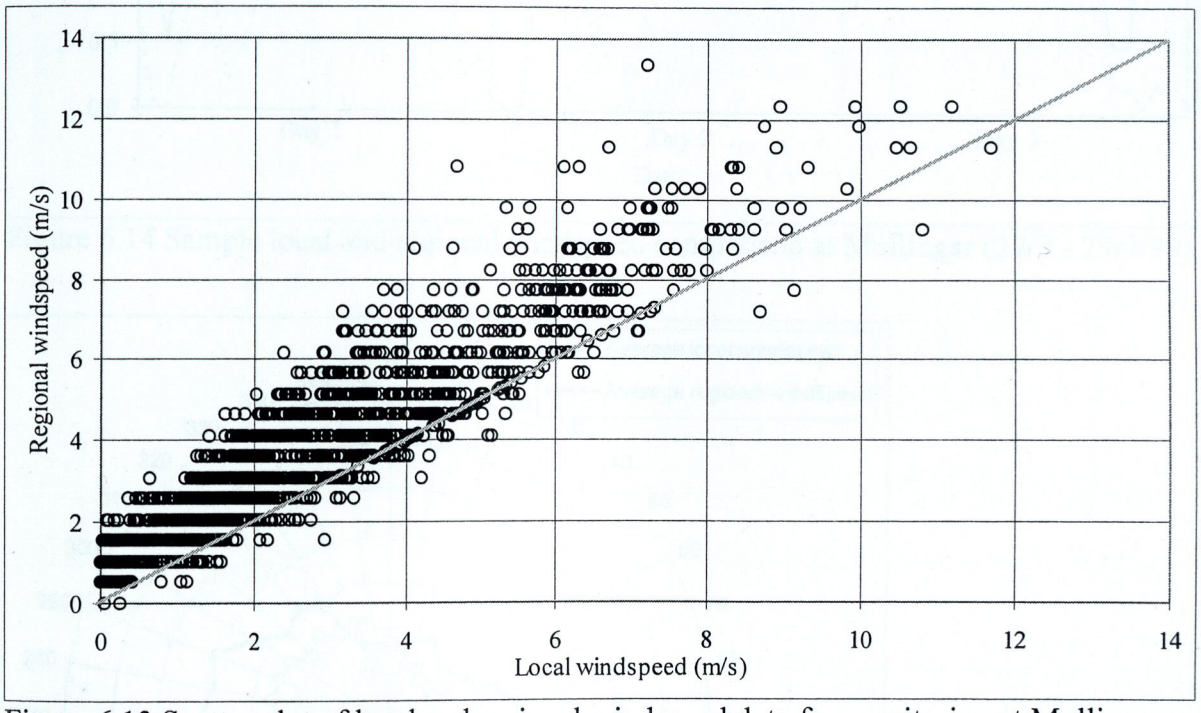


Figure 6.13 Scatter plot of local and regional windspeed data for monitoring at Mullingar

The difference in the magnitude of local and regional windspeed is obvious from the time-series plot in Figure 6.14. The windspeed variation indicates that the regional windspeed is consistently higher. However, the ratio between local and regional data is not consistent over this period, and is likely to be affected by wind direction.

The average windspeed for each ten degree wind direction sector is shown in Figure 6.15. Both local and regional datasets show approximately the same difference in windspeeds for most wind directions, the main exceptions being northerly winds, where the magnitude of the local and regional windspeed is the same, and the sector from 90 to 150 degrees where the regional windspeed is up to four times higher than the local windspeed.

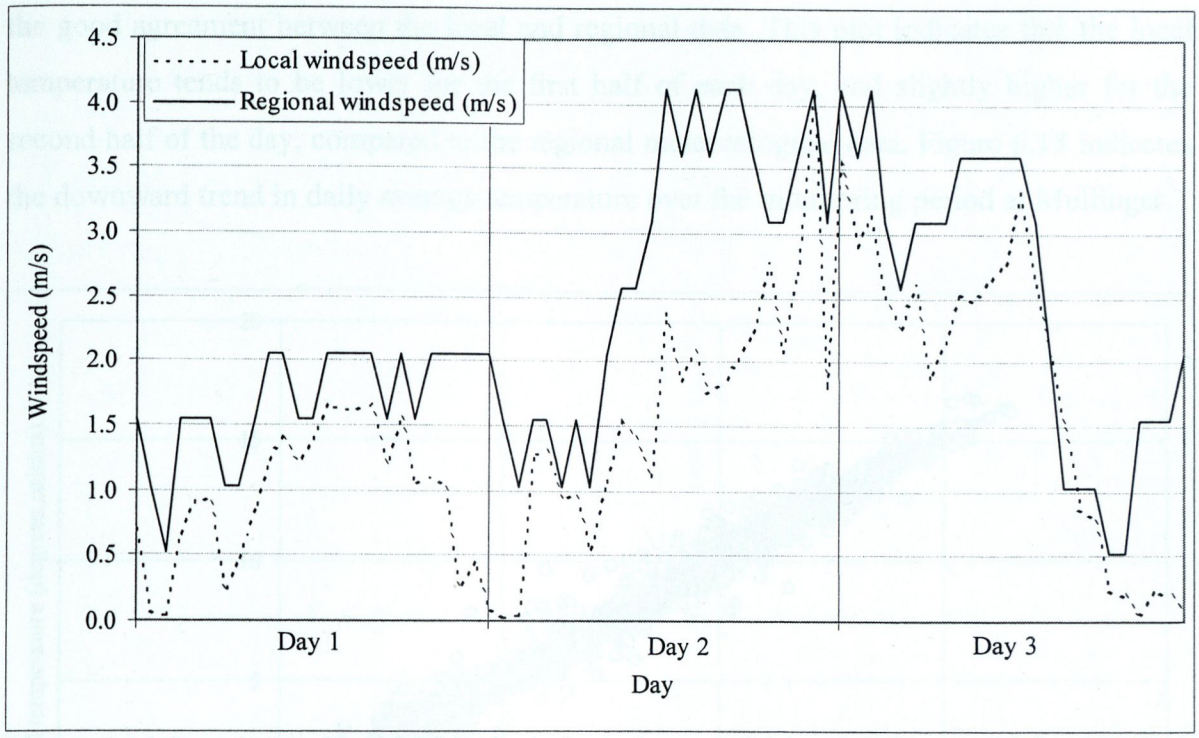


Figure 6.14 Sample local and regional windspeed comparison at Mullingar (27/9 - 29/9/99)

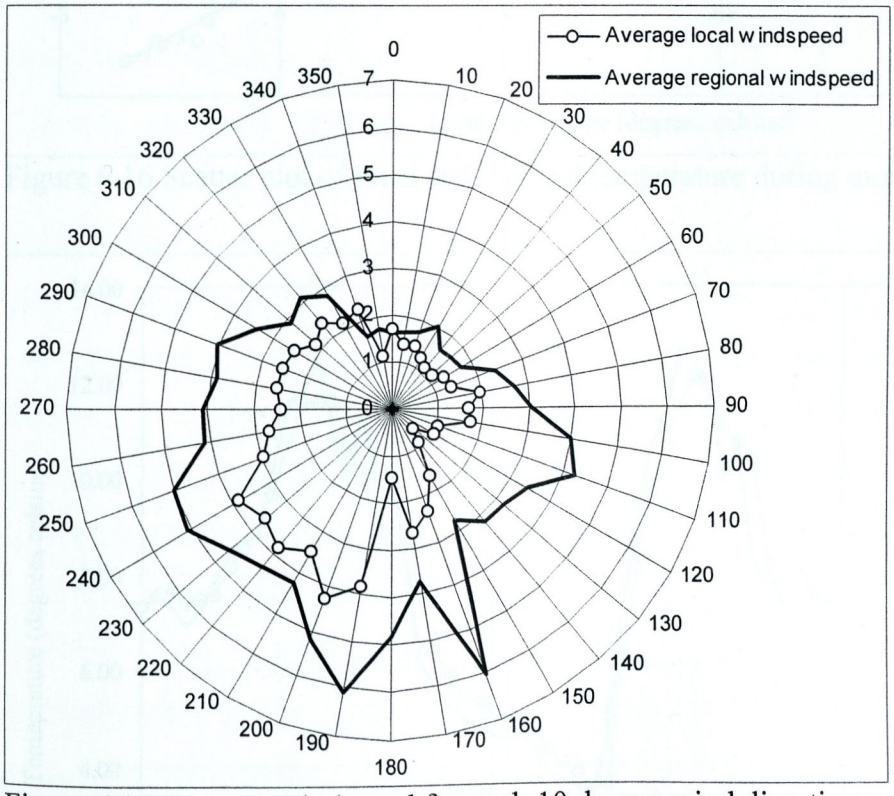


Figure 6.15 Average windspeed for each 10 degree wind direction sector, m/s

6.6.3 Temperature Data

Agreement between local and regional temperature data is excellent as can be seen from the scatter plot in Figure 6.16. There is very little scatter either side of the trend line. A time-series plot for a sample three day period is also given in Figure 6.17, again indicating

the good agreement between the local and regional data. This plot indicates that the local temperature tends to be lower for the first half of each day, and slightly higher for the second half of the day, compared to the regional meteorological data. Figure 6.18 indicates the downward trend in daily average temperature over the monitoring period at Mullingar.

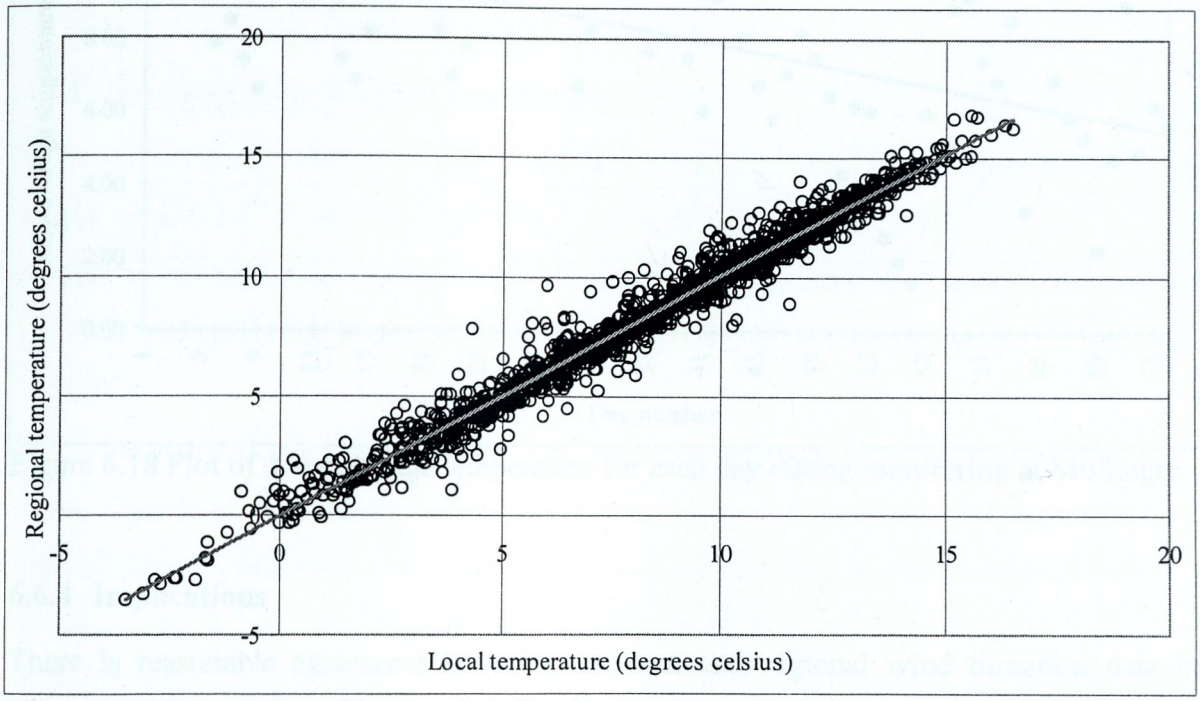


Figure 6.16 Scatter plot of local and regional temperature during monitoring at Mullingar

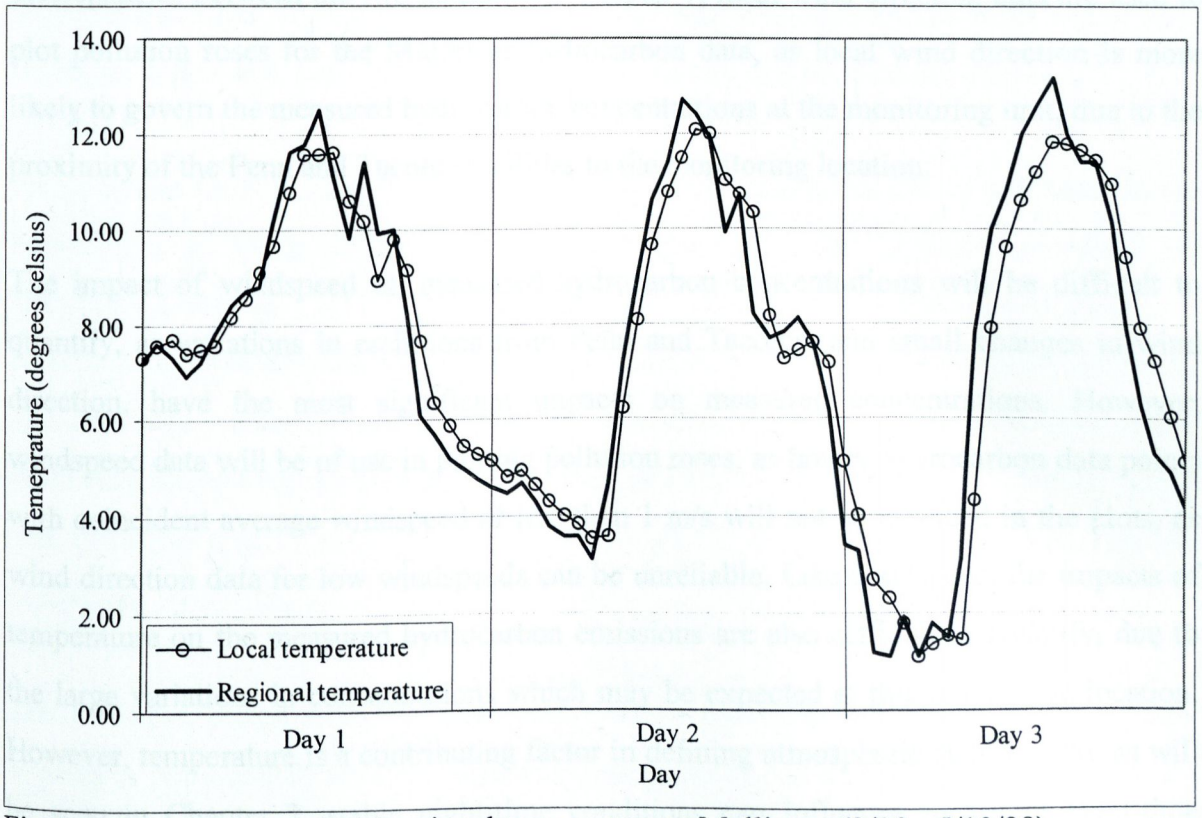


Figure 6.17 Sample local and regional temperature at Mullingar (3/10 - 5/10/99)

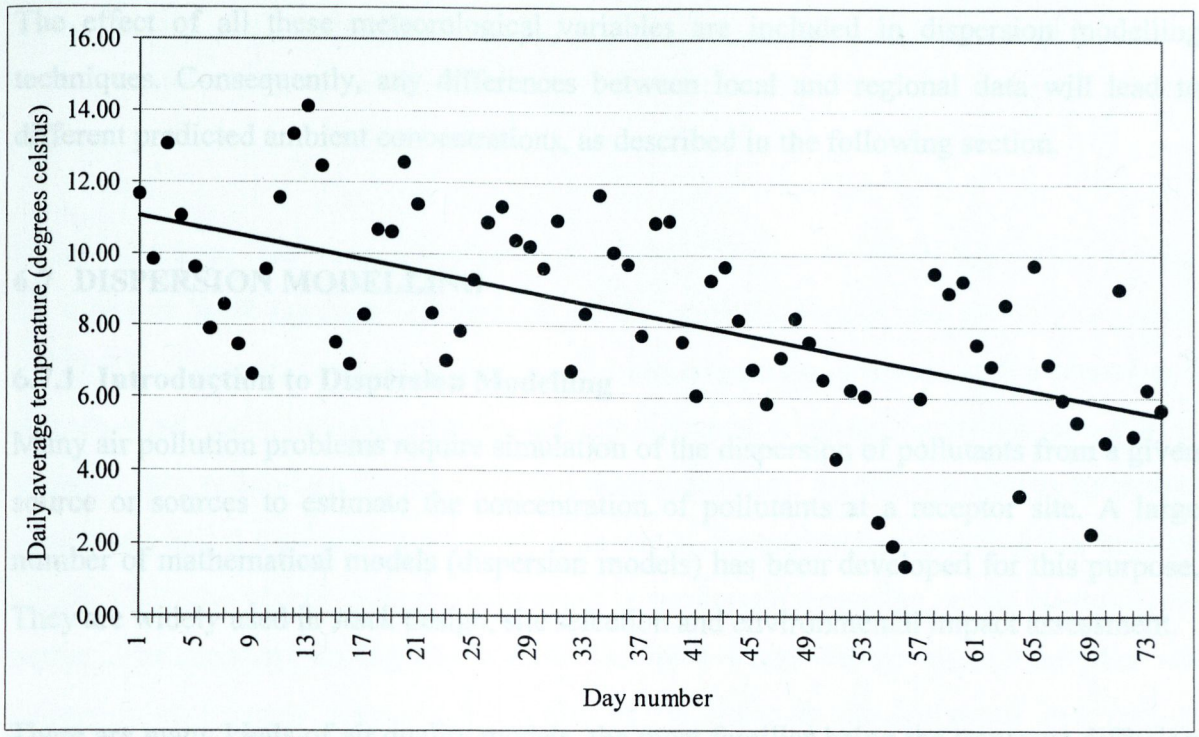


Figure 6.18 Plot of daily average temperature for each day during monitoring at Mullingar

6.6.4 Implications

There is reasonable agreement between the local and regional wind direction data in Mullingar, as opposed to the situation in Dublin, where local obstructions result in large discrepancies between the two datasets. In Chapter 7, local wind direction data are used to plot pollution roses for the Mullingar hydrocarbon data, as local wind direction is more likely to govern the measured hydrocarbon concentrations at the monitoring unit, due to the proximity of the Penn and Taconic facilities to the monitoring location.

The impact of windspeed on measured hydrocarbon concentrations will be difficult to quantify, as variations in emissions from Penn and Taconic, and small changes in wind direction, have the most significant impacts on measured concentrations. However, windspeed data will be of use in plotting pollution roses, as hourly hydrocarbon data points with coincident average windspeed of less than 1 m/s will not be included in the plots, as wind direction data for low windspeeds can be unreliable. Like windspeed, the impacts of temperature on the measured hydrocarbon emissions are also difficult to quantify, due to the large variations in concentrations which may be expected at this monitoring location. However, temperature is a contributing factor in defining atmospheric stability and, as will be seen in Chapter 7, stable night-time conditions can influence measured night-time hydrocarbon concentrations.

The effect of all these meteorological variables are included in dispersion modelling techniques. Consequently, any differences between local and regional data will lead to different predicted ambient concentrations, as described in the following section.

6.7 DISPERSION MODELLING

6.7.1 Introduction to Dispersion Modelling

Many air pollution problems require simulation of the dispersion of pollutants from a given source or sources to estimate the concentration of pollutants at a receptor site. A large number of mathematical models (dispersion models) has been developed for this purpose. They are widely used in stack design, site selection and environmental impact assessment.

There are many kinds of air quality models, the most familiar being the transport-diffusion types. Only a limited number of comprehensive validation studies of such models have been performed, and these demonstrate that calculations will only be accurate to within a factor of two at best. This suggests that simple Gaussian models are often as suitable as more complex ones; indeed, investigation of IPC licence applications of Irish facilities, indicate that the vast majority of industrial applications do employ the simpler models, sometimes referred to as screening models. These can be expected to perform best at short distances downwind, with steady winds, uniform terrain and no local obstructions.

Air pollution models quantitatively simulate factors affecting the fate of pollutants in the atmosphere. In air pollution dispersion modelling five major physical processes are simulated (Zannetti, 1990): pollutant advection (transport), diffusion (migration of pollutant due to concentration gradients), deposition, chemical reactions (transformation) and emission. Plume rise and the aerodynamic effects of terrain are also modelled. Model input data include emissions data, meteorological data (such as wind speed, mixing height and diffusion coefficients), site characteristics (such as terrain features) and removal processes.

The Gaussian plume model is a relatively simple mathematical model that is typically applied to point source emitters, such as power stations and industrial plants. One of the key assumptions used in these models is that over short periods of time (such as a few

hours), steady state emissions and meteorological conditions prevail. Air pollution is typically represented by an idealised plume emitted from a stack of known height and diameter.

When this plume reaches its effective stack height, dispersion in three dimensions occurs; the effective stack height being the sum of the stack height and the plume rise (Arya, 1999). The plume rise depends on the initial buoyancy and momentum of the plume, and also on wind speed and atmospheric stability. Dispersion in the downwind direction is normally assumed to be a function of mean wind speed only, while dispersion in the cross-wind and vertical directions is assumed to result in concentration profiles in the form of normal Gaussian curves, with the maximum concentration occurring at the centre of the plume. The standard deviations of these Gaussian distributions, often referred to as dispersion coefficients, represent the spread of the plume in the horizontal and vertical directions. These depend on a variety of meteorological conditions, the most important being the atmospheric stability, which is normally taken to depend on wind speed, insolation, and the extent of the cloud cover (Turner, 1970). The main advantage of Gaussian models is that they are simple and economical, enabling both long-term and real-time forecasts to be obtained (Vazquez, 1996).

As part of the EU air quality framework directive, dispersion modelling has been specified as a key component in urban air quality assessment (European Commission, 1998). Although it is recognised that modelling emissions from known sources, to predict ground level concentrations of stack emissions, does not provide as precise a result as actual measurements, it is not feasible to maintain a large number of monitoring stations throughout the country. Modelling is an efficient way to predict pollutant concentrations over large areas. Also, modelling can be used to predict future concentrations and to assess the impact of future emissions reduction policies.

The following sections describe the Gaussian equation and provide a general introduction to Gaussian dispersion modelling, including required inputs, expected accuracy and limitations.

6.7.2 The Gaussian Equation

The simplest form of the Gaussian plume formula is for a continuous point source in a uniform flow with homogenous turbulence (Arya, 1999):

$$\bar{c}(x,y,z) = \frac{Q}{2\pi\,\bar{u}\,\sigma_y\sigma_z}\ \exp\left[-\frac{y^2}{2\sigma_y^2}-\frac{z^2}{2\sigma_z^2}\right] \qquad 6.4$$

$\bar{c}$ = mean ambient pollutant concentration ($\mu g/m^3$)

Q = emission rate (normally given in grammes/second)

$\bar{u}$ = mean transport velocity (m/s)

σ_y and σ_z = plume dispersion parameters

x = downwind distance (m)

y = crosswind distance from plume centreline (m)

z = vertical distance above ground (m)

However, reflection at the surface is not considered in Equation 6.4. Assuming a perfectly reflecting surface gives the following reflected Gaussian formula (Arya, 1999). Reflection at the top of the boundary layer may also be modelled.

$$\bar{c}(x,y,z;H) = \frac{Q}{2\pi\,\bar{u}\sigma y\sigma z}\times\exp\left[-\frac{y^2}{2\sigma_y^2}\right]\times\left\{\exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right]+\exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right]\right\} \qquad 6.5$$

In Equation 6.5, the effective release height, H, is normally defined as the height of the emissions source from ground level (stack height), plus the plume rise above the level of the emissions point. The plume rise is caused by the buoyancy of the plume (if it is warmer than the surrounding atmosphere). The exit velocity may also result in some plume rise due to momentum effects. The effective height can be double the height of the stack if the plume is particularly buoyant (Arya, 1999).

The Gaussian dispersion equation is simple and includes many assumptions which can result in significant inaccuracies in the resulting predictions. Consequently, long term average concentrations can be predicted with a greater degree of accuracy than short-term (e.g. hourly) concentrations. The results of several model / measurement comparison studies are summarised by Williams (1996), who concludes that annual averages and peak

hourly concentrations due to emissions from a low level source can be predicted within a factor of two. Short-term predictions are likely to contain greater errors if both the location and the time of peak occurrences are required. The UK guidelines on dispersion modelling suggest that if a prediction lies within ± 50 percent of a measurement, a user would not consider that the model has behaved badly (DETR, 1998b). Although 100 percent errors may seem particularly large, as pointed out by Williams (1996), the quality of available model input data (meteorological and emissions data) does not normally justify the increased resources required to set up and run more complex models.

The assumptions generally implied in the basic Gaussian model include (Arya, 1999):

- continuous emissions at a constant rate, at least for the time required for the plume to reach the receptor;
- steady-state flow and constant meteorological conditions, at least for the transport time from the source to the furthest receptor;
- conservation of mass in the plume, even after reflection from the ground surface or at the top of the boundary layer;
- Gaussian or reflected Gaussian distributions of mean concentration in the lateral and vertical directions at any downwind location in the plume;
- a constant mean transport wind in the horizontal plane; obviously this is not true for flows over complex terrain, such as near buildings and hills;
- no wind shear in the vertical direction;
- windspeeds in the downwind direction which are strong enough to make turbulent diffusion in this direction negligible. This is likely to be invalid very close to the source.

The plume dispersion parameters, σ_y and σ_z, are important parameters in the dispersion equation, but unfortunately they are also difficult to quantify accurately. These dispersion parameters are a function of the atmospheric turbulence in the boundary layer. The primary parameters which influence turbulence are the friction velocity, the surface heat flux, and the depth of the boundary layer (Arya, 1999). Close to the emissions point, small scale turbulence dominates plume growth, as the dimensions of the plume are small. Further from the source, as the plume dimensions increase, larger scale eddies dominate. This

results in the σ_y and σ_z values increasing with distance from the plume, and they also increase with the time or sampling period over which they are measured (Williams, 1996).

The most popular method for characterising atmospheric turbulence is based on the Pasquill stability classification. This scheme is based on diffusion experiments carried out on rural, flat grassland in which concentrations were measured in a plume released from a source close to the surface over a distance of less than one kilometre. Diffusion parameters for longer distances were extrapolated from these data and from other limited observations (Arya, 1999). In this methodology, the dispersion parameters are given as a function of both the downwind distance from the source (x) and the prevailing atmospheric stability class. Because stability is classified into a small number of classes (six), the estimated dispersion parameters exhibit abrupt changes as the stability class changes. The limited data, collected in the original experiments, on which the curves for calculating the diffusion parameters are based, also imply inherent inaccuracies (Arya, 1999). However, the simplicity of calculating the stability class from standard meteorological data has resulted in the continued popularity of this method.

Other empirical methods have been proposed to characterise atmospheric turbulence including the Brookhaven National Laboratory Scheme and the Tennessee Valley Authority Scheme, both of which were carried out over more complex terrain than the Pasquill experiments. Also, unlike the Pasquill experiments, both the Brookhaven and Tennessee schemes were based on releases from elevated sources, with Brookhaven using non-buoyant and Tennessee highly buoyant emissions. Further details of these schemes are included in Arya (1999). In France, the method of estimating the dispersion parameters proposed by Doury, based on experimental data collected by the Sandia Corporation, is popular (European Process Safety Centre, 1999). The Doury classification is reported to provide more accurate results than Pasquill for lower wind speed situations (< 2 m/s).

It has been reported that, in new generation models, there is a greater tendency to employ continuously varying stability parameters (Tasker, 1997), rather than the traditional discrete Pasquill parameters. These continuously varying parameters are commonly based on the height of the boundary layer and the Monin-Obukhov length (determined by temperature, friction velocity and heat flux) which is a parameter that characterises the stability of the surface layer of the atmosphere and can be calculated from ground-level measurements

(Zannetti, 1990). A recent study carried out by Mohan and Siddiqui (1998), compared the atmospheric stability estimated from seven different stability classification schemes. It was concluded that the Monin-Obukhov length scheme showed the best performance among all the schemes, while the Pasquill classification scheme performed poorly. The Monin-Obukhov length is a continuous function, which allows a more accurate description of atmospheric behaviour compared to methods such as the Pasquill classification scheme, which consists of a small number of discrete classes.

6.7.3 Model Validation and Evaluation

Model validations are normally carried out using existing datasets of pollutant measurement. For example, the ADMS model has been validated against field data sets from Kincaid, Indianapolis, Prairie Grass, Copenhagen and Lillestrom, which are all commonly used standard datasets (CERC, 1999).

ADMS has also been validated against a large set of archived LIDAR (light detecting and ranging) data from five different sites in the UK (Carruthers *et al.*, 1996; Carruthers *et al.*, 1997). Results using the ISC model were also compared to the ADMS results in this study. It was concluded that ADMS provided a more reliable prediction than ISC of the location and magnitude of the maximum ground-level concentration in convective conditions. The absolute performance of the ADMS model relative to the LIDAR data was defined as 'good', in that the error in predictions of maximum ground-level concentration was within a factor of two, on average. However, this validation study involved modelling of emissions from tall stacks over simple terrain. Little information is available on modelling low level emissions over more complex terrain.

In order to promote improved harmonisation between dispersion models used by different countries in the European Union, and to allow more reliable intercomparisons between models, a 'model validation toolkit' has been compiled. This kit is a collection of three experimental data sets accompanied by software for model evaluation. It is a practical tool, meant to serve as a common frame of reference for modellers (Olesen, 1998). This ensures that interpretation of model validation results is more uniform between different studies. This kit was developed as part of the workshop on 'harmonisation within atmospheric dispersion modelling for regulatory purposes' (Moussiopoulos, 1997; Olesen, 1998).

A very simple method for model evaluation and comparison is suggested by Cox and Tikvart (1985). This method restricts analysis to higher concentration values, as these values are of most concern in terms of environmental impacts, and regulatory decisions. The fractional bias and standard deviation of the modelled and measured data are calculated. The model whose fractional statistics are most tightly distributed about the origin is judged to be the more reliable model. This method is used in Chapter 7 to assess the ISC and ADMS results.

The USEPA recommend the following graphical displays for model evaluation studies (Sampson and Guttorp, 1999):

- Time-series plots comparing hourly predicted and observed concentrations;
- Isopleths of observed and predicted concentrations for selected hours and for daily maxima;
- Scatterplots of predictions and observations;
- Quantile plots.

Some of these graphical methods are used in Chapter 7 to compare the modelled and measured results.

It is important to bear in mind, however, that the reliability of dispersion model outputs is intrinsically linked to the quality of the model inputs. The UK guidelines on dispersion modelling indicate that it is not necessarily helpful to invest in an expensive and time-consuming advanced model if only sketchy and inaccurate emissions and meteorological data are available (DETR, 1998b). The inputs which are normally most poorly defined are the source emission parameters, such as the flow rate, exit temperature and pollutant emission rate as, unlike meteorological data, these parameters are rarely measured continuously. Emission inputs for modelling purposes are normally based on grab samples taken at the source. For some source types, where emissions are constant and continuous, results from grab samples may provide satisfactory model results. However, where emissions parameters are variable, results from infrequent grab samples may result in large errors in the model outputs, particularly for prediction of short-term (hourly) concentration estimates. Both of these situations are encountered at the Mullingar monitoring location,

where emissions from Penn are relatively constant and continuous, while emissions from Taconic are neither continuous or constant.

6.7.4 Description of the ISC and ADMS Dispersion Models

The above description of the Gaussian plume equation describes the basis for many dispersion models currently used in air pollutant dispersion calculations. Most dispersion modelling is carried out using modelling packages based on the Gaussian equation, but which also have added features such as algorithms to accommodate terrain data, building effects, and variations in surface roughness. One of the most used Gaussian models is the USEPA-approved ISC model (Industrial Source Complex). The next generation of the ISC model, called AERMOD, has recently been released. The availability of such packages now means that models are increasingly used by non-specialists, and the emphasis has firmly been placed on ensuring quality input data, particularly emissions data (Williams, 1996).

New generation dispersion models have attempted to improve the description of dispersion and turbulence in the atmosphere. The realisation that there are different turbulence and diffusion characteristics at different heights in the atmosphere has led to a more sophisticated parameterisation of the boundary layer. These models are still based on the Gaussian plume equation (Equation 6.5), however under convective atmospheric conditions these models use a skewed probability density function (rather than a Gaussian distribution function) to characterise the vertical concentration distribution in the boundary layer. AERMOD uses such an approach, as does the ADMS (Atmospheric Dispersion Modelling System) model, which was developed in the UK. Rather than using the traditional Pasquill classifications to derive the dispersion coefficients (σ_y and σ_z), new generation models determine these parameters from known relationships with turbulence quantities such as σ_v and σ_w, which are the standard deviations of velocity fluctuations in the y (lateral) and z (vertical) directions, respectively (Perry *et al.*, 1998). It is thought that the Pasquill classification scheme could be in error by up to 25 percent, especially when used for non-level, complex terrain and for large distances ranging up to 50 kilometres or more. Pasquill himself proposed a re-examination of his coefficients and suggested they be revised (Turner, 1970).

The Industrial Source Complex model (ISC) and the Atmospheric Dispersion Modelling System (ADMS) employed in this project represent examples of the conventional and modern Gaussian models, respectively. ADMS was developed by Cambridge Environmental Research Consultants in the UK, while ISC was developed for the USEPA.

Table 6.16 lists the main data inputs required for the ADMS and ISC models. A comparison of these shows that only ADMS requires data on cloud cover and surface roughness, whereas ISC employs the notion of stability class and distinguishes only between urban and rural environments. ADMS employs hour-by-hour cloud cover data, along with the time of year, time of day and latitude of the source to determine the intensity of the sunlight on the ground surface. This is used, in turn, to profile the variation in ground temperature during the day and determine the heat flux from surface to atmosphere. This allows the mixing layer depth and convective turbulence present to be quantified. Dispersion coefficients determined on this basis have been validated for a number of regions in the UK. This approach is in contrast to that used by ISC requiring the user to determine which of six possible stability classes occur in each hour, standard dispersion coefficients derived from experiments in the USA being associated with each class.

Table 6.16 Basic inputs of ADMS and ISC models

ADMS	ISC
Emissions	**Emissions**
Source location	Source location
Emission rate	Emission rate
Volume flow rate or exit velocity	Volume flow rate
Temperature of emissions	Temperature of emissions
Stack height and diameter	Stack height and diameter
Contaminant type	Contaminant type
	Gas exit velocity
Meteorology*	**Meteorology***
Wind speed	Wind speed
Wind direction	Wind direction
Temperature	Temperature
Cloud cover	Stability class
Topography	**Topography**
Terrain height data	Terrain height data
Roughness data	Urban or rural options
Building dimensions and locations	Building dimensions and locations

*Example of typical basic data

Table 6.17 lists the main features of the ADMS and ISC models. Several other modelling systems are available which use the ISC algorithms for calculation purposes, but which also have many of the user utilities of ADMS, such as windows operation and links to GIS (Geographical Information Systems). One such system is the Breeze ISC Suite developed by Trinity consultants. The ISC model used during this study was a MS-DOS based version of ISC-ST3 (Industrial Source Complex, Short-Term, version 3.0).

Table 6.17 Features of ADMS and ISC models

	ADMS	ISC
Model type	**Quasi-Gaussian**	**Gaussian**
Meteorological pre-processor	*	*
Complex terrain module	*	*
Building module	*	*
Coastline module	*	*
Windows based	*	
Commercially or publicly available	**commercial only**	**public**
Developed for European conditions	*	
Plume spread dependent on height	*	
Accepts digitised terrain data	*	
Links to contour plotting and GIS utilities	*	

The ADMS model proved too expensive to purchase for the project. Therefore, modelling was carried out at the AEA Technology headquarters in Culham (Oxfordshire), who hold a site licence for ADMS, version 3.0. The modelling work was carried out over a two day visit to AEA during February 2000.

6.7.5 Modelling Programme at Mullingar

Modelling of emissions from Penn and Taconic was carried out using both the ISC and ADMS dispersion models. The main inputs which were required for both models were meteorological and emissions data.

Windspeed, wind direction and temperature data were required by both dispersion models while Pasquill stability class was required by the ISC model, and cloud cover data by the ADMS model. The models were run using both 'local' and 'regional' meteorological data. The closest Met Eireann monitoring station at which cloud cover or Pasquill stability data

were measured was at Dublin airport and these data were used to supplement both local and regional meteorological input data.

Emissions data were gathered from the emissions sampling reports, which are available in the public file held by the EPA for each IPC licensed facility. Data on other emission parameters such as the emission height and the dimensions of the vent openings were provided by Penn and Taconic. The pollutant emission data used in the model were based on samples which were taken during the monitoring period at Mullingar. As mentioned previously (Section 6.2.1), emissions from Penn are reasonably continuous and constant compared to those from Taconic. Hence, the hexane emission rates used for each of the release points at Penn were simply calculated from averaging the results from the quarterly stack samples, from quarter two and three of 1999. The emissions parameters used for modelling emissions from the Penn facility in both the ISC and ADMS model are presented in Table 6.18. The five emission vents are denoted SOL-1 to SOL-5.

It is more difficult to estimate hydrocarbon emission rates from Taconic because the duration and magnitude of emissions on any given day is variable, especially from the rubber coater production line, which operates infrequently. Monthly sampling results of emissions from the sealcon adhesive line indicate that toluene and xylene emissions rates are reasonably constant during normal operation. Therefore, constant emissions were assumed from the sealcon emissions point from 08:00 to 17:00 each weekday. Although this is not a true reflection of the emissions at Taconic (as production may only occur for two to three hours on some days), it ensures that any elevated concentrations occurring during the working day are predicted. Operation of the rubber coater line is very sporadic, with intervals of weeks possible between production runs. Employing maximum emissions values from this production line in the model would, therefore, significantly overestimate average ambient concentrations. Therefore, emissions from this line were weighted on the basis of, on average, one day of operation per week, assumed to be constantly emitted over the course of the five normal working days, i.e. the emissions rate from the rubber coater was assumed to be 20 percent of its actual operating emissions, but emitted constantly from 08:00 to 17:00, Monday to Friday. Again, this is not a true reflection of the emissions scenario, but this emission rate is most likely to provide an accurate prediction of long term average ambient concentrations. The parameters used to model emissions from Taconic are presented in Table 6.19. The release points for emissions from the sealcon adhesive line

and the rubber coater line are denoted A6 and A7, respectively. The stack co-ordinates given in Table 6.18 and Table 6.19 are the Ordnance Survey grid co-ordinates. The magnitude of the flow for each emissions point is presented as a normalised flow (i.e. at standard temperature and pressure).

Table 6.18 Emission parameters for Penn release points

Stack identification number	SOL - 1	SOL - 2	SOL - 3	SOL - 4	SOL - 5
X co-ordinate (metres)	243659	243657	243653	243650	243642
Y co-ordinate (metres)	252255	252259	252253	252248	252235
Base elevation (metres)	85	85	85	85	85
Release height (metres) above ground level	11	11	11	11	11
Release temp. (°C)	55.45	20.85	22.60	23.55	21.10
Stack diameter (metres)	0.45	0.64	0.45	0.36	0.73
Normalised flow (Nm^3/hr)	10207.50	6053.53	10748.25	2754.22	6931.82
Hexane emission rate (g/s)	9.49	2.10	4.97	0.79	3.69

Table 6.19 Emission parameters for Taconic release points

Stack identification number	A6	A7
X co-ordinate (metres)	243505	243505
Y co-ordinate (metres)	252343	252346
Base elevation (metres)	91.00	91.00
Release height (metres)	11.00	11.00
Release temperature (°C)	57.50	64.00
Stack diameter (metres)	0.40	0.40
Normalised volume flow (Nm^3/hr)	3790.00	3788.00
Toluene emission rate (grammes/second)	0.27	0.76
Xylene emission rate (grammes/second)	0.70	0.00

Flat terrain was assumed in both models; however, building effects were taken into account, although it has been suggested that the simplifying assumptions in the building effects algorithms of dispersion models (even new generation models such as ADMS) can result in poor ambient concentration prediction in the near field (Air Quality Management, 1997). Only the buildings on which the stacks are located and other very close buildings were considered. Including all the buildings in the estate would have resulted in very lengthy calculation times for the models, and would have made little difference to the results, as those buildings closest to the emission point have the greatest effect on pollutant dispersion (Abbott, 2000). For buildings with low level emissions points, such as in this study, building downwash can be an important factor. Building downwash occurs when the emitted pollutants are entrained in the turbulent air resulting from the prevailing wind

blowing over and around the building. The UK Department of the Environment suggest that building downwash is likely to be an important factor if the stack height is less than 2.5 times the height of the building upon which it sits (DETR, 1998b). Such a condition pertains at both Penn and Taconic. Building effects are discussed further in Section 7.5.3.

The location of the mobile monitoring unit, passive tube sampling locations and the pumped tube sampling locations were used as the receptor positions in each of the models. ADMS was also run with a gridded receptor output, as this allowed contour plots of concentration in the vicinity of the industrial estate to be plotted using the built-in contour plotting software. Sample plots are given in Section 7.5.3.

7. ANALYSIS OF PHASE 2 RESULTS

7.1 INTRODUCTION

Analysis of the hydrocarbon monitoring results from Mullingar and Rhode are presented in the following sections. The short-term variations in the on-line hydrocarbon data collected at Lynn industrial Estate, Mullingar, are presented in Section 7.2, including correlation analysis of the hourly hydrocarbon data. Section 7.3 investigates the impact of local meteorological data on the measured hydrocarbon concentrations, while Section 7.4 assesses the accuracy and utility of the pumped and passive sampling results. Summary results obtained from dispersion modelling of emissions from two facilities in Lynn Industrial Estate are presented in Section 7.5. The accuracy of these results is assessed in Section 7.6, by comparing the results from the models with the on-line hydrocarbon measurements. Analysis of the hydrocarbon data from Rhode is presented in Section 7.7.

7.2 SHORT-TERM VARIATIONS IN HYDROCARBON CONCENTRATIONS

7.2.1 Diurnal Patterns

The diurnal concentration patterns followed by the compounds measured at Lynn Industrial Estate are markedly different to those exhibited by the data collected at the Dublin roadside site (see Section 5.1.1). At this site, the concentrations of several of the measured hydrocarbons are dominated by emissions from two point sources in the industrial estate, hence, the typical double peaked diurnal pattern observed in the roadside data is not seen at this site. Because ambient concentrations are dominated by point source emissions, the diurnal pattern can vary significantly from day to day, thus the concept of the average and representative day used in Section 5.1.1 and 5.1.2 cannot be applied to these data.

A sample diurnal plot for n-hexane is presented in Figure 7.1. Concentrations during the early hours of the morning are very high, indicating high emissions during this period, though poor night-time atmospheric mixing is likely to have contributed to the measured concentrations. A shift in wind direction in the evening period results in measured concentrations reducing to close to zero. The diurnal pattern for cyclo-hexane is identical to that of n-hexane, as cyclo-hexane is also emitted from the Penn facility, although the magnitude of the cyclo-hexane concentrations is smaller.

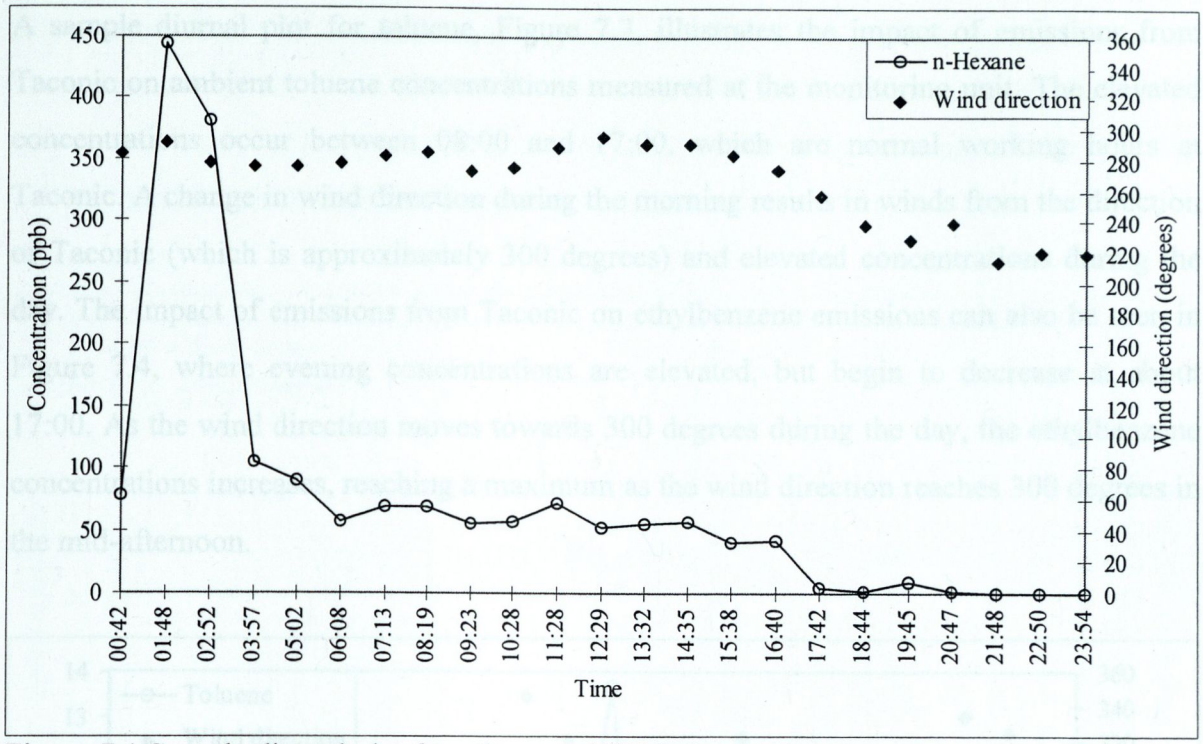


Figure 7.1 Sample diurnal plot for n-hexane (6/11/99)

A sample diurnal plot for benzene is given in Figure 7.2. During the peak in concentration measured in the evening, the wind direction changes from 340 degrees to 280 degrees, which is roughly from the direction of Taconic, thus suggesting that Taconic emissions may be responsible for this peak, though the measured concentrations are very low.

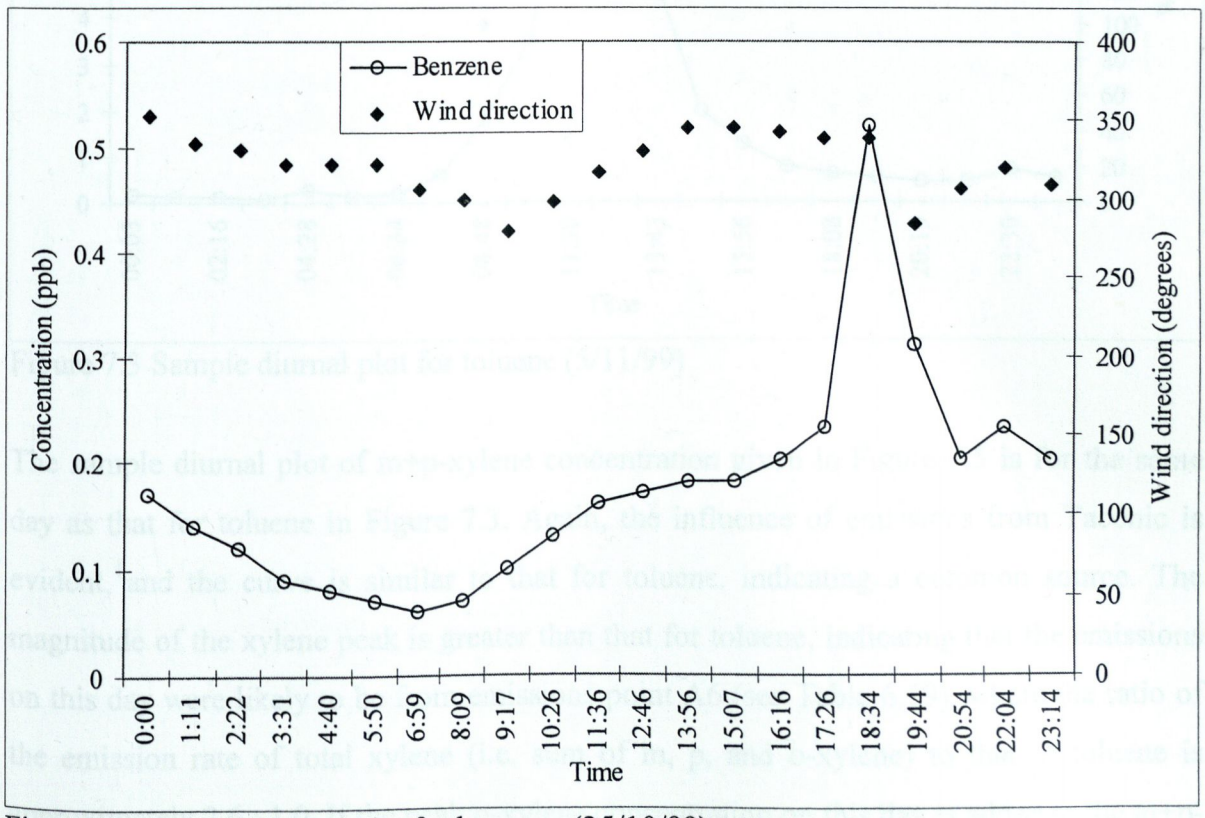


Figure 7.2 Sample diurnal plot for benzene (25/10/99)

A sample diurnal plot for toluene, Figure 7.3, illustrates the impact of emissions from Taconic on ambient toluene concentrations measured at the monitoring unit. The elevated concentrations occur between 08:00 and 17:00, which are normal working hours at Taconic. A change in wind direction during the morning results in winds from the direction of Taconic (which is approximately 300 degrees) and elevated concentrations during the day. The impact of emissions from Taconic on ethylbenzene emissions can also be seen in Figure 7.4, where evening concentrations are elevated, but begin to decrease at about 17:00. As the wind direction moves towards 300 degrees during the day, the ethylbenzene concentrations increases, reaching a maximum as the wind direction reaches 300 degrees in the mid-afternoon.

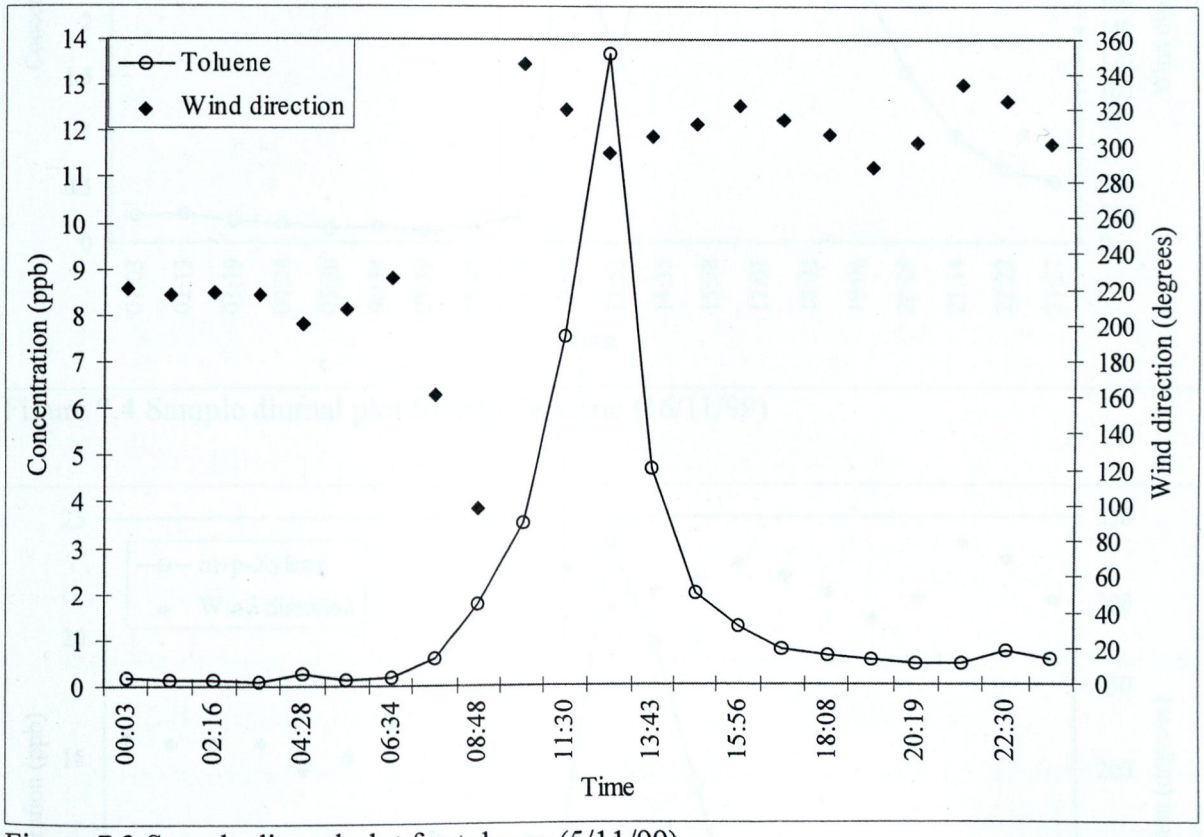


Figure 7.3 Sample diurnal plot for toluene (5/11/99)

The sample diurnal plot of m+p-xylene concentration given in Figure 7.5 is for the same day as that for toluene in Figure 7.3. Again, the influence of emissions from Taconic is evident, and the curve is similar to that for toluene, indicating a common source. The magnitude of the xylene peak is greater than that for toluene, indicating that the emissions on this day were likely to be from emissions point A6 (see Table 6.19), where the ratio of the emission rate of total xylene (i.e. sum of m, p, and o-xylene) to that of toluene is approximately 2.6 : 1.0. If the peak o-xylene concentration on this day is added to the m+p-

xylene peak, the total xylene peak concentration is 29.55 ppb. When compared to the toluene peak of 13.67 ppb, a ratio of approximately 2.2 : 1.0 is attained. Concentrations of m+p-xylene and o-xylene are strongly correlated (see correlation analysis later in this section), hence their diurnal patterns are very similar.

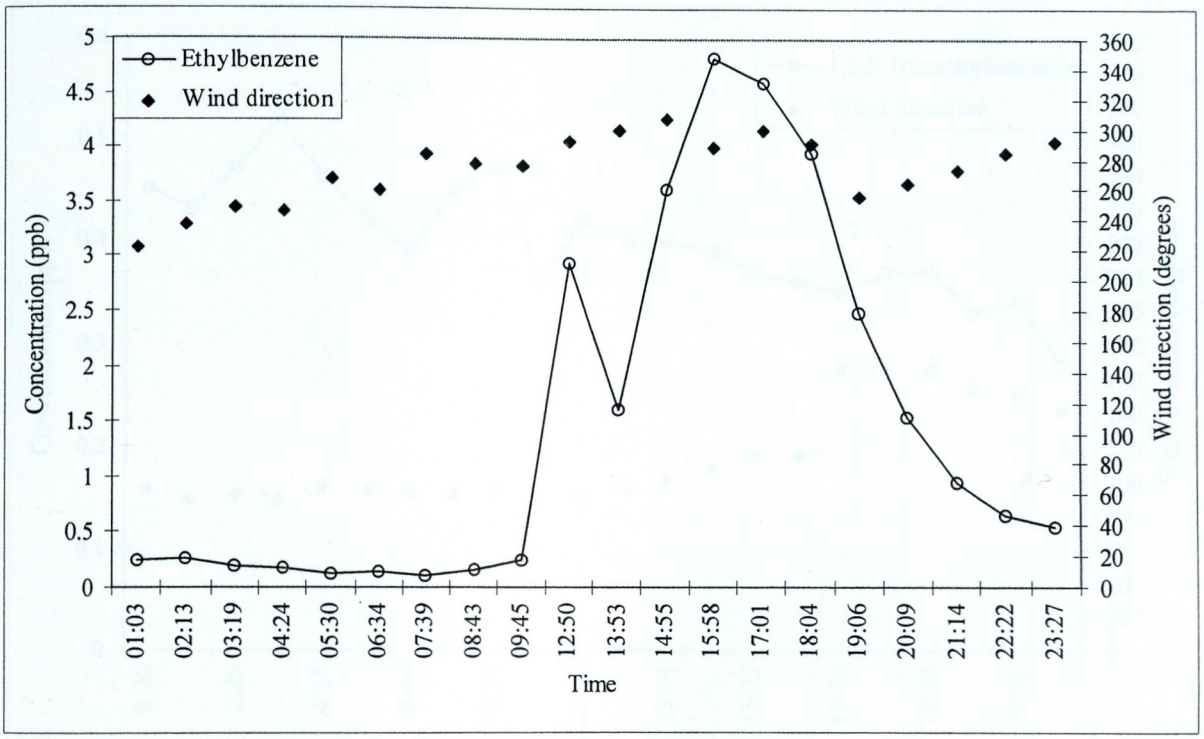


Figure 7.4 Sample diurnal plot for ethylbenzene (16/11/99)

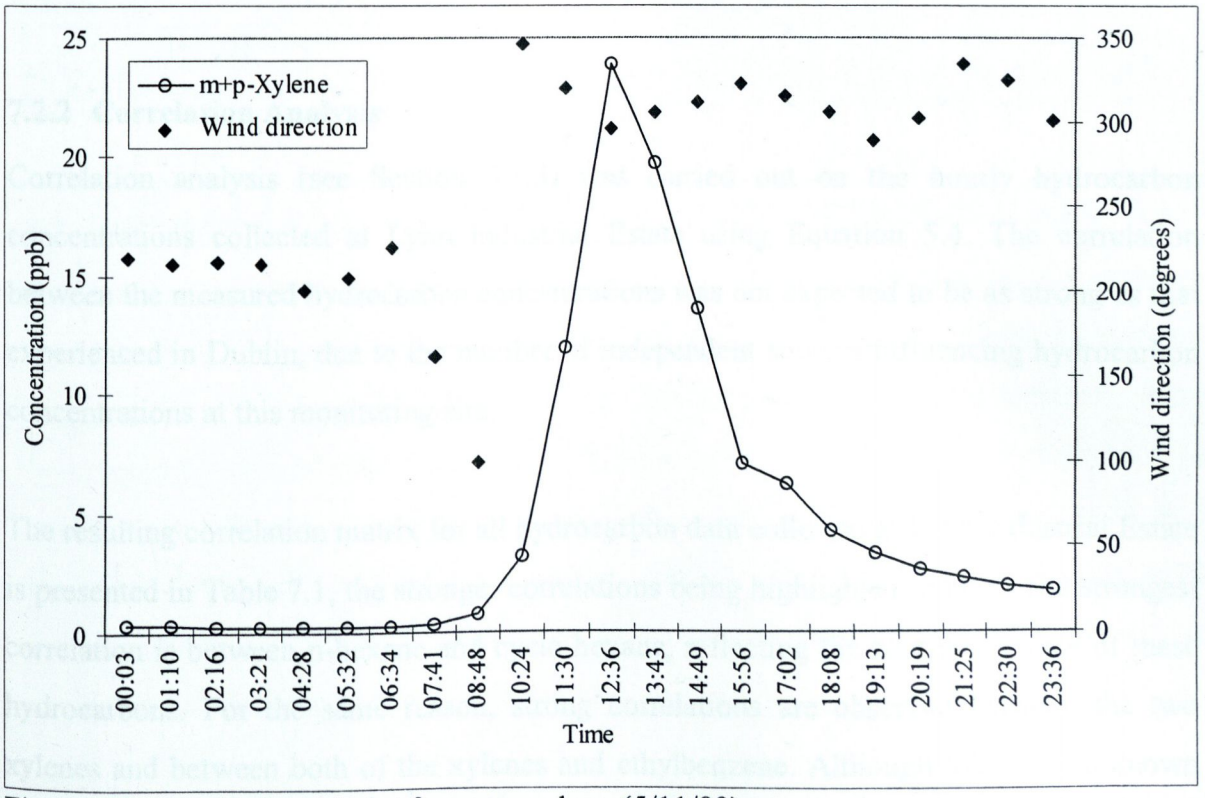


Figure 7.5 Sample diurnal plot for m+p-xylene (5/11/99)

The trimethylbenzenes often display relatively constant ambient concentrations, as the example plot in Figure 7.6 indicates. No source of either trimethylbenzene was identified throughout the monitoring period, however, some peaks in concentrations were noted. Concentrations were generally less variable than those of other measured hydrocarbons.

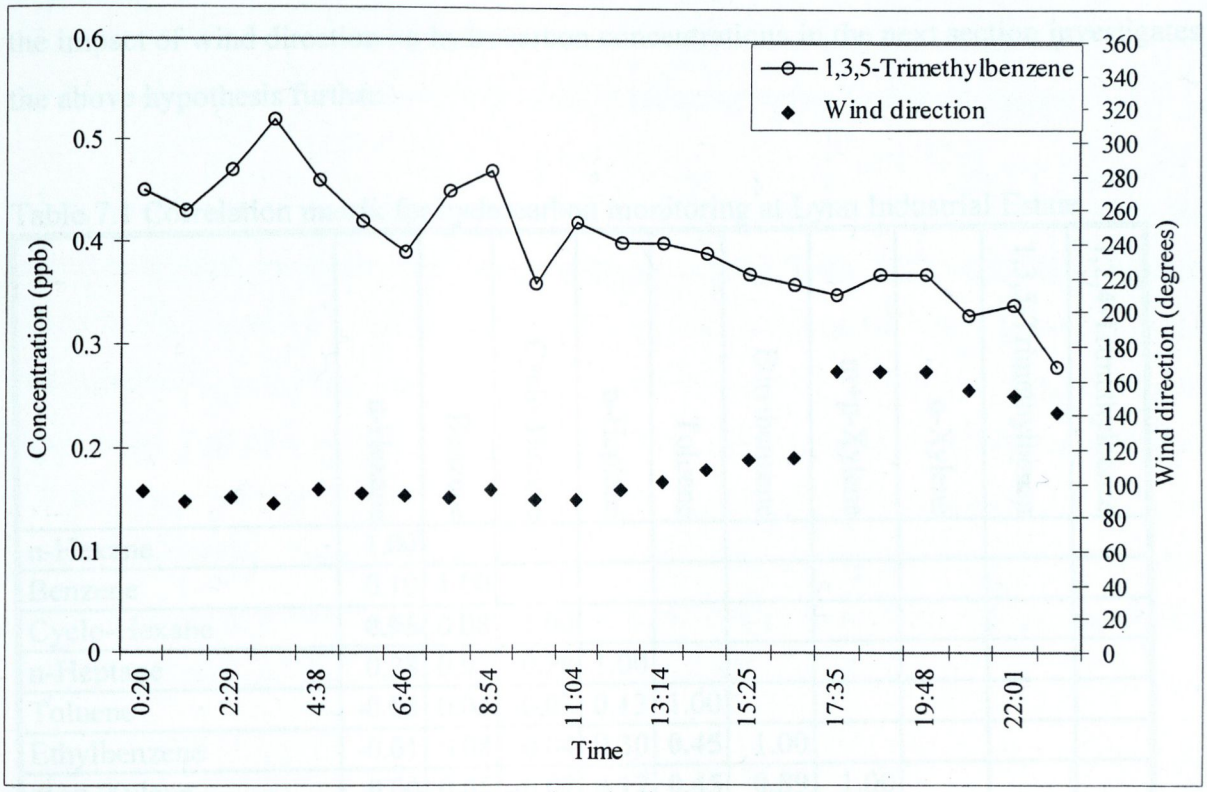


Figure 7.6 Sample diurnal plot for 1,3,5-trimethylbenzene (23/10/99)

7.2.2 Correlation Analysis

Correlation analysis (see Section 5.1.3) was carried out on the hourly hydrocarbon concentrations collected at Lynn Industrial Estate using Equation 5.4. The correlation between the measured hydrocarbon concentrations was not expected to be as strong as that experienced in Dublin, due to the number of independent sources influencing hydrocarbon concentrations at this monitoring site.

The resulting correlation matrix for all hydrocarbon data collected at Lynn Industrial Estate is presented in Table 7.1, the stronger correlations being highlighted in bold. The strongest correlation is between n-hexane and cyclo-hexane, reflecting the common source of these hydrocarbons. For the same reason, strong correlations are observed between the two xylenes and between both of the xylenes and ethylbenzene. Although toluene is a known emission from Taconic, its correlation with the xylenes and ethylbenzene is weak,

reflecting the variability of toluene emissions from this source, as described in Section 6.7.5. There is a weak but appreciable correlation between 1,3,5-trimethylbenzene and o-xylene, indicating that Taconic may be a source of 1,3,5-trimethylbenzene, though no emissions of this compound are detailed in the plant's IPC licence. The correlation of 1,3,5-trimethylbenzene with other compounds emitted from Taconic is weaker. Analysis of the impact of wind direction on hydrocarbon concentrations in the next section investigates the above hypothesis further.

Table 7.1 Correlation matrix for hydrocarbon monitoring at Lynn Industrial Estate

	n-Hexane	Benzene	Cyclo-Hexane	n-Heptane	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene	1,3,5-Trimethylbenze	1,2,4-Trimethylbenze
n-Hexane	1.00									
Benzene	0.10	1.00								
Cyclo-Hexane	**0.95**	0.08	1.00							
n-Heptane	0.28	0.07	0.28	1.00						
Toluene	-0.03	0.08	-0.03	0.13	1.00					
Ethylbenzene	-0.01	0.08	-0.04	0.30	**0.45**	1.00				
m+p-Xylene	0.00	0.05	-0.02	0.12	**0.45**	**0.89**	1.00			
o-Xylene	-0.04	0.09	-0.06	0.23	**0.48**	**0.94**	**0.92**	1.00		
1,3,5-Trimethylbenzene	-0.12	0.09	-0.09	0.17	0.27	0.31	0.23	**0.39**	1.00	
1,2,4-Trimethylbenzene	0.17	0.00	0.18	0.02	0.02	-0.08	-0.07	-0.10	-0.07	1.00

7.3 HYDROCARBON CONCENTRATIONS AND METEOROLOGICAL DATA

This section concentrates mainly on the influence of wind direction on the measured concentrations, as ambient hydrocarbon concentrations in the industrial estate are greatly influenced by variations in wind direction. The influence of ambient temperature and windspeed is very difficult to quantify, as hour-to-hour variations in concentrations are much more affected by variations in emissions, and changes in the prevailing wind direction. The influence of atmospheric stability on the night-time hydrocarbon concentrations is also investigated, though this is not possible for hexane concentrations, as production at the Penn facility is continuous.

7.3.1 Hydrocarbon Pollution Roses

When measuring pollutant concentrations in the vicinity of point sources, wind direction is the most important factor. If the wind blows stack emissions towards the monitoring location, elevated concentrations will be measured; however, emissions from the point source will have no impact on measured concentrations if the wind is blowing in the opposite direction. The number of occurrences of each ten degree wind direction, measured at the monitoring unit over the course of the monitoring period, is given in Figure 6.11.

The prevailing wind direction is between 190 and 270 degrees. The directions from the monitoring unit to Penn and Taconic were approximately 250 and 300 degrees, respectively. Figure 6.11 indicates that neither of these bearings are within the range of the most frequently occurring wind directions, however, some occurrences of these directions were noted. Pollution roses for all of the measured hydrocarbons are presented in Figure 7.7 to Figure 7.16, giving the average measured hydrocarbon concentration for each ten degree wind sector. These pollution roses were calculated using all measured hourly data points (including weekends), in which the average hourly windspeed was greater than 1 m/s. Wind direction data for windspeeds below 1 m/s are not reliable.

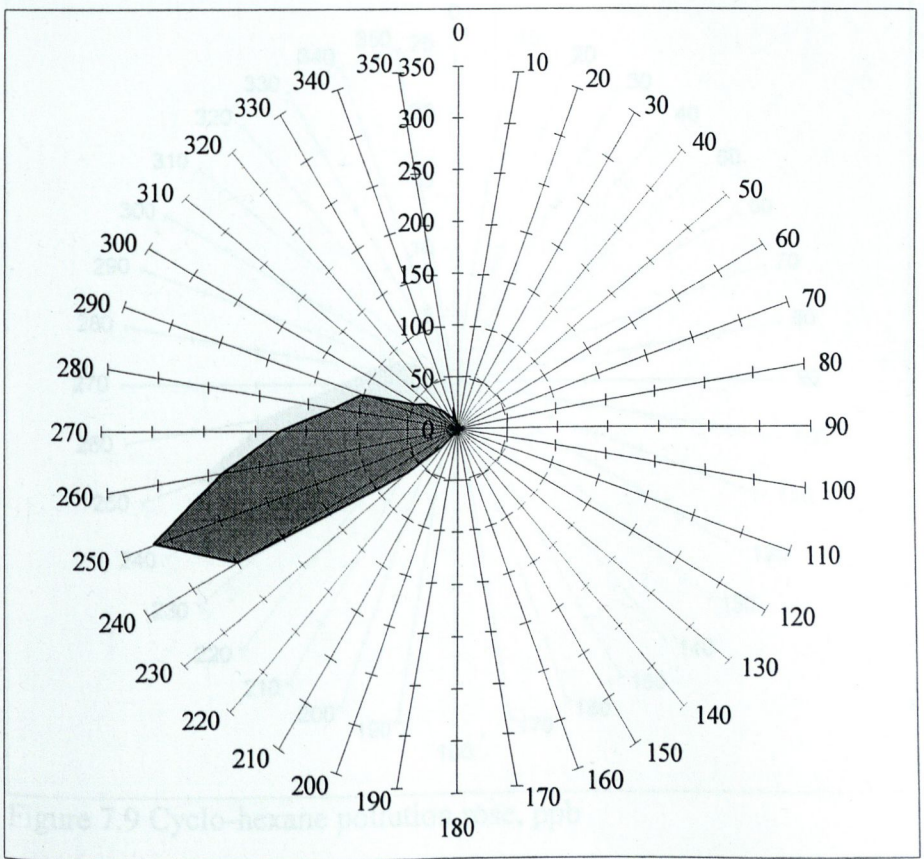


Figure 7.7 n-Hexane pollution rose, ppb

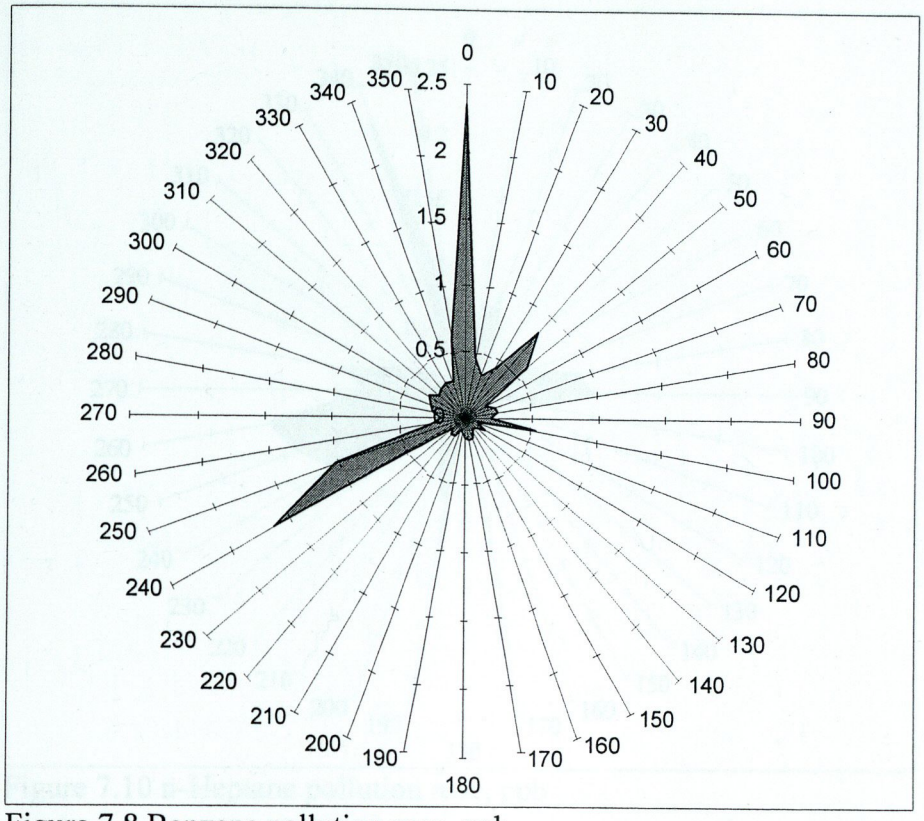


Figure 7.8 Benzene pollution rose, ppb

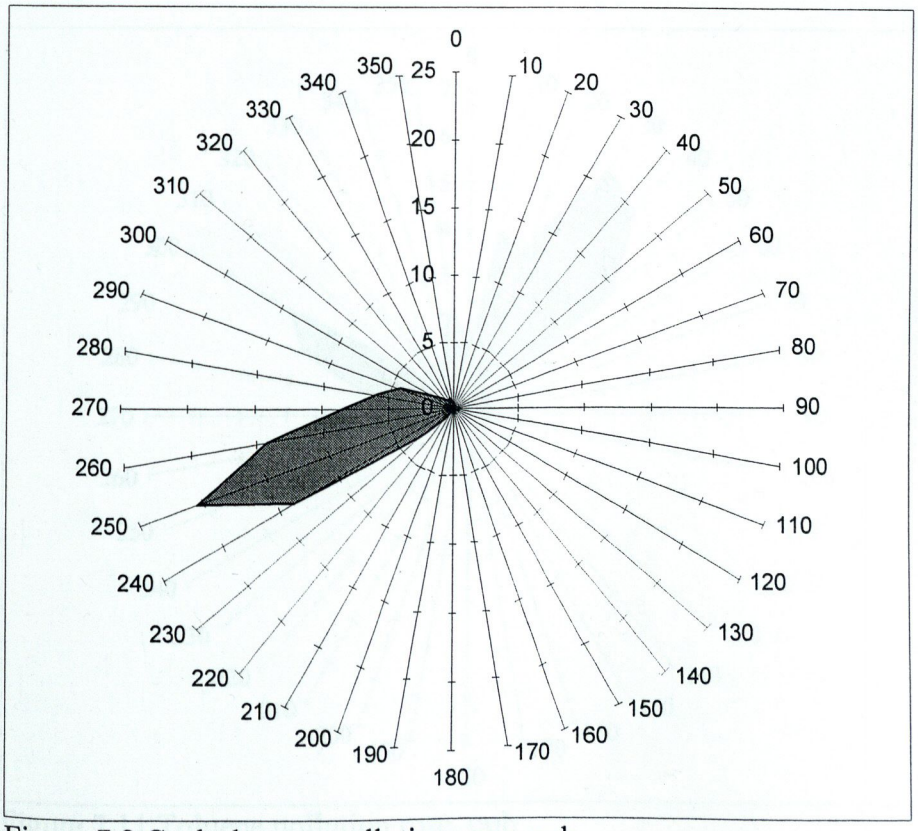


Figure 7.9 Cyclo-hexane pollution rose, ppb

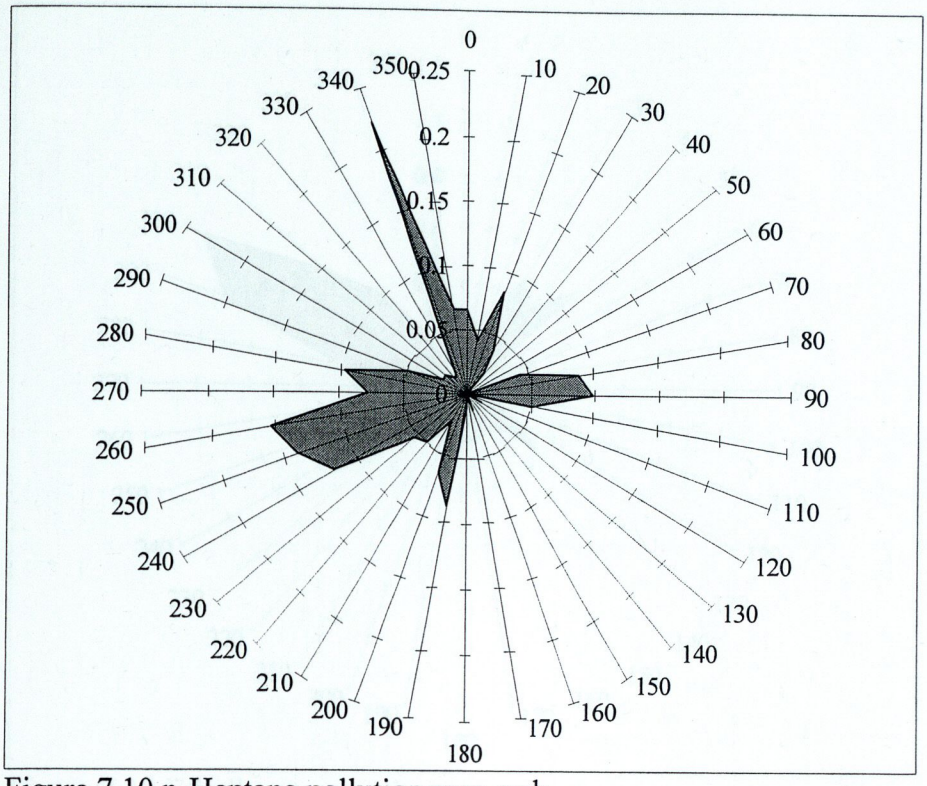


Figure 7.10 n-Heptane pollution rose, ppb

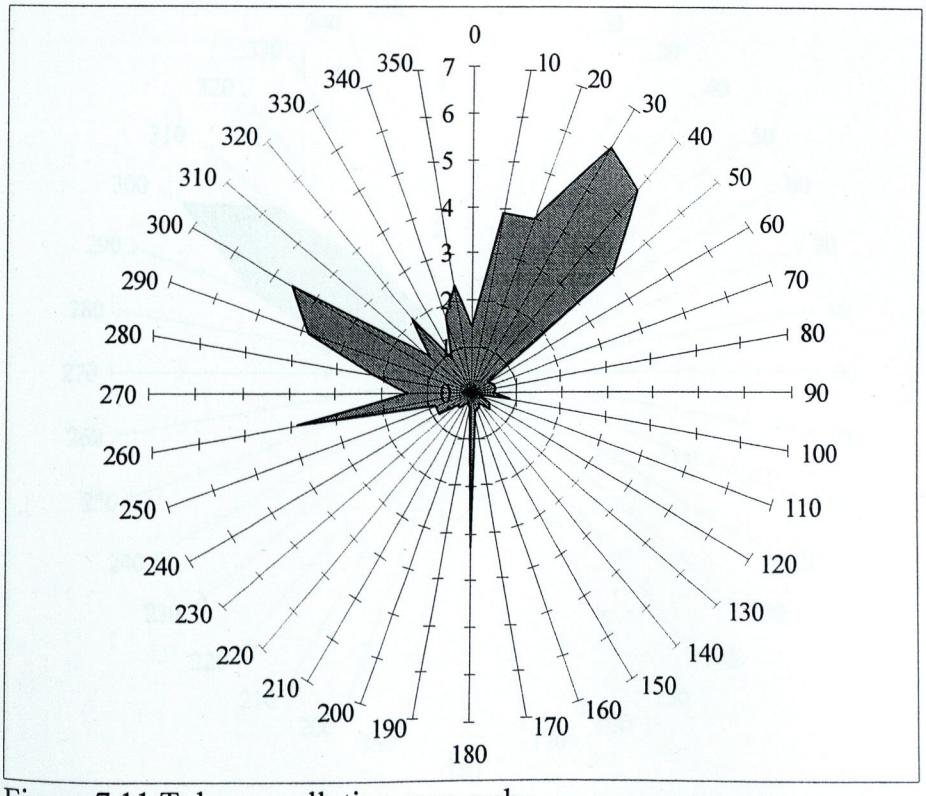


Figure 7.11 Toluene pollution rose, ppb

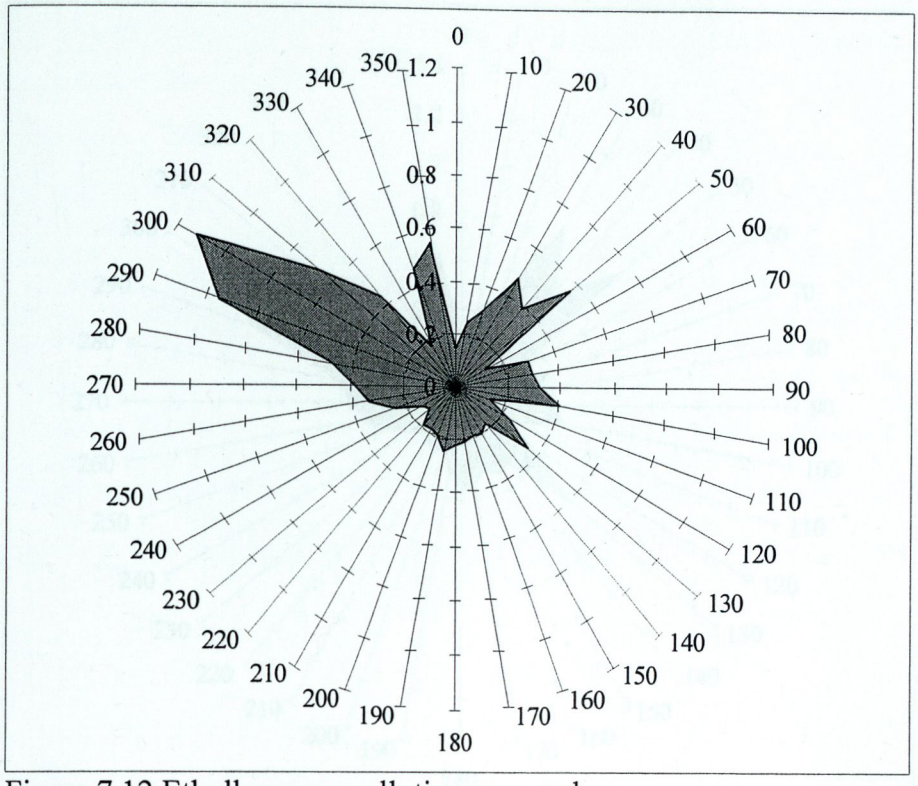


Figure 7.12 Ethylbenzene pollution rose, ppb

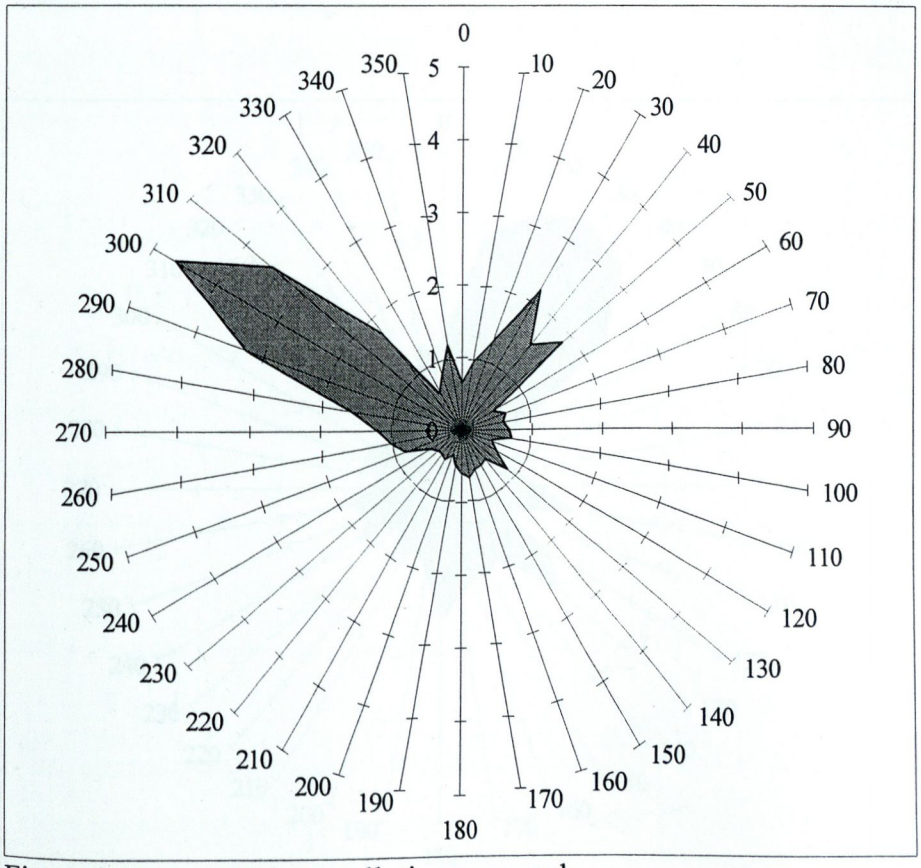


Figure 7.13 m+p-Xylene pollution rose, ppb

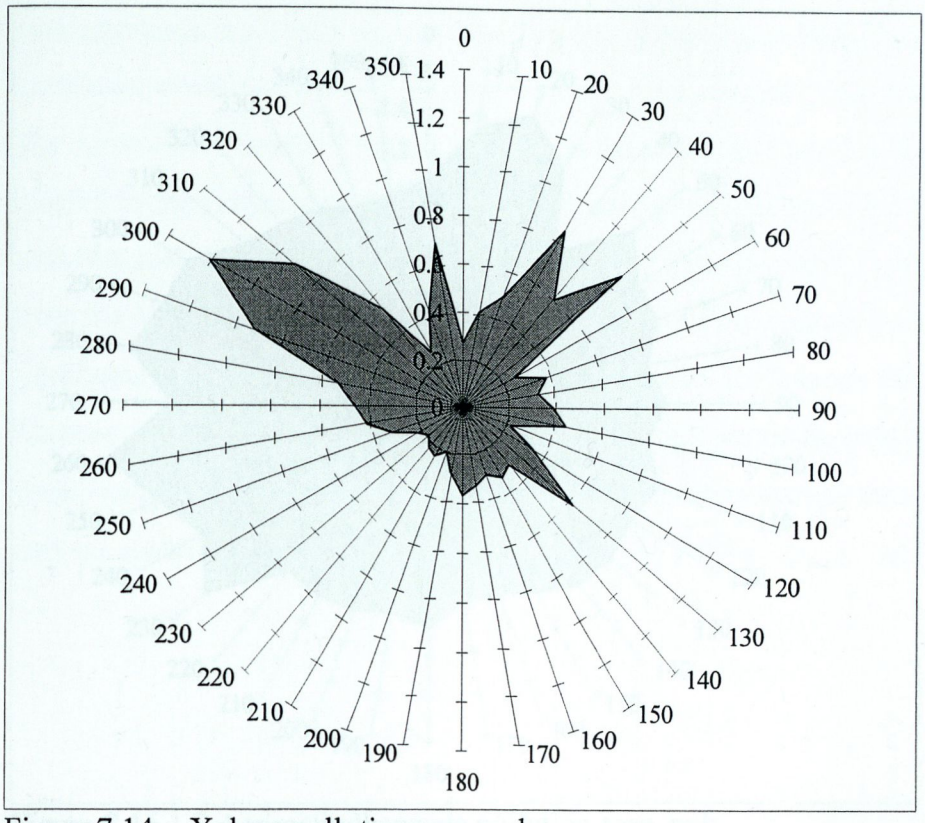


Figure 7.14 o-Xylene pollution rose, ppb

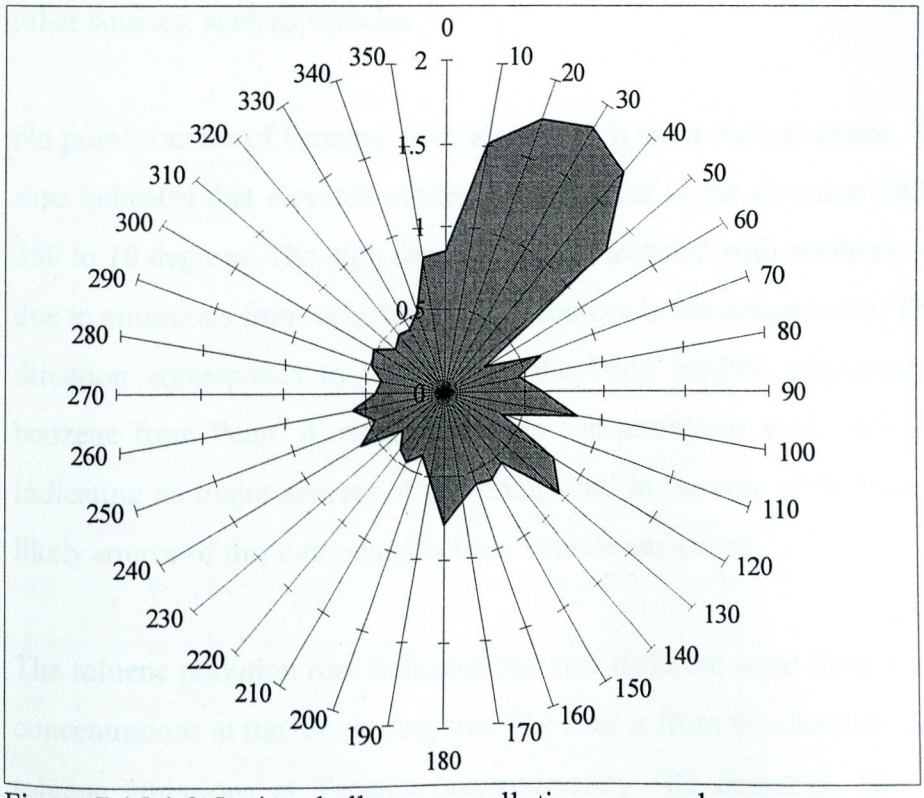


Figure 7.15 1,3,5-trimethylbenzene pollution rose, ppb

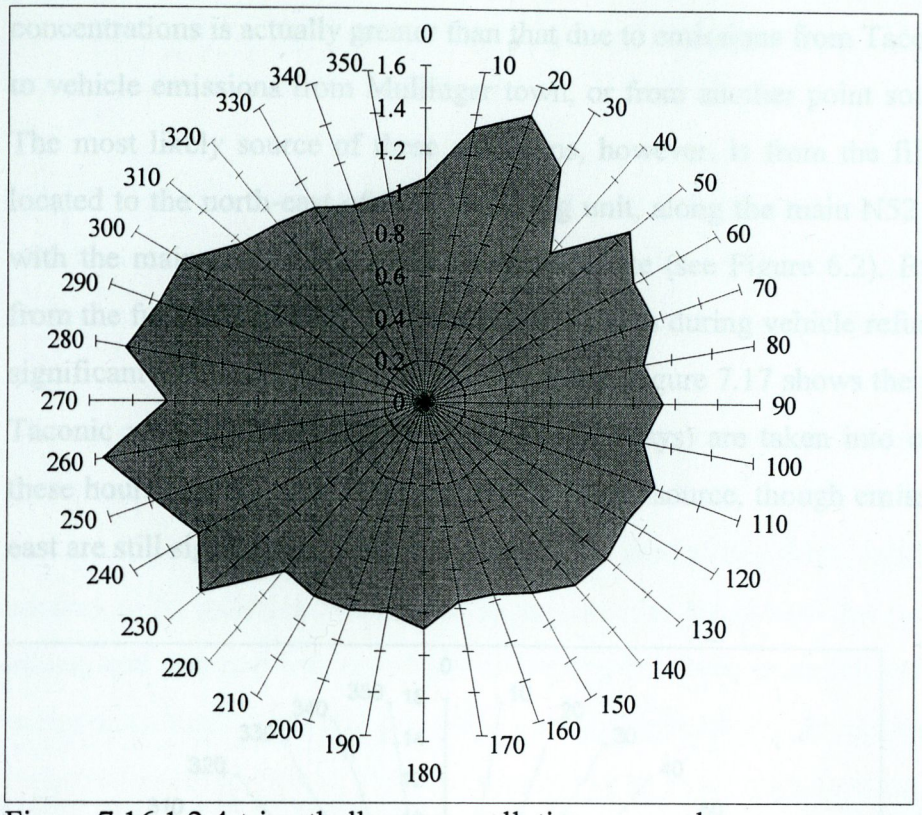


Figure 7.16 1,2,4-trimethylbenzene pollution rose, ppb

The pollution roses for n-hexane and cyclo-hexane indicate that emissions from Penn dominate the measured concentrations at the monitoring unit. This is attributable to the proximity of the monitoring unit to Penn, and the generally low emissions of hexane from other sources, such as vehicles.

No point sources of benzene were identified in the industrial estate. The benzene pollution rose indicates that elevated concentrations occur in the direction 240 to 260 degrees, and 350 to 10 degrees. The high concentrations measured with northerly winds are likely to be due to emissions from vehicles or other sources in Mullingar town. The 240 to 260 degrees direction corresponds to winds from the Penn facility, suggesting small emissions of benzene from Penn. Average n-heptane concentrations were very low for all directions, indicating no major sources of this compound in the area of the monitoring site. The most likely source of this compound is from vehicle emissions.

The toluene pollution rose indicates that two different wind directions resulted in elevated concentrations at the monitoring site. The first is from the direction of the known source of toluene emissions at Taconic (approximately 300 degrees). The second direction lies between approximately 10 and 60 degrees, where the magnitude of the measured

concentrations is actually greater than that due to emissions from Taconic. This may be due to vehicle emissions from Mullingar town, or from another point source in this direction. The most likely source of these emissions, however, is from the filling station which is located to the north-east of the monitoring unit, along the main N52 road, at the junction with the main road through the industrial estate (see Figure 6.2). Evaporative emissions from the fuel storage tanks and fugitive emissions during vehicle refuelling are likely to be significant sources of a range of hydrocarbons. Figure 7.17 shows the pollution rose if only Taconic working hours (08:00 to 17:00, weekdays) are taken into consideration. During these hours, Taconic emissions are the dominant source, though emissions from the north-east are still significant.

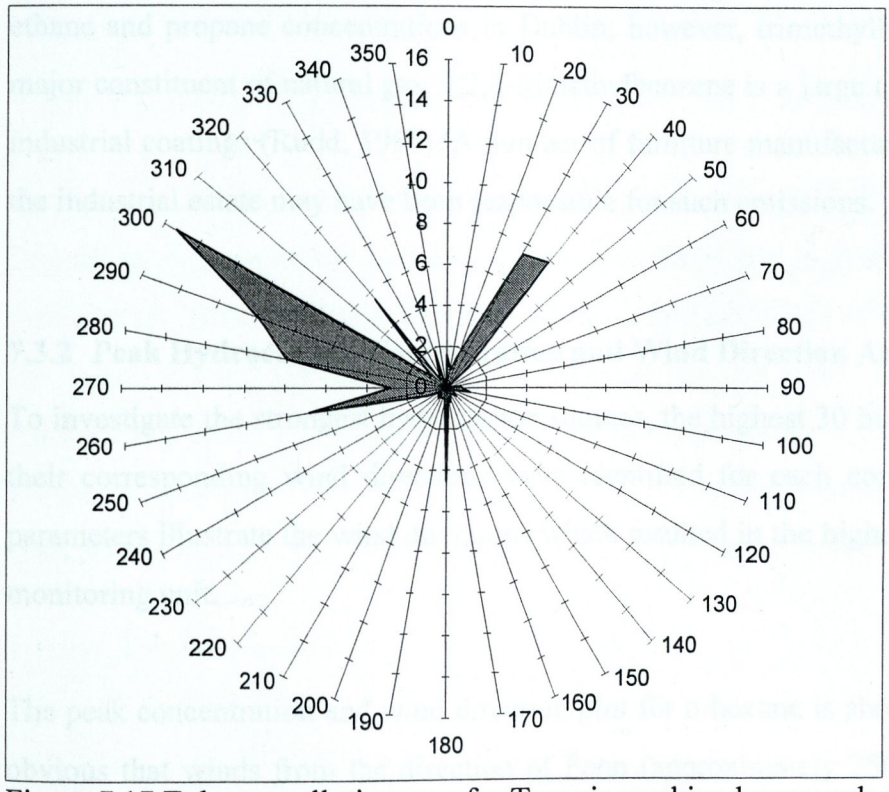


Figure 7.17 Toluene pollution rose for Taconic working hours, ppb

The pollution roses for ethylbenzene, m+p-xylene and o-xylene clearly show the influence of emissions from Taconic on the measured concentrations of these compounds. The highest average concentrations are exhibited by m+p-xylene, with ethylbenzene and o-xylene exhibiting similar concentrations. For each of these compounds, a smaller peak can also be seen for winds from the north-east, similar to that for toluene. Again, the most likely source of these compounds is the filling station located north-east of the monitoring unit (see Figure 6.2). Other studies which measured hydrocarbon concentrations in the vicinity of petrol stations in Ireland (Nugent, 1999) and the UK (Uren, 2000) measured

significant ambient hydrocarbon concentrations, though the range of measured compounds was limited to benzene, toluene and xylene.

1,3,5-trimethylbenzene also exhibits a peak for winds from the north-east. The magnitude of this peak is relatively large compared to those for ethylbenzene and o-xylene, indicating that emissions from the filling station are a significant source of this compound.

1,2,4-trimethylbenzene exhibits an unusual pollution rose, displaying relatively constant concentrations for all wind directions, with only small increases in measured concentrations for north-easterly and westerly winds. This high background concentration appears to be indicative of an area source, such as the natural gas leakage contribution to ethane and propane concentrations in Dublin; however, trimethylbenzene is not a known major constituent of natural gas. 1,2,4-trimethylbenzene is a large component of paints and industrial coatings (Rudd, 1995). A number of furniture manufacturing facilities located in the industrial estate may have been responsible for such emissions.

7.3.2 Peak Hydrocarbon Concentration and Wind Direction Analysis

To investigate the strongest hydrocarbon sources, the highest 30 hourly concentrations and their corresponding wind directions were identified for each compound. Plots of these parameters illustrate the wind directions which resulted in the highest concentrations at the monitoring unit.

The peak concentration and wind direction plot for n-hexane is shown in Figure 7.18. It is obvious that winds from the direction of Penn (approximately 250 degrees) result in the highest measured concentrations. However, the range of wind directions which result in high concentrations is large (230 to 300 degrees). This is because significant fluctuations in wind directions can occur over the course of an hour. However, the meteorological monitoring equipment only records the wind direction which was most often experienced, and cannot describe the variations encountered over the course of an hour. Cyclo-hexane displays a similar pattern to n-hexane, as would be expected.

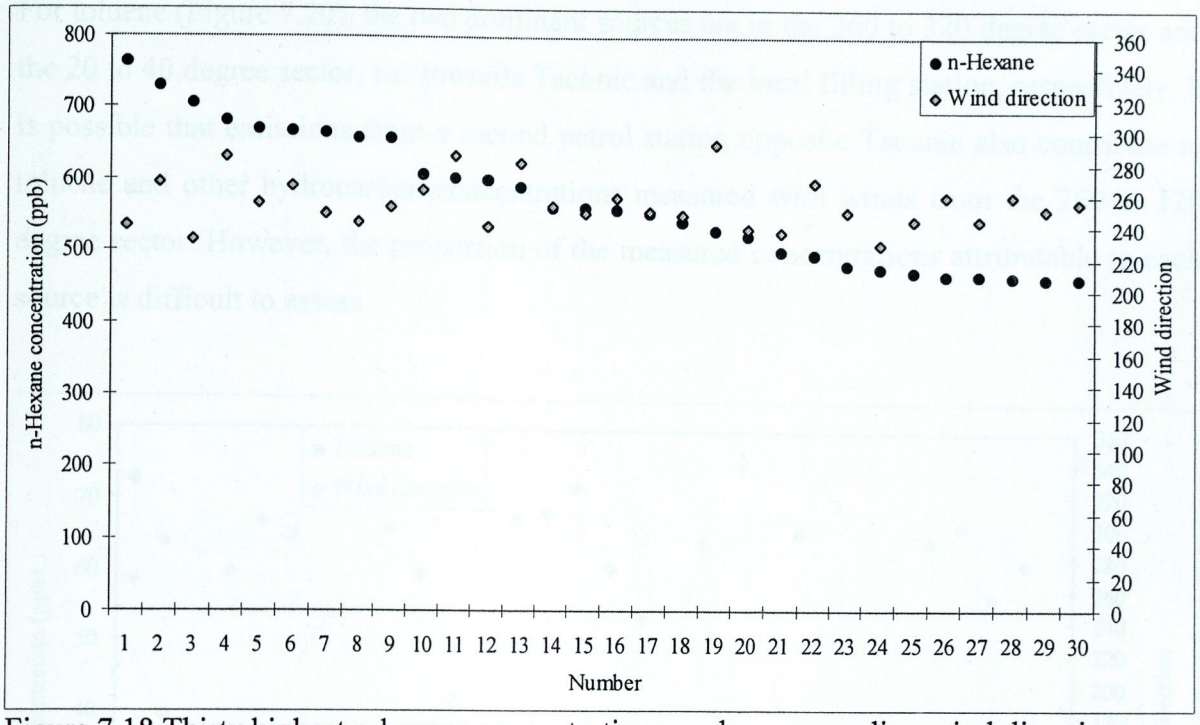


Figure 7.18 Thirty highest n-hexane concentrations, and corresponding wind direction

For benzene (see Figure 7.19), only six hourly concentrations above 4 ppb were noted, with remaining concentrations being very low. For these six highest hourly concentrations, winds from 260 degrees (the direction to Penn), and from 0 to 60 degrees (the direction to the filling station) are identified. The remainder of the higher measured concentrations occur mostly in the range 200 to 300 degrees, encompassing the industrial estate. This may be due to local traffic or emissions from facilities in the industrial estate. Benzene is a product of stationary combustion (see Table 2.9), and many local facilities operate boilers.

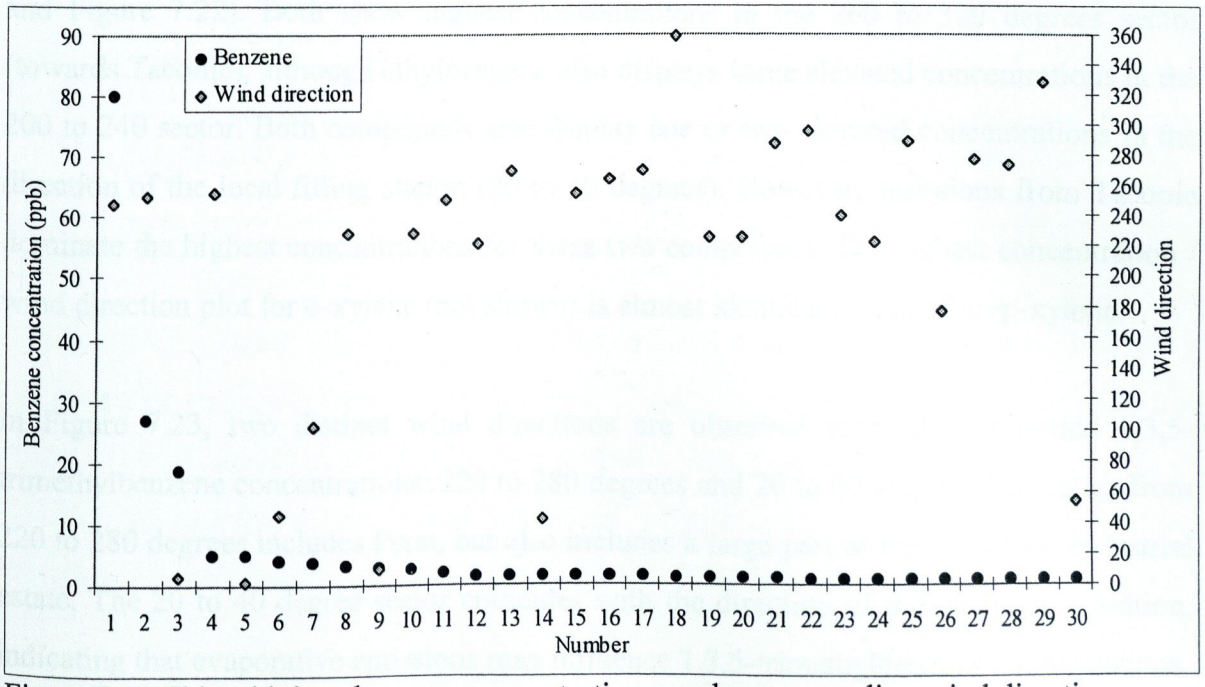


Figure 7.19 Thirty highest benzene concentrations, and corresponding wind direction

For toluene (Figure 7.20), the two dominant sources are in the 260 to 320 degree sector and the 20 to 40 degree sector, i.e. towards Taconic and the local filling station, respectively. It is possible that emissions from a second petrol station opposite Taconic also contribute to toluene and other hydrocarbon concentrations measured with winds from the 260 to 320 degree sector. However, the proportion of the measured concentrations attributable to each source is difficult to assess.

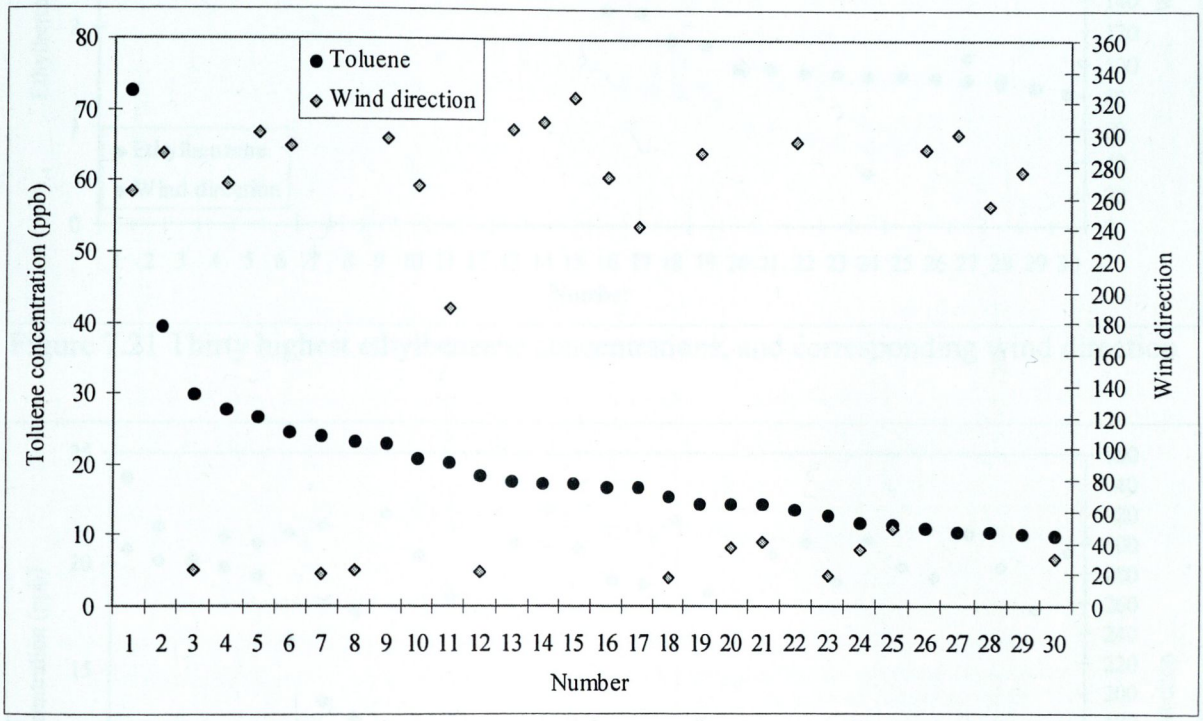


Figure 7.20 Thirty highest toluene concentrations, and corresponding wind direction

Ethylbenzene and m+p-xylene display similar elevated concentration patterns (Figure 7.21 and Figure 7.22). Both show highest concentrations in the 260 to 320 degrees sector (towards Taconic), although ethylbenzene also displays some elevated concentrations in the 200 to 240 sector. Both compounds also display one or two elevated concentrations in the direction of the local filling station (20 to 40 degrees). However, emissions from Taconic dominate the highest concentrations for these two compounds. The highest concentration / wind direction plot for o-xylene (not shown) is almost identical to that of m+p-xylene.

In Figure 7.23, two distinct wind directions are observed to produce elevated 1,3,5-trimethylbenzene concentrations: 220 to 280 degrees and 20 to 60 degrees. The range from 220 to 280 degrees includes Penn, but also includes a large part of the rest of the industrial estate. The 20 to 40 degree sector coincides with the direction of the local petrol station, indicating that evaporative emissions may influence 1,3,5-trimethylbenzene concentrations.

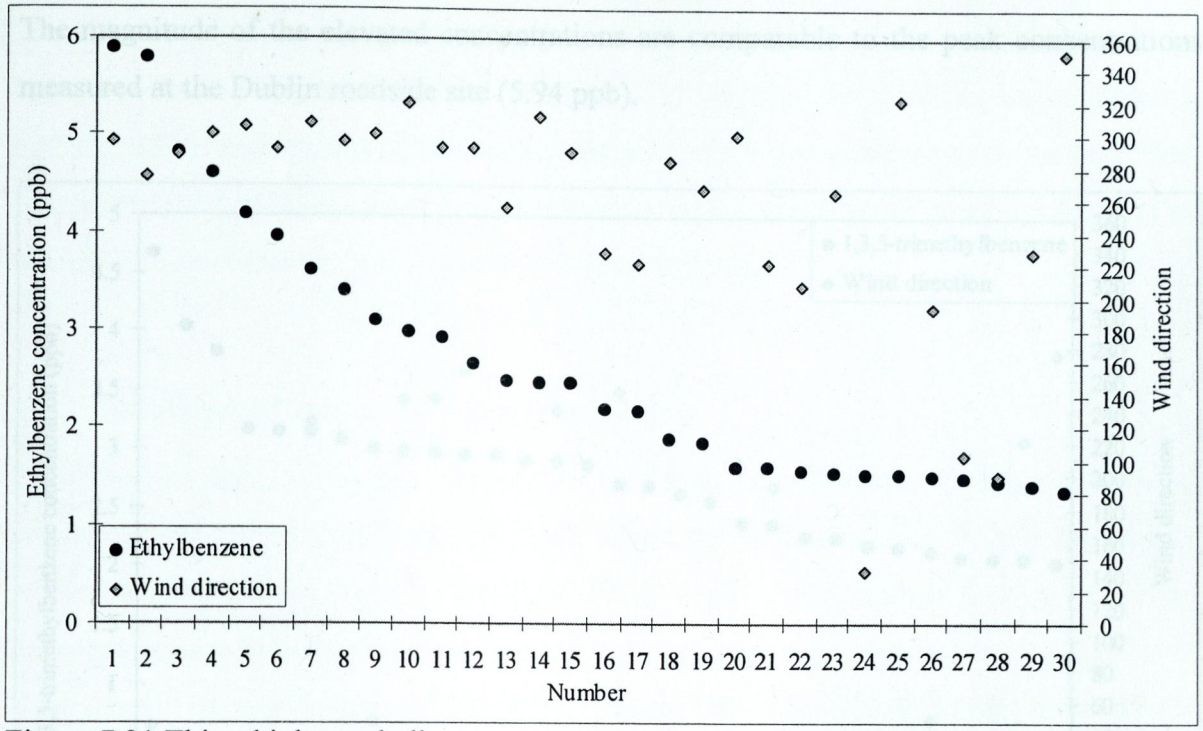


Figure 7.21 Thirty highest ethylbenzene concentrations, and corresponding wind direction

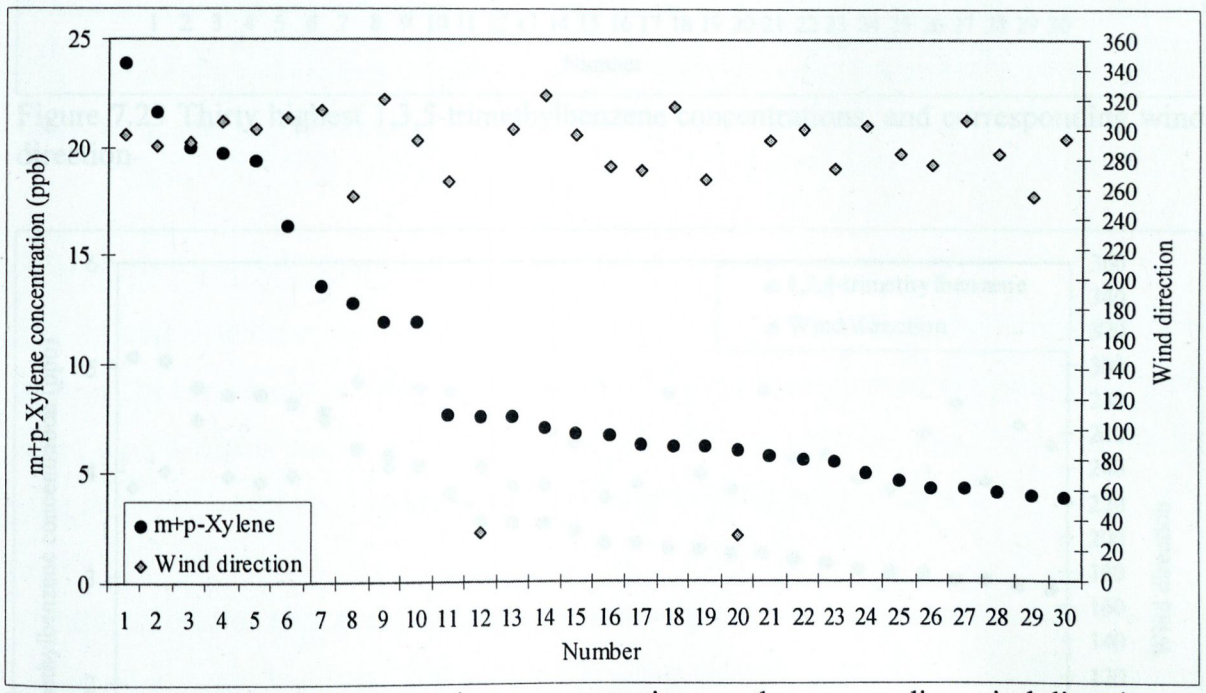


Figure 7.22 Thirty highest m+p-xylene concentrations, and corresponding wind direction

The highest measured 1,2,4-trimethylbenzene concentrations (Figure 7.24) are found for a very specific range of wind directions, from 220 to 280 degrees, which is similar to the range of wind directions displayed for elevated n-hexane concentrations in Figure 7.18. This indicates Penn as a possible source of 1,2,4-trimethylbenzene, even though this compound is not specified in reports of emissions measurements carried out at the plant.

The magnitude of the elevated concentrations are comparable to the peak concentrations measured at the Dublin roadside site (5.94 ppb).

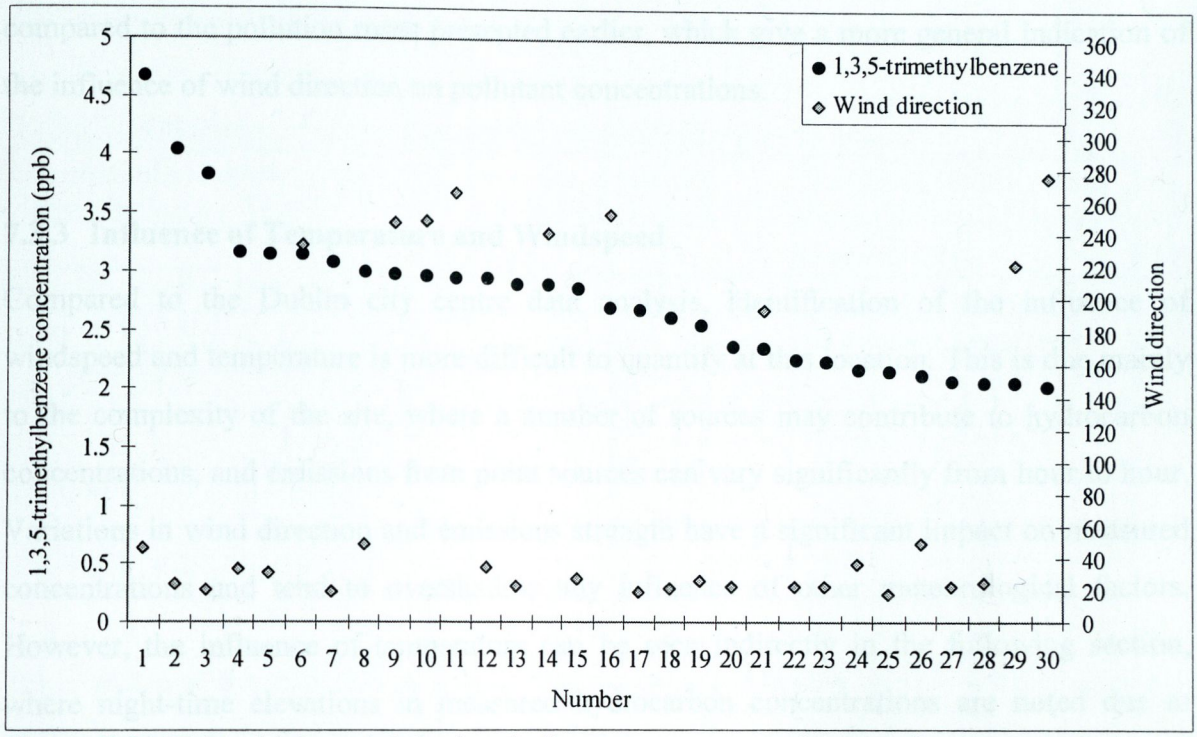


Figure 7.23 Thirty highest 1,3,5-trimethylbenzene concentrations, and corresponding wind direction

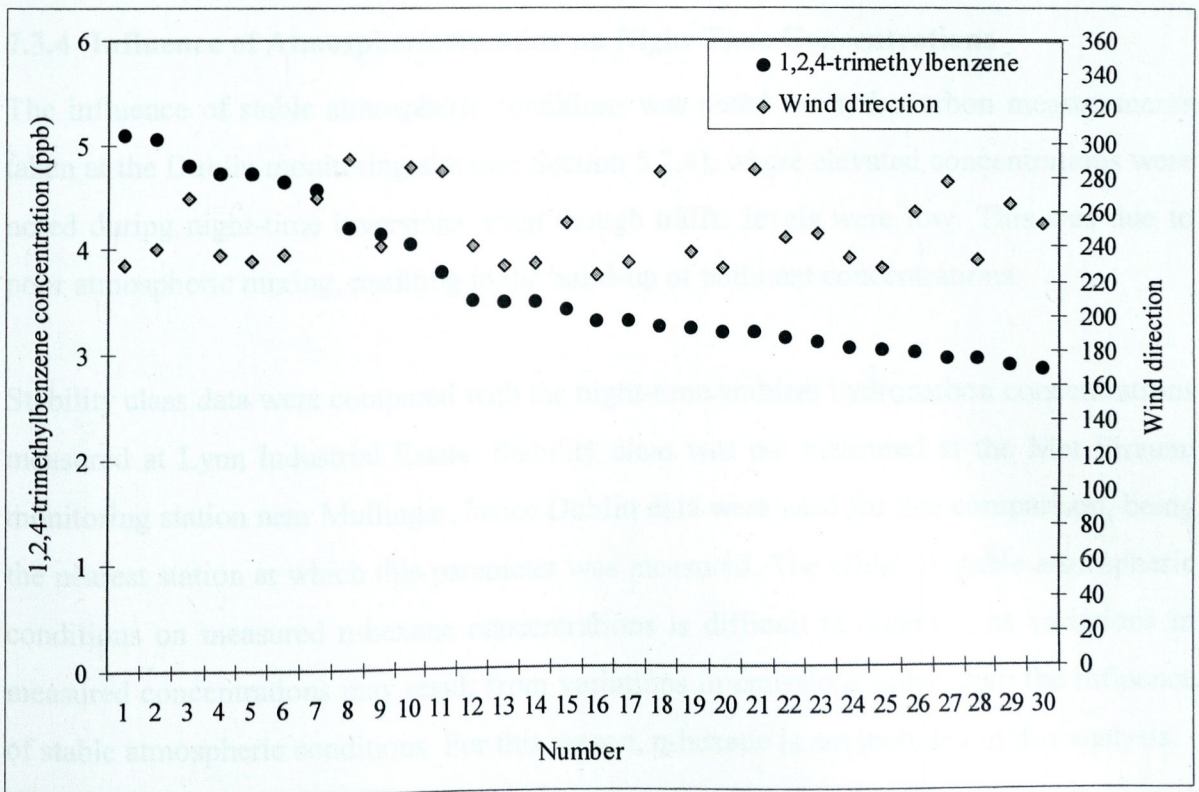


Figure 7.24 Thirty highest 1,2,4-trimethylbenzene concentrations, and corresponding wind direction

The above analysis provides a good indication of the wind directions which result in the highest measured hydrocarbon concentrations. This aids in the identification of primary and secondary sources, giving a clearer indication of the most important wind directions compared to the pollution roses presented earlier, which give a more general indication of the influence of wind direction on pollutant concentrations.

7.3.3 Influence of Temperature and Windspeed

Compared to the Dublin city centre data analysis, identification of the influence of windspeed and temperature is more difficult to quantify at this location. This is due mainly to the complexity of the site, where a number of sources may contribute to hydrocarbon concentrations, and emissions from point sources can vary significantly from hour to hour. Variations in wind direction and emissions strength have a significant impact on measured concentrations and tend to overshadow any influence of other meteorological factors. However, the influence of temperature can be seen indirectly in the following section, where night-time elevations in measured hydrocarbon concentrations are noted due to stable atmospheric conditions.

7.3.4 Influence of Atmospheric Stability on Night-Time Concentrations

The influence of stable atmospheric conditions was noted for hydrocarbon measurements taken at the Dublin monitoring site (see Section 5.2.4), where elevated concentrations were noted during night-time inversions, even though traffic levels were low. This was due to poor atmospheric mixing, resulting in the build-up of pollutant concentrations.

Stability class data were compared with the night-time ambient hydrocarbon concentrations measured at Lynn Industrial Estate. Stability class was not measured at the Met Eireann monitoring station near Mullingar, hence Dublin data were used for this comparison, being the nearest station at which this parameter was measured. The effect of stable atmospheric conditions on measured n-hexane concentrations is difficult to quantify, as variations in measured concentrations may result from variations in emissions rather than the influence of stable atmospheric conditions. For this reason, n-hexane is not included in this analysis.

Analysis was carried out by identifying the concentration peaks which occurred partly or entirely outside normal working hours (08:00 to 16:00). The dominant stability class during

this time was then identified. The details of this analysis for total measured xylene (sum of m, p and o-xylene) are presented, as an example, in Table 7.2. Elevated night-time concentrations are noted on several occasions; all but one exhibited stability class F, indicating that inversions resulted in a build-up of hydrocarbon concentration.

Table 7.2 Occurrences of elevated night-time total xylene concentration

Duration of elevated xylene concentration (> 3 ppb)	Average measured xylene concentration (ppb)	Dominant stability class during period of elevated concentration
29/9/99 18:00 to 30/9/99 16:00	5.49	F (during night hours)
5/10/99 22:00 to 6/10/99 03:00	3.77	F (during night hours)
12/10/99 20:00 to 13/10/99 04:00	4.73	F / E
13/10/99 21:00 to 14/10/99 01:00	3.26	F
28/10/99 20:00 to 29/10/99 04:00	5.37	E / F
8/11/99 15:00 to 9/11/99 05:00	4.78	D / F
10/11/99 17:00 to 11/11/99 03:00	4.23	E / F
15/11/99 17:00 - 23:00	5.95	D

An example of the variation in toluene concentration during the course of an inversion is given in Figure 7.25. Stability class F occurs before midnight on the first day, and continues throughout the early morning of the following day. During this period, toluene concentrations rise to a peak of 14 ppb, and remain high until early the following morning. Similar behaviour is also evident for the other compounds.

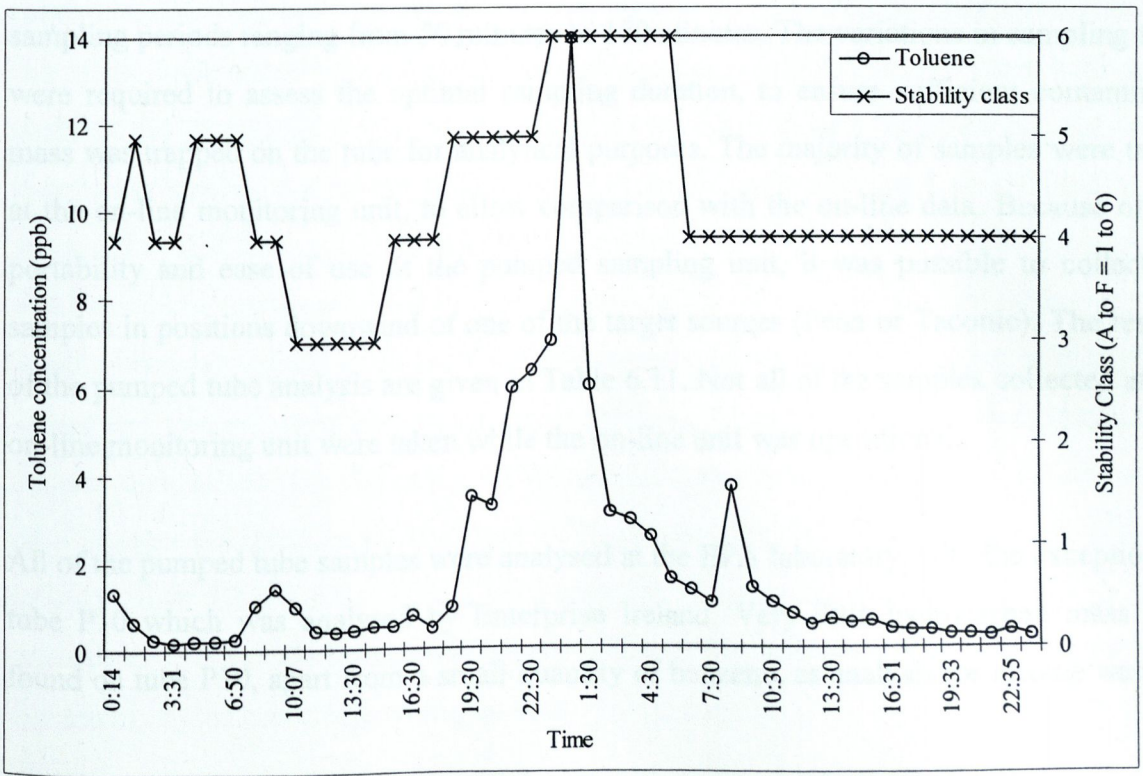


Figure 7.25 Toluene concentration and stability class over a two day period

During the course of monitoring at Lynn Industrial Estate, stability class F was observed on only 7.3 percent of occasions, compared to 75 percent for class D and 13.5 percent for class E. However, while most occurrences of stability class F occur at night, they have significant impacts on observed night-time hydrocarbon concentrations, if the stable conditions persist for several consecutive hours. As the stability class data were measured at Dublin Airport, the timings of the stable conditions may not be exact, but it is likely that stable conditions occurred at Mullingar at approximately the same time.

7.4 ANALYSIS OF PUMPED AND PASSIVE TUBE SAMPLING RESULTS

Results from pumped and passive tube studies are assessed in the following sections. Several sets of tubes were located beside the on-line monitoring unit, thus allowing direct comparison of results from different sampling and analysis methods. The locations of all pumped and passive tubes deployed during the project are presented in Figure 6.2. The on-line measurements were in better agreement with analysis results from pumped tubes than from the passive tubes, as the passive tubes tended to give lower results than either the pumped or on-line methods.

7.4.1 Pumped Tube Results

Fifteen pumped tubes were sampled during the course of monitoring at Mullingar, with sampling periods ranging from 50 minutes to 180 minutes. The variations in sampling time were required to assess the optimal sampling duration, to ensure sufficient contaminant mass was trapped on the tube for analytical purposes. The majority of samples were taken at the on-line monitoring unit, to allow comparison with the on-line data. Because of the portability and ease of use of the pumped sampling unit, it was possible to collect all samples in positions downwind of one of the target sources (Penn or Taconic). The results of the pumped tube analysis are given in Table 6.11. Not all of the samples collected at the on-line monitoring unit were taken while the on-line unit was operational.

All of the pumped tube samples were analysed at the EPA laboratory, with the exception of tube P10 which was analysed by Enterprise Ireland. Very little hydrocarbon mass was found on tube P10, apart from a small quantity of benzene, as analysis for hexane was not

available. Table 6.11 shows that similarly low concentrations of benzene, toluene and xylene were detected by the on-line unit during the same period.

No traces of toluene or xylene were detected on the pumped sample tubes located at the on-line unit. The masses of these compounds trapped on the tubes were likely to be below the detection limits of the analytical method used at the EPA laboratory. However, tubes P1, P8, P14 and P15 did display significant concentrations of benzene. Tube P1, with an equivalent atmospheric benzene concentration of 122 ppb, displayed the highest benzene concentration measured throughout monitoring at Mullingar. This sample was taken in the main yard of the Penn facility, close to, and directly downwind of the stack. However, throughout the course of on-line monitoring at Lynn Industrial Estate, no hourly concentrations as high as that collected on tube P1 were measured, despite several periods where the prevailing wind was from the direction of the Penn emissions location. This suggests that the elevated benzene concentration calculated for tube P1 may be due to contamination of the sampling tube, either due to poor conditioning of the tube after its previous use, or due to leakage of the tube before or after sample collection, even though Swagelok fittings were used at these times.

High concentrations of toluene (19.26 ppb) and xylene (39.00 ppb) were exhibited at the Statoil service station (tube P3), on the opposite side of the road to Taconic. Due to the short distance from the Taconic facility, the average xylene concentration measured over this three hour sampling period was actually greater than the highest one hour value observed by the on-line hydrocarbon monitoring unit at any time during the entire monitoring period. Emissions from the filling station may also have contributed to the measured xylene concentration; however, throughout the course of the sampling period the wind was blowing directly from Taconic, and a noticeable odour was also observed. The batch processing carried on at the Taconic facility means that no consistent ratio between xylene and toluene emissions exists, hence toluene emissions may have been low during the sampling of tube P3. However, whenever stack A6 alone is operational, the emissions ratio is approximately 2.6 parts xylene : 1.0 part toluene, which compares well with the ratio on tube P3 of 2.0 : 1.0. The production process related to stack A7 is used infrequently but results in higher toluene emissions. No hexane was detected on tube P3, due mainly to the prevailing wind direction.

Tube P2 was sampled in the Taconic car park when the wind was from the direction of the Penn facility, located over 200 m to the east. Hence, only a small quantity of xylene was detected, while the n-hexane concentration was reasonably high (139 ppb). However, even at this short distance from the Penn stack, the measured n-hexane concentration had decreased considerably compared to samples taken closer to the emissions point. Tube P4 was sampled at the entrance to the industrial estate beside National Route N52. The wind direction was from the Penn facility; however, concentrations of benzene (2.3 ppb), toluene (3.21 ppb) and xylene (1.67 ppb) were also detected during analysis, suggesting a contribution from vehicle emissions. Again, although an elevated n-hexane concentration was measured (147.51 ppb), this was not as high as samples taken closer to the Penn emission points. The distances from Penn to the sampling location of tubes P2 and P4, are similar, and both tubes display practically the same downwind measured n-hexane concentration, indicating the accuracy of the pumped tube sampling method.

Of the pumped samples taken at the online unit, seven were obtained while the on-line unit was operational. The results of the analysis of six of these samples and the corresponding average concentrations determined by the on-line unit during these sampling periods are compared in Table 7.3. Results for tube P10 are not included as this tube was analysed by Enterprise Ireland and no n-hexane measurement was provided.

Table 7.3 Comparison of on-line and pumped tube derived hydrocarbon concentrations

	Pumped tube results				On-line results				
Tube no.	Benzene ppb	n-Hexane ppb	Toluene ppb	Xylene ppb	Benzene ppb	n-Hexane ppb	Toluene ppb	Xylene ppb	n-Hexane ratio
P8	14.27	647.28	0.00	0.00	1.73	527.96	0.67	1.32	1.23
P9	0.00	605.13	0.00	0.00	2.59	599.21	0.1	1.13	1.01
P11	0.00	236.70	0.00	0.00	0.05	303.8	0.12	0.41	0.78
P12	0.00	277.86	0.00	0.00	0.2	325.62	0.1	0.3	0.85
P13	0.00	223.83	0.00	0.00	0.02	274.93	1.92	1.94	0.81
P14	20.12	501.70	0.00	0.00	0.2	601.39	0.16	0.5	0.83

All of the toluene and xylene concentrations for tube samples taken at this site are zero and the corresponding on-line measurements are very low (< 2ppb). The benzene concentrations are also generally low, but agreement between the benzene measurements is poor: two slightly elevated benzene concentrations being identified by pumped samples when the on-line results remained relatively low. As the ambient concentrations are higher, the n-hexane concentration results provide a more useful basis for comparison. There is

very good agreement between the on-line n-hexane concentrations and those determined from the pumped sample tubes. The column on the right of Table 7.3 presents the ratio between the pumped tube and on-line results. Tubes P8 and P9 indicated concentrations slightly higher than their contemporary on-line measurements, while the concentrations indicated by the remainder of the tubes were approximately 80 percent of the on-line value. Figure 7.26 illustrates the strong relationship between the two datasets.

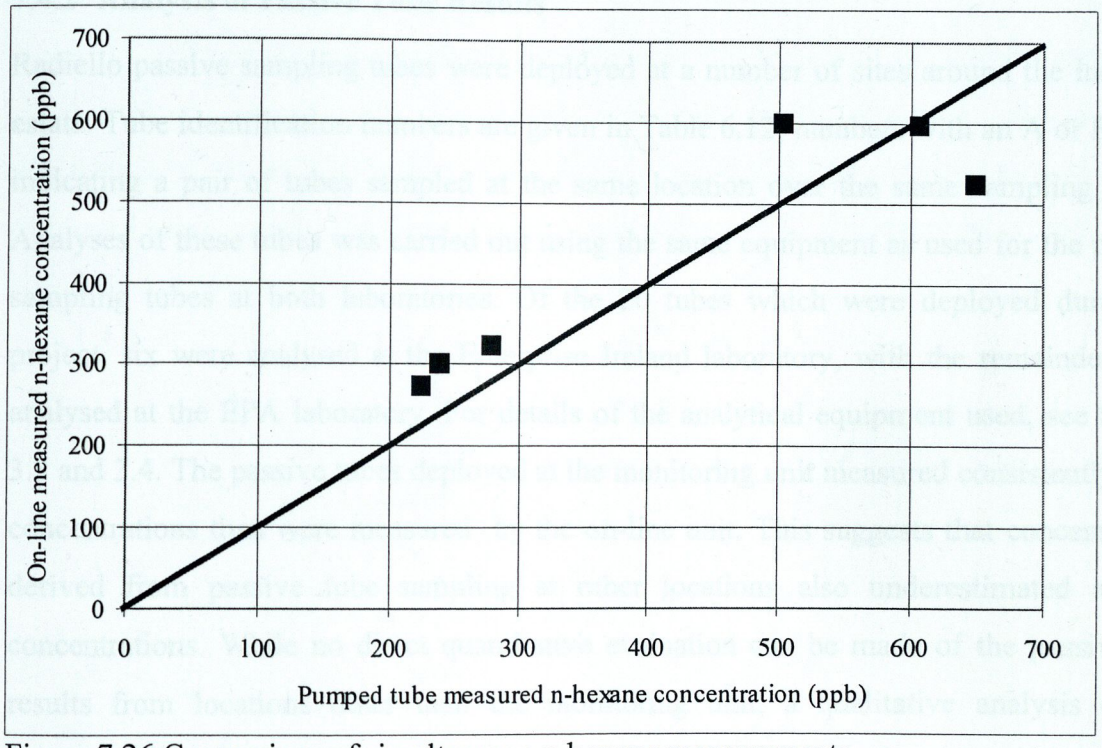


Figure 7.26 Comparison of simultaneous n-hexane measurements

Compared to the passive sampling tubes, the pumped tubes appear to provide results for hexane which agree strongly with the on-line data. The maximum difference observed between any two contemporary samples was 23 percent, with an average difference of 16 percent. USEPA test method 0031 specifies that sampling errors in the region of ± 20 percent are generally held to be acceptable (USEPA, 1996c). The pumped samples indicated lower concentrations on four occasions and higher values on two occasions. This suggests that the pumped sample may tend to slightly underestimate mean ambient concentrations. However, an overall assessment of this comparison indicates a satisfactory level of accuracy in both measurement methods. Another study comparing the results of on-line and pumped tube methods reported on-line / pumped ratios between 0.70 and 1.38 (Field, 1995). This is a wider range than found in this study (0.78 to 1.23), though a larger number of samples were compared. A similar study in Spain (Alonso *et al.*, 1999)

compared results from an automated gas chromatography system and pumped tube samples. Good agreement was found between the methods. A correlation coefficient of approximately 0.85 was observed between the two methods. The correlation between simultaneous n-hexane measurements in Mullingar is 0.92, though the number of simultaneous samples is smaller than measured by Alonso *et al.*

7.4.2 Analysis of Passive Tube Results

Radiello passive sampling tubes were deployed at a number of sites around the industrial estate. Tube identification numbers are given in Table 6.12, numbers with an A or B suffix indicating a pair of tubes sampled at the same location over the same sampling period. Analyses of these tubes was carried out using the same equipment as used for the pumped sampling tubes at both laboratories. Of the 20 tubes which were deployed during the project, six were analysed at the Enterprise Ireland laboratory, with the remainder being analysed at the EPA laboratory. For details of the analytical equipment used, see Section 3.3 and 3.4. The passive tubes deployed at the monitoring unit measured consistently lower concentrations than were measured by the on-line unit. This suggests that concentrations derived from passive tube sampling at other locations also underestimated ambient concentrations. While no direct quantitative evaluation can be made of the passive tube results from locations other than the monitoring unit, a qualitative analysis can be employed by comparing concentrations measured by passive tube pairs and by tubes sampled at the same location in different periods, and also by assessing the frequency of wind directions towards the tube location from either Penn or Taconic.

Samples Collected at the Mobile Unit

Four tubes were deployed at the on-line monitoring site (tube numbers R7A, R7B, R8A and R8B). The average concentration measured by the on-line monitoring unit during the deployment of these tubes was significantly higher than the mean concentration inferred from the mass of contaminant trapped on the tubes (see Table 6.12). For example, laboratory analysis of tube number R8A determined a hexane concentration of 10.78 ppb, while the on-line system measured an average concentration of 72.75 ppb during the same period (though on-line data do not cover the complete passive tube monitoring period). Similar results can be seen for tube R7A, and overall, the tube samples detected only 8.8

percent of the concentration measured by the on-line system. Benzene, toluene and xylene concentrations at the on-line monitoring site are low for both the passive tube and on-line estimates, although the passive tube results are again the lower. Considering the successful analysis of pumped sampling tubes at both laboratories, it seems unlikely that the performance of the analytical equipment was responsible for these low measurements.

Samples Collected Close to Penn

Tubes R1, R2 and R3 were deployed to determine the impact of emissions from Penn, being located approximately 40 metres from the stacks. However, the n-hexane concentrations detected were still much lower than the average on-line concentrations during the same period. The wind direction frequency rose for the sampling period of tube R2 is shown in Figure 7.27.

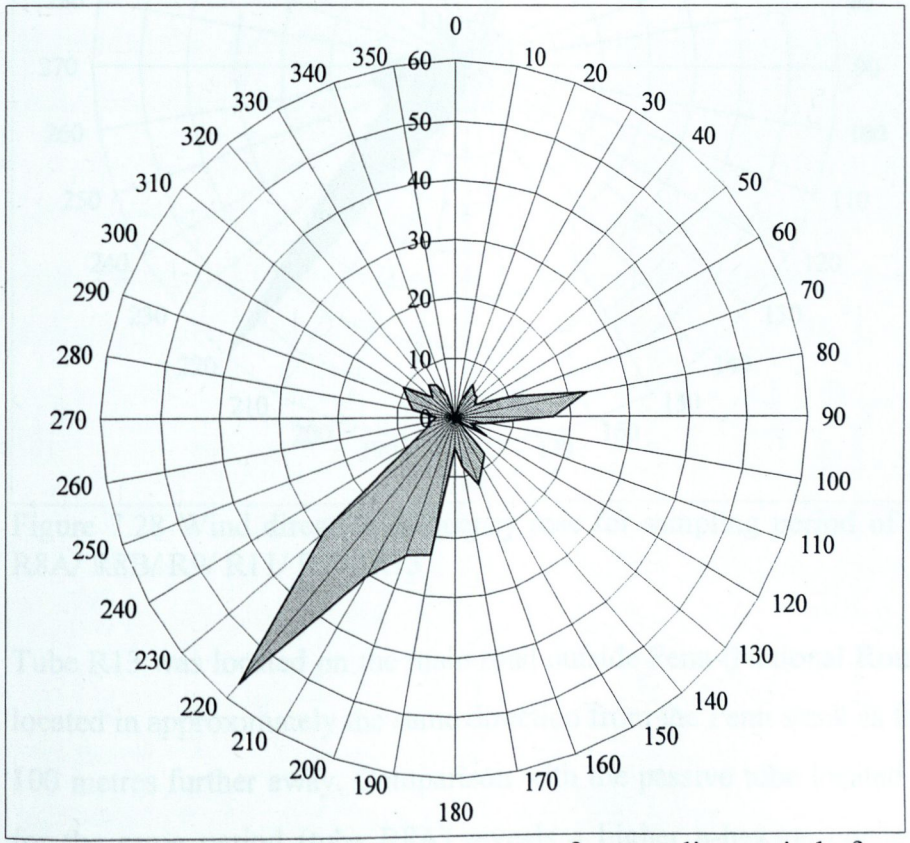


Figure 7.27 Wind direction frequency rose for sampling period of passive tubes R2/R5/ R7A/ R7B/ R10A/ R10B

Tube R3 displays elevated toluene (2.15 ppb) and xylene (3.07 ppb) concentrations which may be attributed to emissions from Taconic. The wind rose for the sampling period of tube R3 is shown in Figure 7.28. The wind direction required to cause the plume from Taconic to pass over the locations of tubes R2 and R3 is approximately 270 to 290 degrees.

Figure 7.28 suggests that the mean 1-hour wind direction was in this range on 20 – 30 occasions during the tube R3 sampling period. During tube R2 sampling period, the number of occurrences of winds from the 270 to 290 degree sector is smaller. Similarly, wind directions of between 130 and 150 degrees were required to cause high hexane concentrations due to Penn emissions at the location of tubes R2 and R3. Figure 7.27 and Figure 7.28 indicate few occurrences of these wind directions.

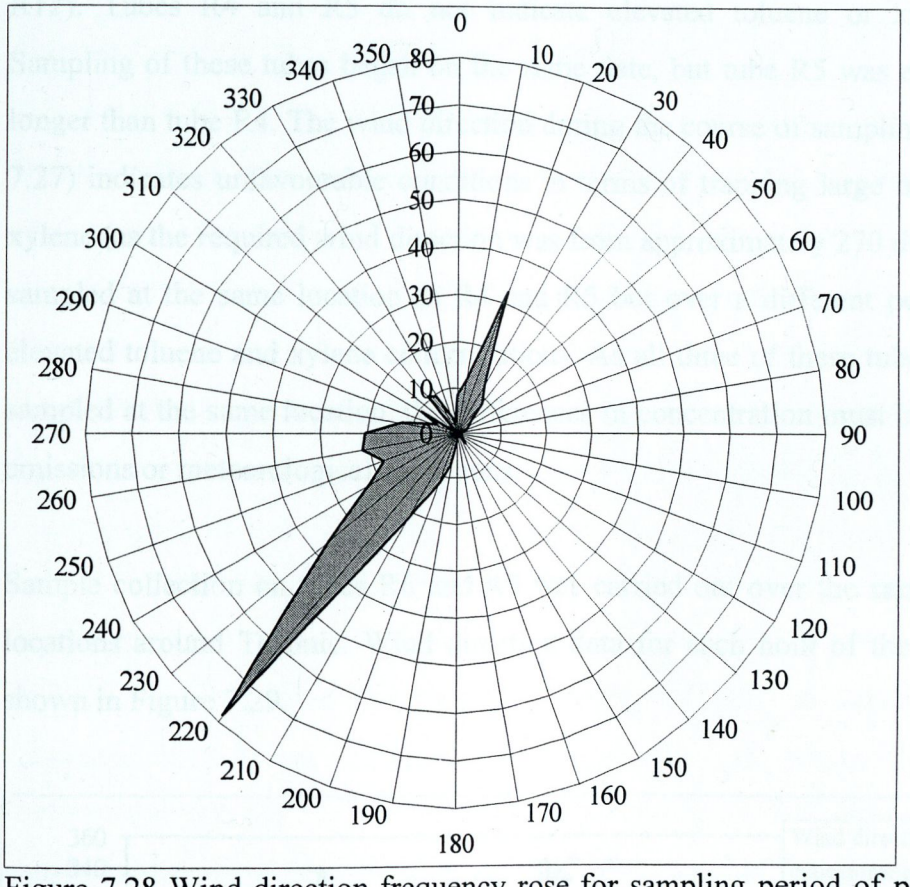


Figure 7.28 Wind direction frequency rose for sampling period of passive tubes R3/ R6/ R8A/ R8B/ R9/ R11/ R12/ R13

Tube R13 was located on the main road outside Penn (National Route N52). The tube was located in approximately the same direction from the Penn stack as the monitoring unit, but 100 metres further away. Comparison with the passive tube located at the monitoring unit for the same period (tube R8A) reveals a higher n-hexane concentration at the on-line monitoring unit site, but higher toluene and xylene concentrations at the roadside site. Elevated toluene and xylene concentrations could be attributed to vehicle emissions; however, these should also have caused elevated benzene concentrations. A wind direction of approximately 280 degrees from the Taconic stack should have resulted in elevated concentrations at the roadside site. The wind direction frequency rose in Figure 7.28 covers the sampling period for tubes R13 and R8A. This indicates that several hours of wind

directed from Taconic (particularly from the 280 degrees direction) occurred during sampling and may have contributed to the elevated toluene and xylene concentrations.

Samples Collected Close to Taconic

Some passive tubes deployed close to Taconic display higher concentrations of toluene and xylene. In all, five tubes were located to trap emissions from Taconic (R4, R5, R6, R9 and R12). Tubes R4 and R5 do not indicate elevated toluene or xylene concentrations. Sampling of these tubes began on the same date, but tube R5 was exposed for one week longer than tube R4. The wind direction during the course of sampling for tube R5 (Figure 7.27) indicates unfavourable conditions in terms of trapping large masses of toluene and xylene (as the required wind direction was from approximately 270 degrees). Tube R6 was sampled at the same location as R4 and R5 but over a different period, and does show elevated toluene and xylene concentrations. As all three of these tubes (R4, R5, R6) were sampled at the same location, the differences in concentration must be due to variations in emissions or meteorological conditions.

Sample collection on tubes R6 and R9 was carried out over the same period at different locations around Taconic. Wind direction data for each hour of the sampling period are shown in Figure 7.29.

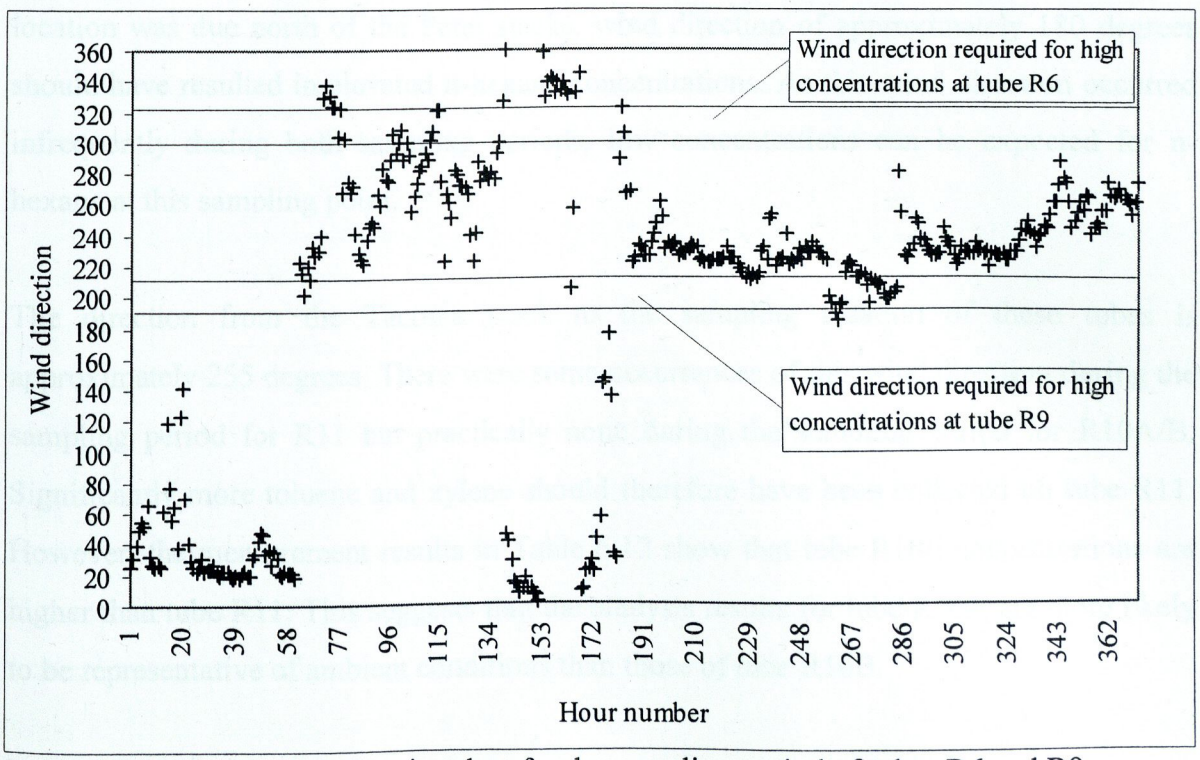


Figure 7.29 Hourly wind direction data for the sampling period of tubes R6 and R9

The wind direction sector which would be expected to result in high concentrations at either of the sampling points is also indicated. It is clear that the wind direction during this period was more favourable for tube R9, and as would be expected, the toluene and xylene concentrations were higher at this location. Tube R12, which was located close to tube R9, and sampled over the same period, also displays elevated toluene and xylene concentrations.

Samples Collected Between Penn and Taconic

Tubes R10A, R10B and R11 were deployed approximately equidistant from both sources. R10A and R10B were sampled at the same time and location, however R10B was analysed one month after R10A. The results for toluene and xylene from both analyses are significantly different, with three to four times more contaminant detected on tube R10B. This may be due to some reaction in the tube during storage of tube R10B or differences in the uptake rates of the two tubes during sampling. However, because the concentrations are low, some discrepancies during analysis may also have occurred.

Tube R11 was sampled at the same location as R10A/B, but at a later date. Analysis of tube R11 was carried out at Enterprise Ireland. The sampling duration is similar to that of R10A/B. The sampling periods for R10A/B and R11 produced the wind direction frequency roses shown in Figure 7.27 and Figure 7.28, respectively. As the sampling location was due north of the Penn stacks, wind direction of approximately 180 degrees should have resulted in elevated n-hexane concentrations. As this wind direction occurred infrequently during both sampling periods, low concentrations can be expected for n-hexane at this sampling point.

The direction from the Taconic stack to the sampling location of these tubes is approximately 255 degrees. There were some occurrences of this wind direction during the sampling period for R11 but practically none during the sampling period for R10A/B. Significantly more toluene and xylene should therefore have been collected on tube R11. However, the measurement results in Table 6.12 show that tube R10B concentrations are higher than tube R11. This suggests that the analysis results for tube R10A are more likely to be representative of ambient conditions than those of tube R10B.

Two pairs of tubes, R14A/B and R15A/B were located at a greater distance from both sources, in the direction of Mullingar town. Very low benzene concentrations were measured on all the tubes. Tubes R14A and R14B were both analysed (on the same date) by the EPA laboratory in Cork and display very similar concentrations, indicating the precision of the analytical method used. Tubes R15A and R15B were also sampled at the same time and location; however, tube R15A was analysed at the Enterprise Ireland laboratory, while tube R15B was analysed at the EPA laboratory. The results provided by the EPA are two to three times higher than the Enterprise Ireland results. The wind direction frequency rose for the sampling period of these tubes is given in Figure 7.30.

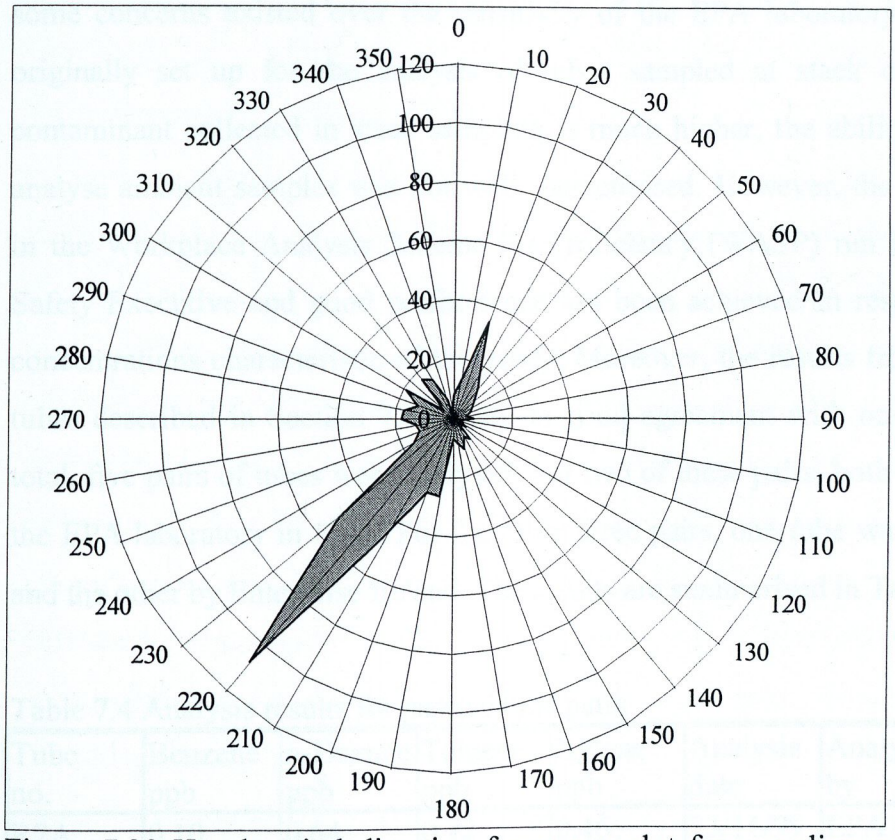


Figure 7.30 Hourly wind direction frequency plot for sampling period of tubes R14A / R14B / R15A / R15B

For comparison purposes, results from the tubes analysed at the EPA laboratory (tube R15B) are used. The direction from the Penn stack to the sampling locations is approximately 210 to 220 degrees. During sampling, this direction occurred frequently, resulting in higher mean n-hexane concentrations than observed at other sampling locations closer to the emissions point. The direction from the Taconic stack to the sampling sites is approximately 250 degrees for the sampling location of tubes R15A/B and 230 degrees for tubes R14A/B. Wind from 230 degrees occurred more frequently than from 250 degrees.

This may account for the fact that the measured toluene and xylene concentrations are very similar at both sites, even though site R14A/B is further from the Taconic stack. Again, the influence of vehicle emissions can be discounted as benzene concentrations remain low. The elevated toluene and xylene emissions indicate that emissions from Taconic have an influence on ambient hydrocarbon concentrations at both locations.

Analysis of Tube Pairs

Several pairs of passive tubes were employed during the monitoring study to assess the precision and accuracy of the sampling and analysis methods. As mentioned previously, some concerns existed over the sensitivity of the EPA laboratory equipment, as it was originally set up for the analysis of tubes sampled at stack exits. As the mass of contaminant collected in stack sampling is much higher, the ability of this equipment to analyse ambient samples was not well characterised. However, the laboratory participates in the Workplace Analysis Scheme for Proficiency (WASP) run by the UK Health and Safety Executive and good performance has been achieved in respect of BTX assays at concentrations characteristic of this study. Moreover, the results from analysis of pumped tubes described in Section 7.4.1 were in good agreement with on-line measurements. In total, five pairs of tubes were analysed. For two of these pairs, both tubes were analysed at the EPA laboratory in Cork. For the other three pairs, one tube was analysed by the EPA and the other by Enterprise Ireland. The results are summarised in Table 7.4.

Table 7.4 Analysis results for passive tube pairs

Tube no.	Benzene ppb	n-Hexane ppb	Toluene ppb	Xylene ppb	Analysis date	Analysed by
R7A	0.10	0.64	0.72	0.46	23/11/99	EPA Cork
R7B	0.09	NA	0.92	0.71	16/12/99	EI
R8A	0.19	10.78	1.50	1.80	20/12/99	EPA Cork
R8B	0.02	NA	0.67	0.92	16/12/99	EI
R10A	0.15	0.98	1.27	0.71	23/11/99	EPA Cork
R10B	0.52	1.17	4.16	2.85	20/12/99	EPA Cork
R14A	0.21	0.95	1.95	1.83	20/12/99	EPA Cork
R14B	0.21	1.04	2.05	1.83	20/12/99	EPA Cork
R15A	0.08	NA	0.72	0.90	16/12/99	EI
R15B	0.32	3.56	2.00	2.13	20/12/99	EPA Cork

One of each of tube R7A and R7B was analysed by the EPA Cork and Enterprise Ireland laboratories. For all contaminants, the results were very low. One tube from each of the

pairs R8A/B and R15A/B were analysed by each laboratory. In both cases, lower concentration estimates were determined by the Enterprise Ireland analysis. For each of the above tube pairs, results are in reasonable agreement given variations in analytical approaches between the two laboratories.

Two pairs of tubes were analysed by the EPA laboratory. Tubes R10A/B show some discrepancy in their results, particularly for toluene and xylene; this may be due to the length of time between either analysis, as described above. In comparison, the results for tubes R14A and R14B, which were analysed at the same time, are in very good agreement for all compounds.

7.4.3 Assessment of Passive Tube Results

Inspection of the n-hexane contamination rose in Figure 7.7 indicates that with wind directions in the range 230 to 320, significant concentrations of n-hexane are measured at the monitoring unit, i.e. for approximately 45 degrees either side of the exact direction from the Penn stacks to the monitoring unit. For winds in this range, an average n-hexane concentration of 127 ppb was measured at the on-line unit. If this concentration were taken as a typical average concentration at a receptor approximately 80 to 90 metres downwind of the stack, then the number of occurrences of this concentration at any of the passive sampling sites at similar distances can be estimated by inspecting the hourly wind direction data during the relevant tube sampling period. If it is also assumed that concentrations outside this range of wind sectors are zero, then the average concentration at a passive tube sampling site can be estimated from the finite number of elevated hourly concentrations occurring within a band of wind directions. This estimate should provide a lower bound for the expected average concentration at a given site, and can be compared with the concentration determined from passive tube analyses to further evaluate their accuracy. Several examples are given below.

Tube R3

For example, sampling tube R3 was located 80 metres due north of the Penn stack. Therefore, an hourly wind direction of 180 ± 45 degrees would be expected to provide an hourly concentration at this point of, on average, 127 ppb. During the sampling period of

tube R3, 124 hourly wind direction values in the 135 to 225 sector occurred over the 503 hour sampling period. If it is assumed that wind directions outside this range result in zero concentrations then the average hexane concentration at this site can be approximated as:

$$\frac{124 \text{ hours} \times 127 \text{ ppb}}{503 \text{ hours}} = 31.30 \text{ ppb}$$

The actual average concentration resulting from the analysis of tube R3 was 0.51 ppb. This is 60 times less than the estimated concentration.

Tube R8A

Performing the same analysis on a tube exhibiting higher n-hexane concentrations should allow more confidence in the results. Tube R8A was sampled at the on-line monitoring unit and analysis indicated an average concentration of 10.78 ppb. On-line results for this sampling period indicate an average concentration of approximately 72 ppb. The sampling period was the same as that of R3 above but the required wind direction from the Penn stack is approximately 255 degrees. During sampling, 244 hourly wind directions in the 210 to 300 sector occurred. Again, if it is assumed that the wind directions outside the 210 to 300 degree sector result in zero concentrations at the sampling site, then the average hexane concentration at this site can be approximated as:

$$\frac{244 \text{ hours} \times 127 \text{ ppb}}{503 \text{ hours}} = 61.6 \text{ ppb}$$

The actual results from the tube analysis, of 10.78 ppb is six times lower than the estimated concentration of 61.6 ppb. The estimated concentration using this method is, however, close to that measured by the on-line unit (72 ppb), indicating that the method is a useful tool in estimating the expected concentration at passive tube locations near the monitoring unit. Compared to tube R3, the greater number of occurrences of the correct wind direction for the sampling location of tube R8A would be expected to give a higher passive tube result. Accordingly, the estimated concentration for tube R8A (61.6 ppb) is approximately twice that estimated for tube R3 (31.3 ppb), however the actual result of the tube analysis is 21 times higher.

Tube R1

The sampling duration for tube R1 was 336 hours at a location 80 metres due north of the Penn stack. During this period 113 hourly wind directions in the 135 to 225 degrees sector were noted. The average concentration can therefore be expected to be:

$$\frac{113 \text{ hours} \times 127 \text{ ppb}}{336 \text{ hours}} = 42.71 \text{ ppb}$$

The average concentration estimated from tube R1 is approximately 2.80 ppb. As for the other tubes, the estimated concentration is significantly greater than the measured value.

These results, and the comparison of on-line and passive tube results, show that the passive tubes tend to severely underestimate the ambient n-hexane concentration. Comparison of on-line and passive results for toluene, benzene and xylene indicate better agreement, with results normally lying within a factor of two to three of each other.

Analysis of the passive tube results suggests that the average ambient concentrations estimated by the Radiello passive sampling method tend to underestimate those measured by the on-line monitoring system, and are generally below the levels which would be expected, particularly for measured n-hexane concentrations. Early work carried out with Radiello passive sampling tubes by Bates *et al.* (1997) also encountered problems with underestimation of ambient pollutant concentrations. It was observed that, under certain conditions, the longer the device was exposed to the atmosphere, the less sample was collected. The results from this study are presented in Table 7.5, where Radiello tubes were exposed for varying lengths of time, with ambient concentrations also being measured using another method. The most striking aspect of these results is, that while no benzene was detected on the tube when a seven day sampling period was used, agreement between the Radiello tube results and the standard methods improved as the sampling period was shortened. This effect is also noticeable for toluene, though not to the same extent, with little or no effect being observed for the xylenes. Unfortunately, the impact of different sampling periods on measured n-hexane concentrations was not investigated by Bates *et al.*

This behaviour has been attributed to competitive effects between the different hydrocarbons being adsorbed onto the adsorbent material used. The mass of a compound

adsorbed onto a given adsorbent is dependant on a number of factors and can be expressed as follows (Bates *et al.*, 1997):

$$m_j = \frac{b_j c_j m_{\max_j}}{1 + \sum_{i=1}^{n} b_i c_i} \qquad 7.1$$

m_j = mass adsorbed for compound j in a mixture of n compounds

b_j = distribution coefficient for compound j

c_j = concentration of compound j in the gaseous phase

m_{maxj} = maximum adsorbable mass of compound j for a given adsorbent

Table 7.5 Results from ambient hydrocarbon measurements using Radiello sampling tubes and standard methods (Bates *et al.*, 1997)

Duration	Sampling device	Benzene $\mu g/m^3$	Toluene $\mu g/m^3$	m+p-Xylene $\mu g/m^3$	o-Xylene $\mu g/m^3$
7 days	Axial tube	1.9	8.1	4.4	1.4
	Radiello	0.0	6.0	4.3	1.3
6 days	Axial tube	1.7	5.3	2.7	0.9
	Radiello	0.4	4.8	3.0	1.0
11 hours	Canister	16.3	59.2	24.3	8.6
	Radiello	7.2	55.5	27.0	9.7
6 hours	Pumped tube	2.8	8.3	2.6	1.0
	Radiello	2.8	8.5	3.1	1.2

For a given adsorbent, m_{maxj} is different for each individual hydrocarbon, and m_j is directly proportional to m_{maxj}. It has been shown for Radiello tubes, that the affinity of the adsorbent for different compounds results in the relative masses adsorbed following the trend (Bates *et al.*, 1997) :

$$m_{benzene} < m_{toluene} < m_{xylene}$$

This 'competitiveness at equilibrium' of the adsorbent used in Radiello tubes means that compounds which are adsorbed preferentially by this adsorbent may displace other compounds which have a lower affinity on the adsorbent.

Such effects have also been noted for conventional passive sampling methods (Ballesta *et al.*, 1992; Krupa and Legge, 2000), though the impact on the resultant concentrations is not

as significant as that observed by Bates *et al.* for Radiello tubes. In particular, Roche *et al.* (1999) noted unusual behaviour for n-hexane and benzene. The diffusive uptake rate of these compounds onto an adsorbent was observed to decrease rapidly with increasing ambient concentration. During monitoring at Mullingar, this effect would be particularly significant for n-hexane, as very high concentrations of this compound (close to 1 ppm) were measured in the vicinity of Penn. This effect would also explain the very low benzene concentrations measured on the Radiello tubes, despite some samples being collected close to busy roads. Field (1995) reported that there still exists significant uncertainty in the diffusive uptake rate of pollutant / adsorbent combinations under ambient conditions. Such uncertainty in uptake rates would likely impact the measured concentrations at Mullingar.

This problem was noted by the manufacturers of Radiello tubes. To combat the problem, the effective uptake rate was reduced by altering the geometry of the adsorbent cartridge (see Section 3.4) which protects the adsorbent from direct atmosphere exposure. The study by Bates *et al.* (1997) indicates that no competitive effects were noted for these upgraded Radiello tubes during experiments where the tubes were exposed for seven days. However, the results of the present study indicate that the problem can still occur for sampling periods which are extended beyond seven days. The results from passive tube sampling at Lynn Industrial Estate suggest that competitive effects between compounds particularly affected n-hexane, and also benzene, which displayed lower than expected concentrations. The agreement between Radiello and on-line predictions of toluene and xylene concentrations is much better, compared to n-hexane. This is in agreement with Bates' *et al.* (1997) study which showed that these compounds were least affected by competitive effects, and is further investigated in the following section where monitoring results are compared with dispersion modelling predictions.

7.5 DISPERSION MODELLING SUMMARY RESULTS

The ISC and ADMS dispersion models were used to predict the contribution of emissions from Penn and Taconic to ambient concentrations of n-hexane, toluene and the xylenes, using both local and regional meteorological data, and emissions estimates based on monthly and quarterly stack sampling programmes at Taconic and Penn, respectively. Background information on dispersion modelling, and on the emissions data used during this project is included in Section 6.7. The models were set up to provide hourly average

concentrations at a number of receptors, corresponding to the location of the monitoring unit, and of the pumped and passive sampling tubes around the industrial estate.

7.5.1 Measured and Modelled Concentrations at the Monitoring Unit

Summary results for predicted and measured n-hexane concentrations at the monitoring unit are given in Table 7.6. The results are averaged for working hours at Penn (24 hours / day, Monday to Saturday lunch-time), with zero emissions assumed for other periods.

Table 7.6 Modelled and measured n-hexane concentrations at the monitoring unit, ppb

	Average	Median	Standard deviation	Maximum	90th percentile	95th percentile	98th percentile
Measured n-hexane	**68.90**	**3.03**	**134.08**	**764.28**	**276.54**	**398.78**	**464.76**
ISC, local met. data	82.03	0.00	208.84	970.08	338.72	655.89	868.36
ISC, regional met. data	89.44	0.00	207.64	910.22	411.05	642.36	819.66
ADMS, local met. data	66.74	0.81	135.05	650.90	296.20	426.81	490.03
ADMS, regional met. data	77.69	0.03	157.59	693.83	265.97	464.39	634.74

The model prediction closest to the measured n-hexane concentration is given by the ADMS model, using local meteorological data. The agreement between the modelled (66.74 ppb) and measured (68.90 ppb) average concentrations is excellent. The standard deviation for this modelled dataset is also in good agreement with the measured results, though the median value is lower for the model data. The low median values associated with all of the modelled datasets reflects the larger number of zero concentrations predicted by the models, compared to the measured data. The measured concentration rarely drops to zero, even when the wind is not blowing in the direction of the monitoring unit, due to background n-hexane concentrations. However, the models are not capable of predicting these concentrations, which are normally very low (1 to 2 ppb). ADMS, using local meteorological data, slightly underpredicts the maximum measured concentrations, as does ADMS using regional meteorological data; however, both predicted maximum concentrations are within 85 percent of the measured maximum.

The ISC model predicts similar concentrations using both meteorological datasets, however, as with the ADMS model, the local meteorological data provides a slightly lower average concentration than the regional data. The average and maximum modelled concentration are overpredicted for both meteorological datasets. The median values of zero indicate the larger number of zero concentrations predicted by ISC compared to the ADMS model. This is because the ISC model is reported to calculate a narrower plume width compared to the ISC model (Abbott, 2000). ISC also predicts higher percentile values, despite the large number of zero concentrations predicted.

Summary results for toluene and the xylenes (sum of measured xylene concentrations) are presented in Table 7.7 and Table 7.8, respectively. Again results are calculated only for normal operating hours at Taconic (08:00 - 17:00, Monday to Friday). Xylene results are presented as sum of m+p-xylene and o-xylene.

Table 7.7 Modelled and measured toluene concentrations at the monitoring unit, ppb

	Average	Median	Standard deviation	Maximum	90th percentile	95th percentile	98th percentile
Measured toluene	**2.31**	**0.61**	**4.56**	**38.06**	**6.52**	**10.53**	**17.34**
ISC, local met. data	0.82	0.00	3.66	29.98	0.06	2.34	16.51
ISC, regional met. data	1.23	0.00	4.66	38.59	0.37	10.53	18.87
ADMS, local met. data	1.28	0.00	3.75	34.82	5.20	9.45	13.06
ADMS, regional met. data	1.43	0.00	3.34	22.68	5.37	8.29	12.91

Bearing in mind the uncertainties regarding the magnitude of toluene emissions, described in Section 6.7.5, both models have performed well in predicting toluene concentrations at the monitoring unit. As regards the average measured concentration, the ADMS model predicts the closest values. It is not surprising that both models underpredict the average concentration by around 1 ppb, as the models do not take other sources, such as emissions from vehicles and the nearby filling stations into account. These results suggest that emissions from Taconic result in at least a doubling of the average toluene concentration which would otherwise have occurred at the monitoring location due to emissions from other sources. The median value for both model predictions are zero, indicating the large number of zero concentrations predicted by the models. The ISC model results using

regional meteorological data are in good agreement with the measured data for all of the parameters (except the median). The ADMS model performs more strongly using local meteorological data.

The predicted average xylene concentrations at the monitoring site using both models are much lower than the measured concentrations, suggesting that xylene emissions from Taconic have been underestimated or that a significant contribution to ambient concentrations is made by emissions from other sources. Again, the models predict a large number of zero concentrations, as indicated by the zero median value. The ADMS model using local meteorological data comes closest to the results measured at the monitoring unit, particularly for the maximum and percentile values, though all models underpredict the 98th percentile by a factor of two. The fact that the maximum and 98th percentile concentrations are underpredicted suggests that the emissions values used in the models may be less than the maximum emissions which occurred during the course of the monitoring study, as the maximum measured concentrations were all observed for winds from the direction of Taconic.

Table 7.8 Modelled and measured xylene concentrations at the monitoring unit, ppb

	Average	Median	Standard deviation	Maximum	90th percentile	95th percentile	98th percentile
Measured total xylene	**2.15**	**1.13**	**3.79**	**29.55**	**3.97**	**6.73**	**15.98**
ISC, local met. data	0.46	0.00	1.76	11.36	0.13	4.12	7.54
ISC, regional met. data	0.59	0.00	2.06	18.32	0.89	4.34	7.45
ADMS, local met. data	0.77	0.00	2.26	21.08	3.09	5.67	7.62
ADMS, regional met. data	0.85	0.00	1.98	13.47	3.20	4.94	7.66

Table 7.6 to Table 7.8 confirm that both models performed well in predicting long-term pollutant concentrations due to emissions from local low level emissions points, with both maximum and average concentrations being within a factor of two of the measured values on most occasions. However, background concentrations of xylene and toluene resulted in higher measured concentrations. Initial results suggest that ADMS performed slightly better than ISC in this situation. Further analysis in Section 7.6 provides a clearer indication of the relative performance of the two models on a short-term (hourly) basis.

7.5.2 Measured and Modelled Concentrations at the Tube Sampling Locations

The ADMS model was also used to predict the hourly concentrations at each of the tube sampling locations throughout the complete monitoring period. However, the ISC model could only be used to calculate average concentrations at each of these locations, as the run time to calculate hourly values was extremely lengthy. The average concentration predicted by the ADMS model for each of the tube sampling studies is compared to the measured results in Table 7.9 and Table 7.10.

The ADMS model predictions of hydrocarbon concentrations for the same locations and time periods as the pumped tube results are presented in Table 7.9. The best comparison between the modelled and measured results is obtained by comparing the n-hexane concentrations. The low ambient (background) concentrations of toluene and xylene present during most of the pumped sampling periods resulted in very small masses of hydrocarbons being collected on the tubes during the short sampling period, precluding quantitative analysis of these compounds by the analytical system used. On two occasions, where samples were collected downwind of Taconic (tubes P3 and P4), measurable quantities of xylene and toluene were trapped on the tubes, however, the ADMS predictions of these average concentrations are lower than those measured.

Table 7.9 Comparison of pumped tube sampling and ADMS predicted results

Tube	ADMS predicted (ppb)			Pumped tube results (ppb)			ADMS / pumped		
no.	n-Hexane	Toluene	Xylene	n-Hexane	Toluene	Xylene	n-Hexane	Toluene	Xylene
P1	385.02	0.00	0.00	341.33	2.57	1.39	1.13		
P2	559.65	0.00	0.00	138.93	0.00	2.93	4.03		
P3	0.00	5.26	9.10	0.00	19.26	39.00	both zero	0.27	0.23
P4	350.18	0.37	0.56	147.51	3.21	1.67	2.37	0.12	0.34
P5	NA	NA	NA	221.91	0.00	0.00	NA		
P6	NA	NA	NA	166.72	0.00	0.00	NA		
P7	48.60	0.00	0.00	0.00	0.00	0.00	-		
P8	340.81	0.38	0.47	647.28	0.00	0.00	0.53		
P9	470.48	1.97	2.58	605.13	0.00	0.00	0.78		
P10	105.77	0.00	0.00	NA	0.00	0.00	NA		
P11	202.28	0.02	0.03	236.70	0.00	0.00	0.85		
P12	210.93	0.04	0.04	277.86	0.00	0.00	0.76		
P13	259.24	0.08	0.09	223.83	0.00	0.00	1.16		
P14	635.40	6.22	8.59	501.70	0.00	0.00	1.27		
P15	92.44	15.49	22.75	319.03	0.00	0.00	0.29		

The results from pumped sample measurements of elevated n-hexane concentrations at the monitoring unit (tubes P5 to P15), indicate particularly good performance at higher

concentrations. This suggests that the pumped sampling results are likely to be more accurate than ADMS results. Due to the variable emissions from Taconic, it is possible that emissions during the tube sampling period were lower than those used in the dispersion model. Also, emissions may not have been continuous throughout the sampling period, though this is assumed by the model. On most occasions ADMS predicts low toluene and xylene concentrations, in agreement with the pumped tube data, which indicates mainly zero concentrations, with the main exceptions of the sampling periods of tubes P14 and P15, where elevated toluene and xylene concentrations are predicted by the ADMS model, but the pumped tube results are low. These tubes were sampled at the monitoring unit, with on-line results indicating no elevated toluene or xylene concentrations at this time. It would therefore appear that there were no emissions from the Taconic facility at this time, as the wind was blowing from the direction of the Taconic facility during this sampling period.

ADMS predictions and pumped tube measurements for n-hexane are generally in good agreement. Seven out of 12 comparable results indicate that the ratio of the ADMS prediction to the measured concentration is between 0.5 and 1.5. This level of accuracy would be considered good for prediction of short-term concentrations for a given time period and specific location. Of the other five comparable samples, one (tube P3) indicates zero concentrations for both methods, while ADMS overpredicts the concentration on three occasions (tubes P2, P4 and P7). For the remaining comparable sample (tube P15), ADMS underpredicts the measured concentration. Considering the good agreement previously observed between the pumped tube and on-line analysis methods for n-hexane, the pumped tube analysis results can be assumed to be more reliable than the model predictions.

Results from the ADMS model of predicted hydrocarbon concentrations for the same locations and time periods as the passive tube samples are presented in Table 7.10. The majority of comparisons reveal that the ADMS results tend to be higher than those from analysis of passive tube results, with the ADMS / passive ratio being particularly large for n-hexane. This agrees with the comparison of the on-line and passive tube results presented in Section 7.4.2, where on-line measurements of n-hexane were an order of magnitude greater than concentrations measured using passive sampling tubes.

Comparison of the ADMS and passive results for tube R4 reveals very poor agreement for all compounds. For several tubes, n-hexane ratios between 30 and 40 : 1 are observed.

Even for the pair of hexane results with the best agreement, the ADMS prediction is 3.55 times the concentration measured by the passive sampling tubes. The good agreement found between the pumped sampling results and ADMS is not observed with the passive tube results, again agreeing with previous analyses suggesting that the passive tube method used during the project underestimates the actual n-hexane concentration.

Table 7.10 Comparison of passive tube sampling and ADMS predicted results

Tube	Passive tube results (ppb)			ADMS predicted (ppb)			ADMS / passive		
no.	n-Hexane	Toluene	Xylene	n-Hexane	Toluene	Xylene	n-Hexane	Toluene	Xylene
R1	2.80	0.43	0.28	25.03	1.97	1.22	8.95	4.60	4.38
R2	0.64	0.69	0.63	20.48	3.16	1.96	32.16	4.57	3.13
R3	0.51	2.15	3.07	6.31	3.24	2.07	12.28	1.51	0.67
R4	0.08	0.27	0.28	30.73	2.57	1.56	402.83	9.39	5.54
R5	0.34	0.63	0.40	21.54	3.35	2.03	64.28	5.34	5.06
R6	0.10	2.78	2.89	0.00	2.02	1.30	0.00	0.73	0.45
R7A	0.64	0.72	0.46	20.28	1.75	1.08	31.87	2.44	2.34
R7B	NA	0.92	0.71	20.28	1.75	1.08	NA	1.90	1.51
R8A	10.78	1.50	1.80	38.28	1.25	0.79	3.55	0.83	0.44
R8B	NA	0.67	0.92	38.28	1.25	0.79	NA	1.87	0.85
R9	NA	7.46	6.26	0.00	4.78	2.75	NA	0.64	0.44
R10A	0.98	1.27	0.71	40.37	2.18	1.35	41.24	1.72	1.89
R10B	1.17	4.16	2.85	40.37	2.18	1.35	34.37	0.52	0.47
R11	NA	1.35	1.90	17.94	4.76	2.93	NA	3.53	1.54
R12	NA	5.35	2.80	0.07	13.02	7.85	NA	2.43	2.81
R13	6.31	2.91	4.10	113.44	23.06	14.09	17.98	7.92	3.44
R14A	0.95	1.95	1.83	41.07	2.31	1.44	43.42	1.18	0.79
R14B	1.04	2.05	1.83	41.07	2.31	1.44	39.47	1.12	0.79
R15A	NA	0.72	0.90	77.40	1.71	1.05	NA	2.39	1.17
R15B	3.56	2.00	2.13	77.40	1.71	1.05	21.73	0.86	0.49

Agreement between model and passive results is also poor for xylene and toluene, though considerably better than the hexane comparison. Agreement is stronger if ratios with passive measurements below 1 ppb are ignored, with most ratios then between 0.5 and 1.5. Again, this agrees with previous analyses which indicated better agreement between the on-line and passive results for xylene and toluene, and research by Bates *et al.* (1997), which indicated that these compounds suffer least from competitive effects on Radiello tubes.

Although little confidence can be placed in the accuracy of the passive tube results, the ratios between the ADMS and passive results for the respective compounds are as expected, based on previous analyses of the tube results. Though the quantitative results from the Radiello tubes may be in doubt, the ADMS / passive ratio is reasonably consistent, particularly for toluene and xylene, indicating a consistent reduction factor in the hydrocarbon concentrations calculated from the passive tube analyses.

The above comparisons with on-line, pumped, and passive tube analyses indicates good performance of the ISC and ADMS dispersion models in this situation. Further analysis of short-term concentrations in Section 7.6 allows a more detailed evaluation of the relative performance of either model through statistical and graphical techniques.

7.5.3 Building Effects

It is extremely difficult to simulate how a given plume will be redirected by local obstacles such as building and other structures, as the movement of wind-flows around a building, or group of buildings, can disperse a plume in a wide variety of patterns, depending on variables such as the building density, the angle of incidence and the height of the buildings (Air Quality Management, 1997). The summary model results, presented in Section 7.5.1, suggest that both models performed well in the complex modelling situation present in Lynn Industrial Estate, however, the building modules in these models are based on simplistic assumptions, and it has been suggested that representative behaviour of plumes around buildings can only be estimated using wind tunnels or computational fluid mechanics (Air Quality Management, 1997). For example, in many dispersion models, a complex group of buildings may be idealised as a single block to simplify the required calculations, and shorten the run-time of the model (CERC, 1999). Although the use of wind tunnels or fluid mechanics may provide a more accurate solution, the cost and expertise required for such work is beyond the scope of most projects.

In this section, the impact of modelling building effects are investigated using the results of several analyses from the ADMS model. Pollution data are also presented using concentration contour plots of n-hexane, toluene and xylene using software which is supplied with the ADMS modelling package. These model analyses cover a slightly shorter period than the complete monitoring period, hence the summary statistics of the model data are slightly different to those presented previously.

Results from the ADMS model with and without building effects are compared in Table 7.11. ISC and ADMS model results which are presented in all other sections include building effects. In modelling n-hexane, regional meteorological data were employed, while local data were used in the modelling of toluene and xylene ambient concentrations, though these factors have no impact on the findings of this analysis. The vast majority of

the analyses indicate that higher average and maximum concentrations are measured when building effects are included. This is likely to be due to entrainment of stack gases in the turbulent wake of the building (known as building downwash), resulting in a lower effective release height, and higher ground level concentrations closer to the stack. To avoid the adverse effects of building downwash, it is recommended that height of the stack or chimney should be 1.5 to 2.5 times the height of nearby buildings whose wake may cause plume downwash and entrainment into the recirculating flow region in the lee of the building (Arya, 1999). The stack height to building height ratio for the Penn facility is approximately 1.2, below the recommended value. For Taconic, the height of the roof-line varies, hence the stack to roof height ratio varies between 1.0 and 1.5, again suggesting that building downwash will affect ground level toluene and xylene concentrations.

Table 7.11 Results from ADMS model with and without the inclusion of building effects

Model results with and without building effects	Average	Maximum	95th percentile	98th percentile	Standard deviation
n-Hexane MU, measured	**68.90**	**764.28**	**398.78**	**464.76**	**134.08**
n-Hexane MU, with	67.1	677.0	458.9	643.7	149.9
n-Hexane MU, without	56.4	604.1	336.9	398.2	111.5
n-Hexane ST, with	9.3	463.7	49.7	171.3	45.3
n-Hexane ST, without	8.0	331.1	49.4	168.7	37.4
n-Hexane LT, with	17.6	511.1	151.8	255.4	62.6
n-Hexane LT, without	18.1	520.3	117.7	298.1	66.1
Toluene MU, measured	**2.31**	**38.06**	**10.53**	**17.34**	**4.56**
Toluene MU, with	1.5	51.9	10.5	18.8	5.1
Toluene MU, without	0.8	16.6	7.6	11.8	2.7
Toluene ST, with	4.8	50.0	34.5	40.4	10.9
Toluene ST, without	4.1	52.0	27.2	32.1	8.7
Toluene LT, with	4.9	120.5	26.6	38.2	11.3
Toluene LT, without	2.5	24.9	17.3	20.5	5.3
Xylene MU, measured	**2.15**	**29.55**	**6.73**	**15.98**	**3.79**
Xylene MU, with	0.9	32.6	6.3	11.6	3.2
Xylene MU, without	0.5	10.1	4.7	7.3	1.6
Xylene ST, with	2.9	33.3	21.1	24.9	6.7
Xylene ST, without	2.4	30.8	15.9	19.1	5.1
Xylene LT, with	3.0	73.2	16.4	22.7	6.9
Xylene LT, without	1.5	14.8	10.3	12.5	3.2

MU = concentrations at the monitoring unit
ST = concentrations at the Statoil filling station (see Figure 6.2)
LT = concentrations at Lynn tyres (see Figure 6.2)

Comparing analysis with and without building data, particularly large differences in the concentration of xylene and toluene are noted at Lynn Tyres (LT) and the monitoring unit location, both for the average and maximum values. Significant building effects would be

expected for these two directions, due to the location of buildings close to Taconic. Comparing model and measured data at the monitoring unit it is clear that model results including building effects display much stronger agreement with measured concentrations. This indicates that, for emissions from low level sources with surrounding buildings, including building effects results in much improved model performance.

Concentration contour plots of ambient concentrations due to emissions from Penn and Taconic were calculated using the ADMS model and associated software from the ADMS modelling package. In all cases, building effects were included in the calculations, which were carried out for a 50 m grid, stretching 750 m north, south, east and west of the monitoring site. Calculations were made of the maximum and average concentrations at each receptor over the course of the monitoring period. The plot of average n-hexane concentration in the industrial estate is shown in Figure 7.31. The concentrations are presented in $\mu g/m^3$ in these plots. The ordnance survey grid location (in metres) is shown. The influence of the prevailing south-westerly wind on ambient concentrations is obvious. The influence of the low emission height and building downwash are illustrated in the high concentrations estimated close to the emissions location.

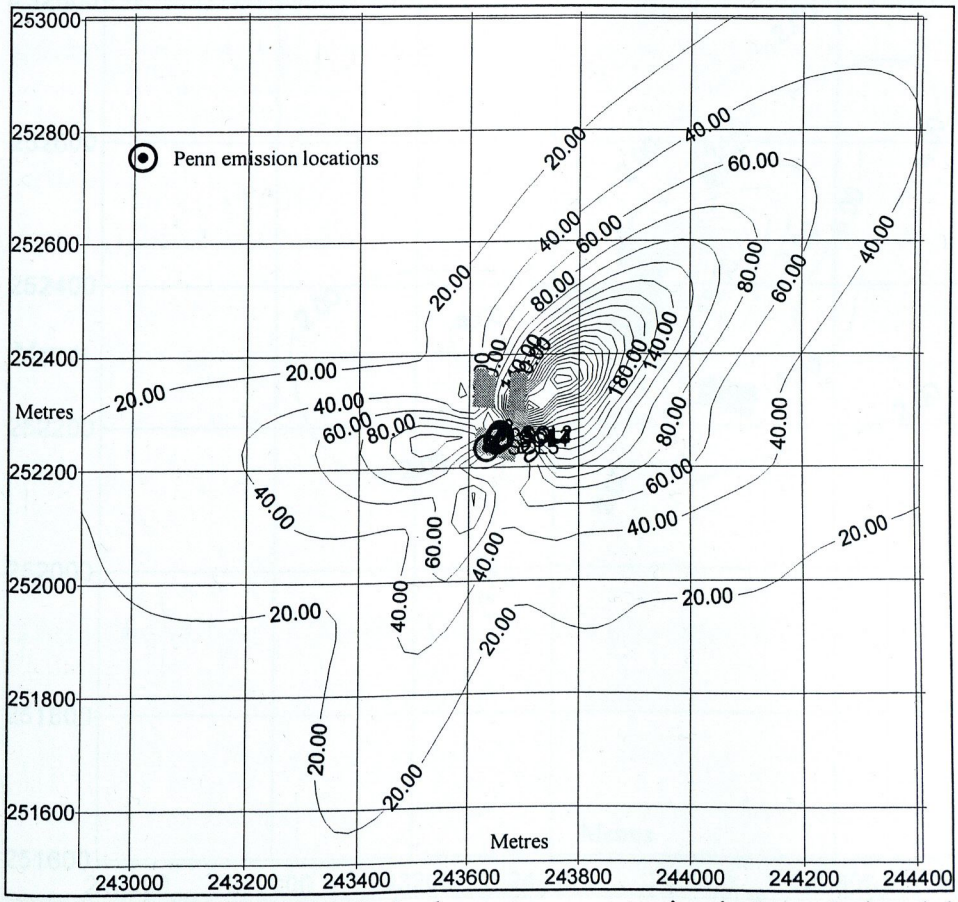


Figure 7.31 Average modelled n-hexane concentration in Lynn Industrial Estate, $\mu g/m^3$

A plot of average xylene concentrations in the industrial estate, due to emissions from Taconic, is given in Figure 7.32. A similar pattern to that shown for n-hexane is observed. Again very high concentrations are observed close to the emissions point, indicated by the very close contours to the north-east of the emission location. The fact that the emissions points are sheltered from north and north-easterly winds by the front part of the Taconic facility can be seen in the very low average concentrations observed to the west and south-west. Though this is also influenced considerably by the prevailing wind direction during the monitoring period (see Figure 6.11).

A plot of the highest modelled hourly toluene concentrations is presented in Figure 7.33. On this occasion the highest concentrations can be seen for winds from the west and north-west, again with the highest concentrations being observed very close to the emissions point.

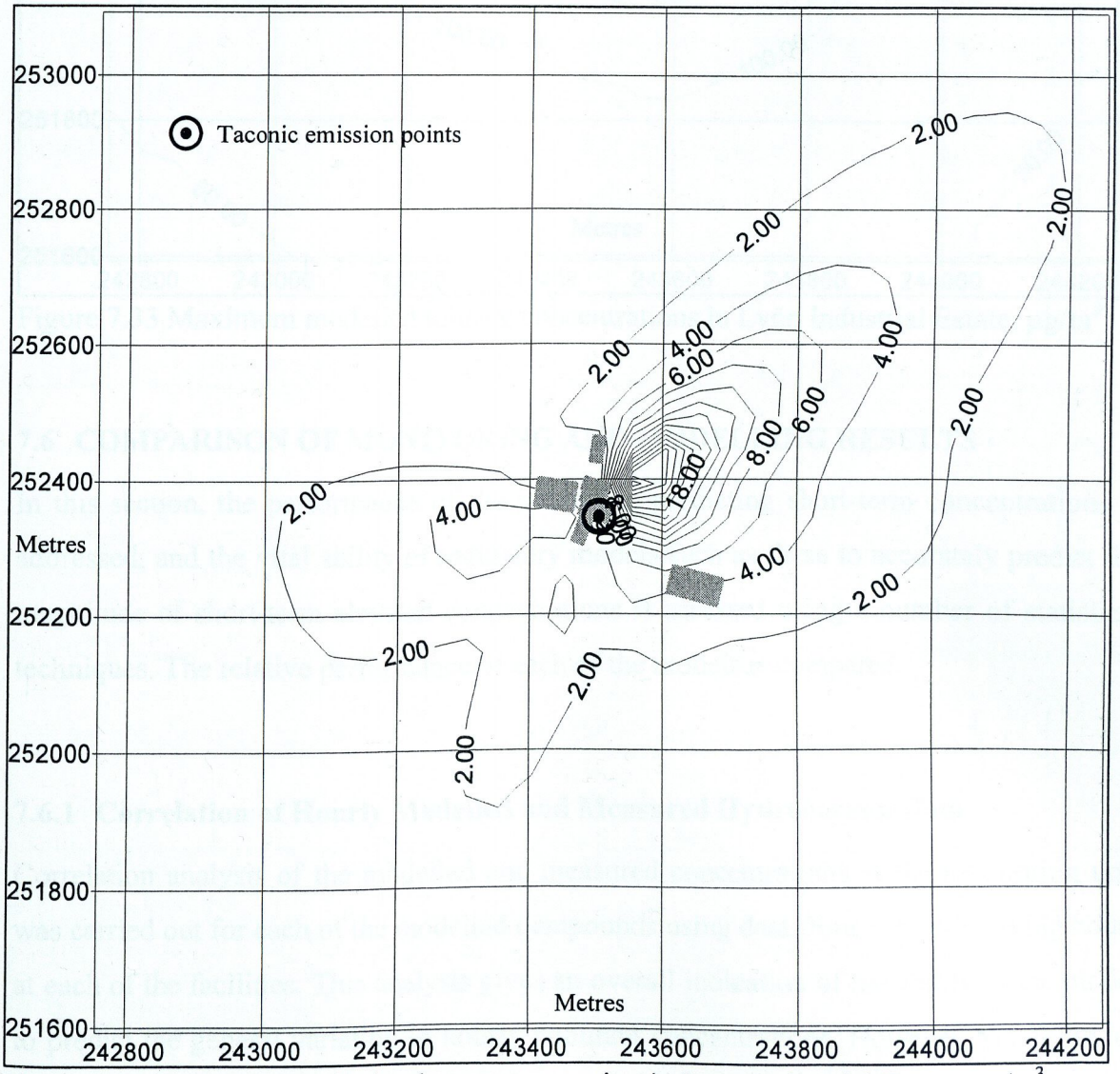


Figure 7.32 Average modelled xylene concentration in Lynn Industrial Estate, $\mu g/m^3$

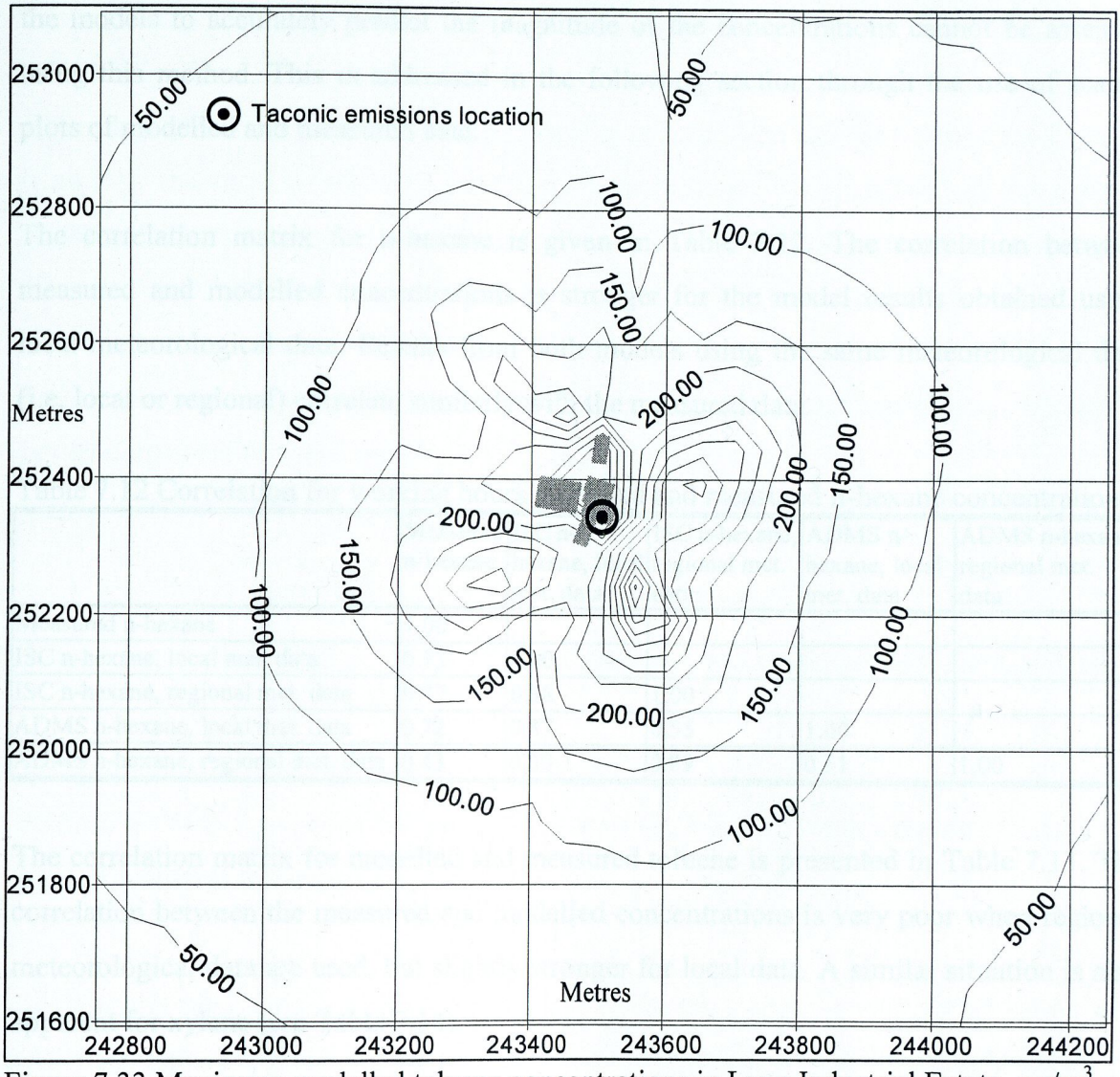


Figure 7.33 Maximum modelled toluene concentrations in Lynn Industrial Estate, $\mu g/m^3$

7.6 COMPARISON OF MONITORING AND MODELLING RESULTS

In this section, the performance of the models in predicting short-term concentrations is addressed, and the vital ability of regulatory models such as these to accurately predict the magnitude of short-term elevated concentrations is assessed using a number of statistical techniques. The relative performance of each of the models is compared.

7.6.1 Correlation of Hourly Modelled and Measured Hydrocarbon Data

Correlation analysis of the modelled and measured concentrations at the monitoring unit was carried out for each of the modelled compounds using data from normal working hours at each of the facilities. This analysis gives an overall indication of the ability of the model to predict the general variation in hourly pollutant concentrations. However, the ability of

the models to accurately predict the magnitude of the concentrations cannot be assessed using this method. This is addressed in the following section through the use of scatter plots of modelled and measured data.

The correlation matrix for n-hexane is given in Table 7.12. The correlation between measured and modelled concentrations is stronger for the model results obtained using local meteorological data. Results from both models using the same meteorological data (i.e. local or regional) correlate similarly with the measured data.

Table 7.12 Correlation for working hours modelled and measured n-hexane concentrations

	Measured n-hexane	ISC n-hexane, local met. data	ISC n-hexane, regional met. data	ADMS n-hexane, local met. data	ADMS n-hexane, regional met. data
Measured n-hexane	1.00				
ISC n-hexane, local met. data	0.73	1.00			
ISC n-hexane, regional met. data	0.47	0.38	1.00		
ADMS n-hexane, local met. data	0.72	0.87	0.55	1.00	
ADMS n-hexane, regional met. data	0.43	0.30	0.89	0.51	1.00

The correlation matrix for modelled and measured toluene is presented in Table 7.13. The correlation between the measured and modelled concentrations is very poor when regional meteorological data are used, but slightly stronger for local data. A similar situation is also apparent for xylene (see Table 7.14).

Table 7.13 Correlation for working hours modelled and measured toluene

	Measured toluene	ISC toluene, local met. data	ISC toluene, regional met. data	ADMS toluene, local met. data	ADMS toluene, regional met. data
Measured toluene	1.00				
ISC toluene, local met. data	0.36	1.00			
ISC toluene, regional met. data	0.19	0.52	1.00		
ADMS toluene, local met. data	0.34	0.55	0.51	1.00	
ADMS toluene, regional met. data	0.17	0.33	0.67	0.61	1.00

Table 7.14 Correlation for working hours modelled and measured xylene

	Measured xylene	ISC xylene, local met. data	ISC xylene, regional met. data	ADMS xylene, local met. data	ADMS xylene, regional met. data
Measured xylene	1.00				
ISC xylene, local met. data	0.39	1.00			
ISC xylene, regional met. data	0.12	0.53	1.00		
ADMS xylene, local met. data	0.45	0.65	0.47	1.00	
ADMS xylene, regional met. data	0.13	0.40	0.66	0.61	1.00

The results for each of the three modelled compounds indicate good model performance, particularly when local meteorological data are used. The correlation for n-hexane is stronger for two reasons. Firstly, the monitoring location was closer to Penn than Taconic. Secondly, and most importantly, emissions from Penn are better defined temporally and quantitatively, than those from Taconic. All modelling assumed constant emissions at Taconic, from 08:00 to 17:00 daily. Though this assumption was known to be inaccurate, it allowed peak ambient concentrations to be predicted. In Section 7.6.3, comparison of the highest measured and modelled concentrations of each compound investigates whether or not this approach was successful.

7.6.2 Graphical Analysis of Short-Term Model Performance

Scatter plots and time-series plots of hourly measured and modelled hydrocarbon data are presented in this section. These provide an indication of the level of short-term agreement between modelled and measured concentrations. The statistical methods presented in later sections quantify the agreement between the datasets, but do not demonstrate as clearly the level of temporal agreement achieved.

Short-Term n-Hexane Concentrations

A sample scatter plot of ADMS modelled and measured n-hexane concentrations is given in Figure 7.34, for normal working hours at Penn. Lines indicating various levels of data agreement are also included on the plot to allow comparison of the modelled and measured data. A large amount of scatter is evident, though the distribution of points either side of the line of slope unity is balanced, with the exception of a number of measured concentrations along the x-axis, for which zero concentrations were predicted. The scatter plot for ISC modelled and measured n-hexane (Figure 7.35) is similar to that for ADMS in Figure 7.34, except that there are a greater number of point above the line of slope unity, as ISC tends to overestimate the hourly hexane concentration at the monitoring unit. This indicates that the ADMS model appears to be less biased towards elevated concentrations than the ISC model. For both models, the scatter is greater when regional meteorological data are used.

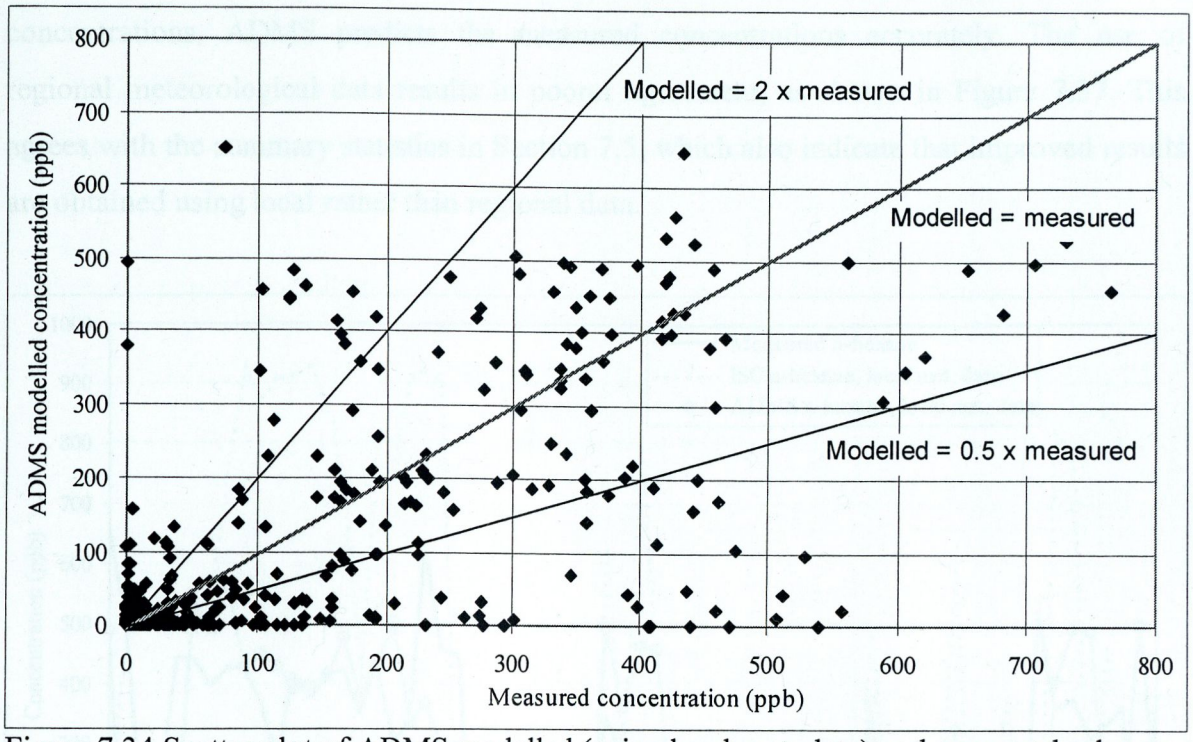


Figure 7.34 Scatter plot of ADMS modelled (using local met. data) and measured n-hexane concentrations at the monitoring unit, ppb

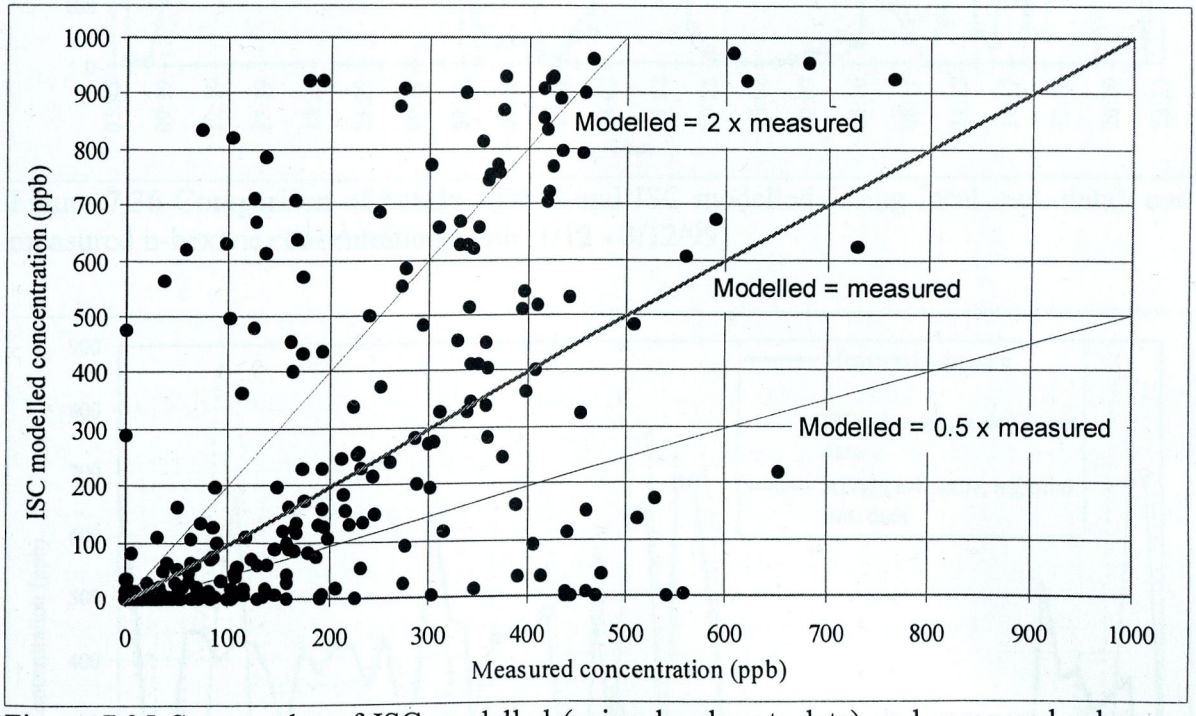


Figure 7.35 Scatter plot of ISC modelled (using local met. data) and measured n-hexane concentrations at the monitoring unit, ppb

A sample time-series plot of the measured and modelled n-hexane concentration is presented in Figure 7.36. Results from both ISC and ADMS are shown, with both model calculations using local meteorological data. Both models predict the hourly n-hexane concentrations very well, though ISC tends to slightly overpredict the measured

concentrations. ADMS predicts the measured concentrations accurately. The use of regional meteorological data results in poorer agreement, as shown in Figure 7.37. This agrees with the summary statistics in Section 7.5, which also indicate that improved results are obtained using local rather than regional data.

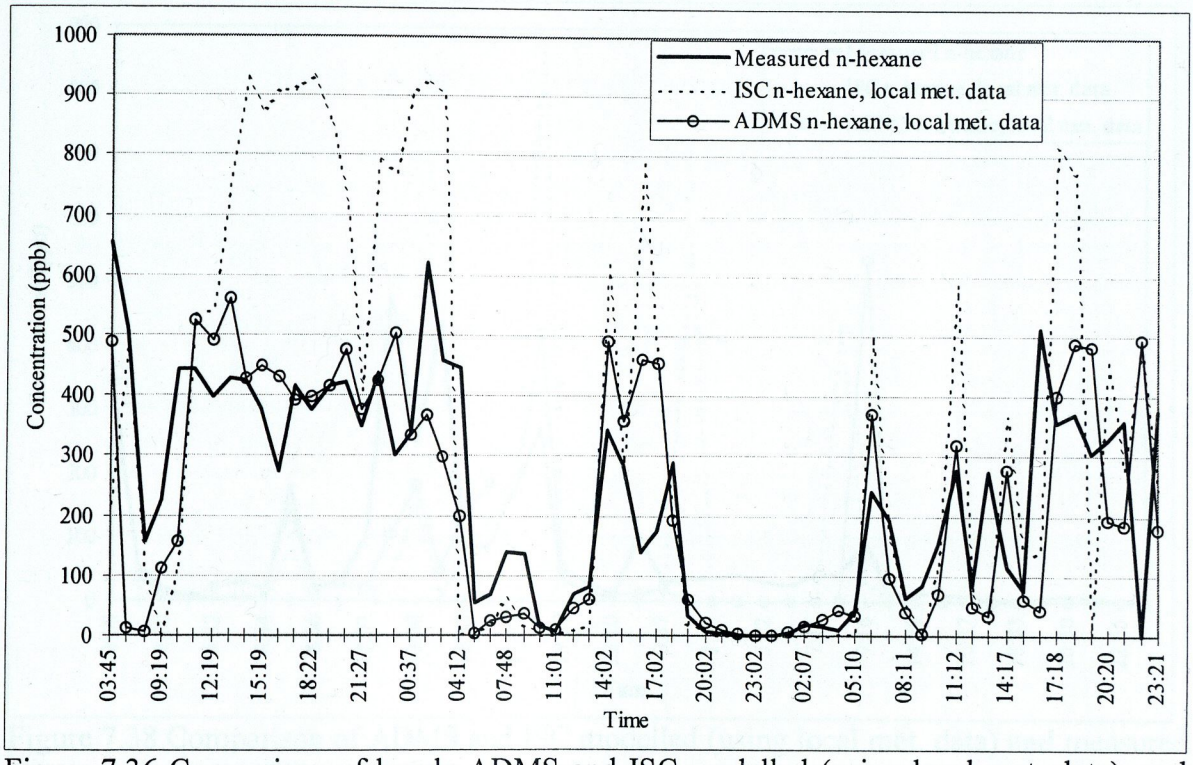


Figure 7.36 Comparison of hourly ADMS and ISC modelled (using local met. data), and measured n-hexane concentrations, ppb (1/12 - 3/12/99)

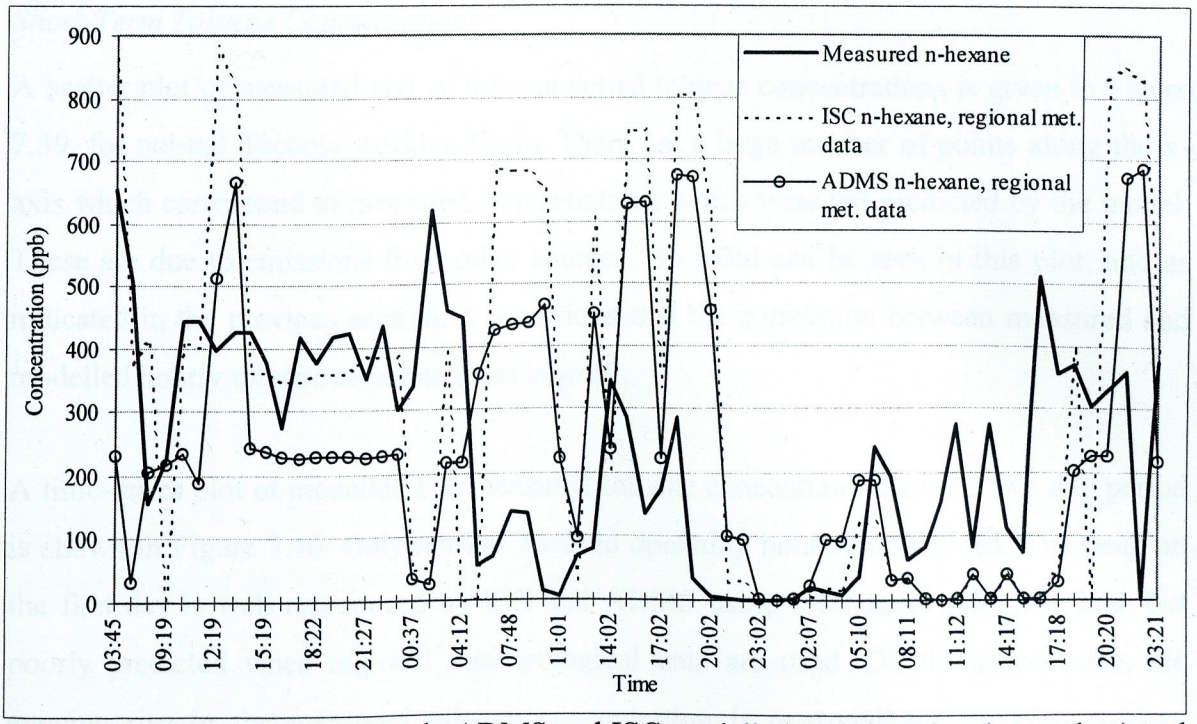


Figure 7.37 Comparison of hourly ADMS and ISC modelled (using regional met. data) and measured n-hexane concentrations, ppb (1/12 - 3/12/99)

Figure 7.36 and Figure 7.37 illustrate a case where good agreement between modelled and measured concentrations is observed. However, agreement is poorer on other occasions, particularly when the measured concentrations are lower. In Figure 7.38, when measured concentrations fall below 100 ppb, modelled concentrations are at or close to zero.

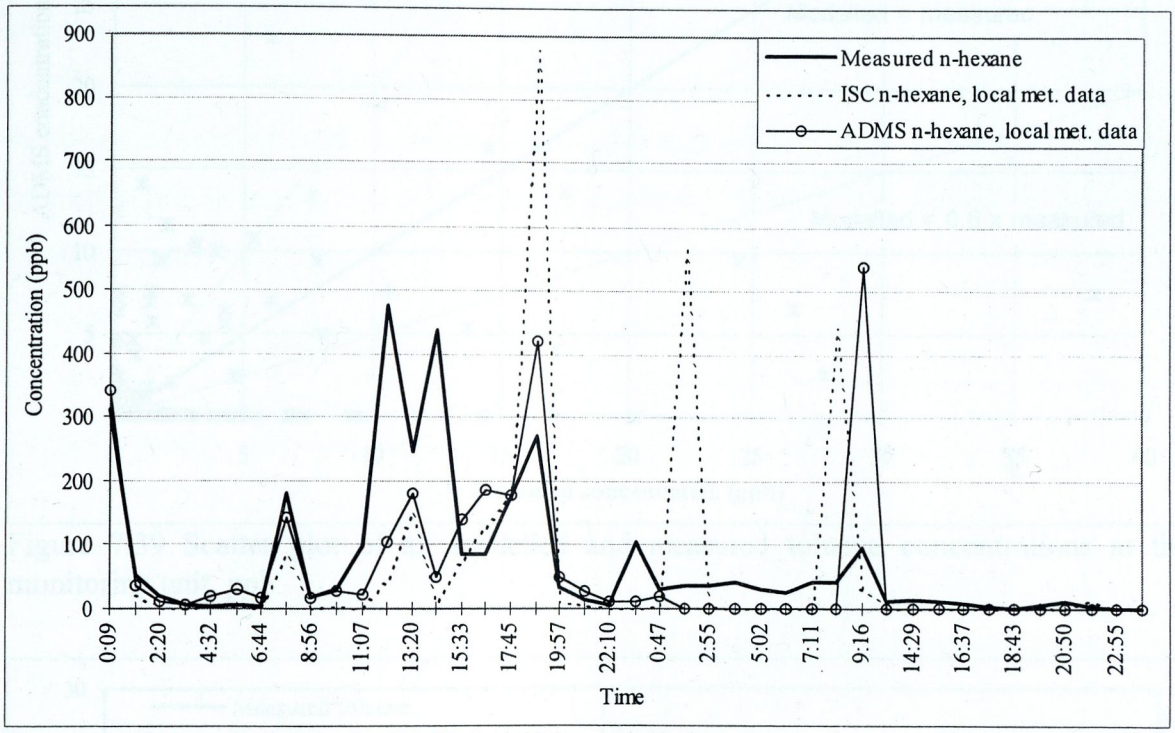


Figure 7.38 Comparison of ADMS and ISC modelled (using local met. data) and measured n-hexane concentrations, ppb (1/10 - 4/10/99)

Short-Term Toluene Concentrations

A scatter plot of measured and ADMS modelled toluene concentrations is given in Figure 7.39, for normal Taconic working hours. There are a large number of points along the x-axis which correspond to measured concentrations which were not predicted by the model. These are due to emissions from other sources. No trend can be seen in this plot, and as indicated in the previous section, it is obvious that the correlation between measured and modelled hourly toluene concentrations is weak.

A time-series plot of modelled and measured toluene concentrations over a two day period is shown in Figure 7.40. Only normal Taconic operating hours are included. The peak on the first day is well reproduced by ISC and ADMS using local meteorological data, but poorly predicted when regional meteorological data are used. On the second day, the evening rise in the measured toluene concentration is overpredicted by both models, probably due to higher emissions being specified in the model, than occurred at this time.

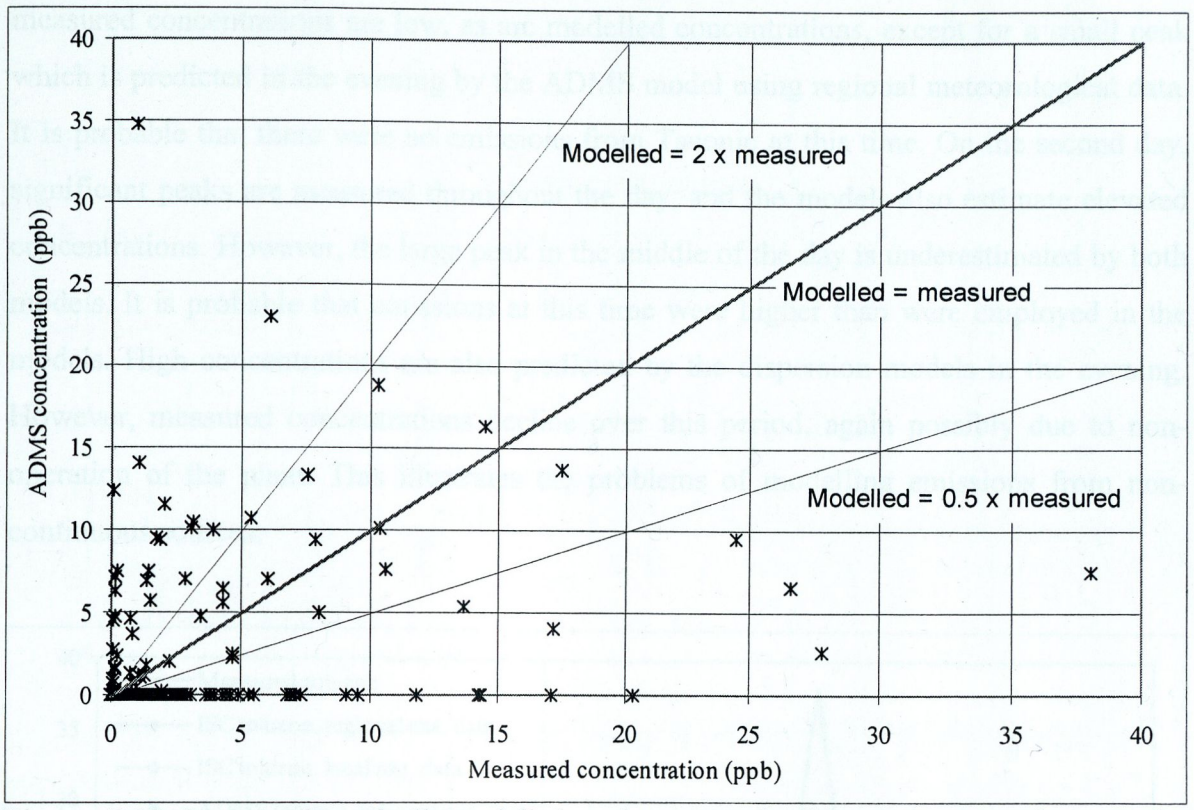


Figure 7.39 Scatter plot of all modelled and measured toluene concentrations at the monitoring unit, ppb

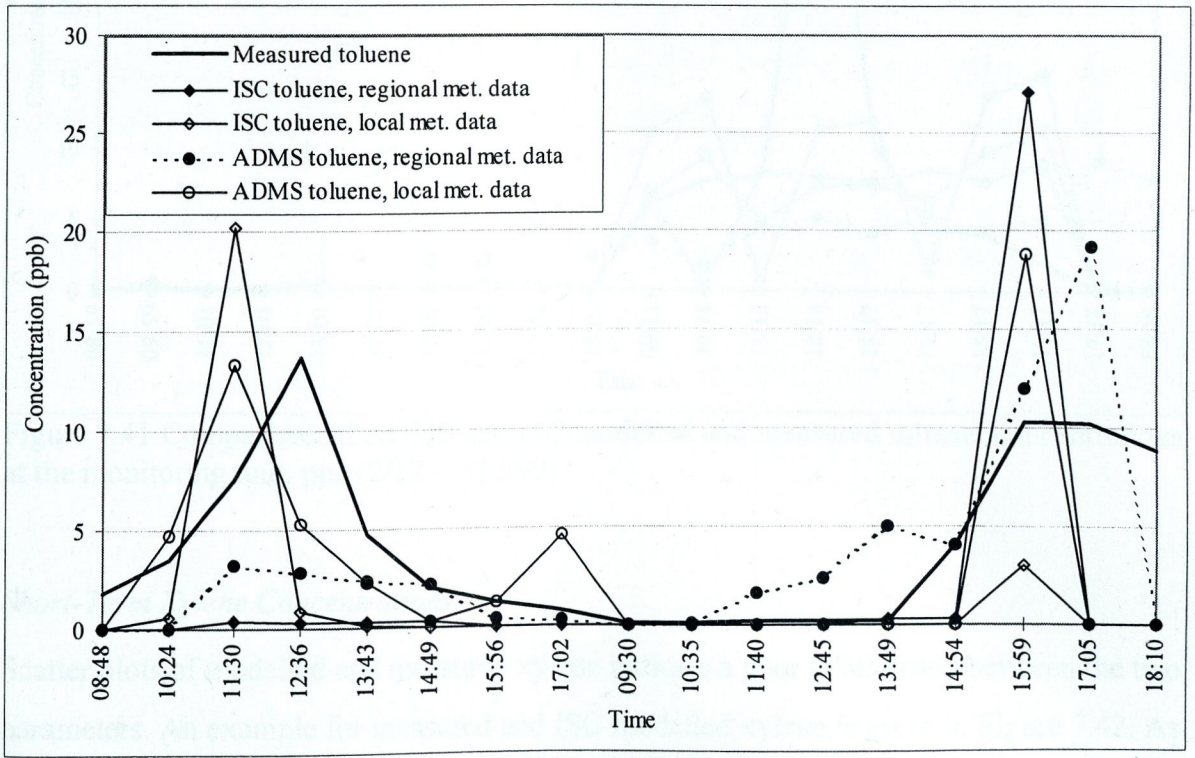


Figure 7.40 Comparison of ADMS and ISC modelled and measured toluene concentrations at the monitoring unit, ppb (5/11 - 8/11/99)

Another time-series plot of modelled and measured toluene is given in Figure 7.41. The results cover two periods of normal operation at Taconic. Throughout the first day,

measured concentrations are low, as are modelled concentrations, except for a small peak which is predicted in the evening by the ADMS model using regional meteorological data. It is probable that there were no emissions from Taconic at this time. On the second day, significant peaks are measured throughout the day, and the models also estimate elevated concentrations. However, the large peak in the middle of the day is underestimated by both models. It is probable that emissions at this time were higher than were employed in the models. High concentrations are also predicted by the dispersion models in the evening. However, measured concentrations decline over this period, again possibly due to non-operation of the plant. This illustrates the problems of modelling emissions from non-continuous sources.

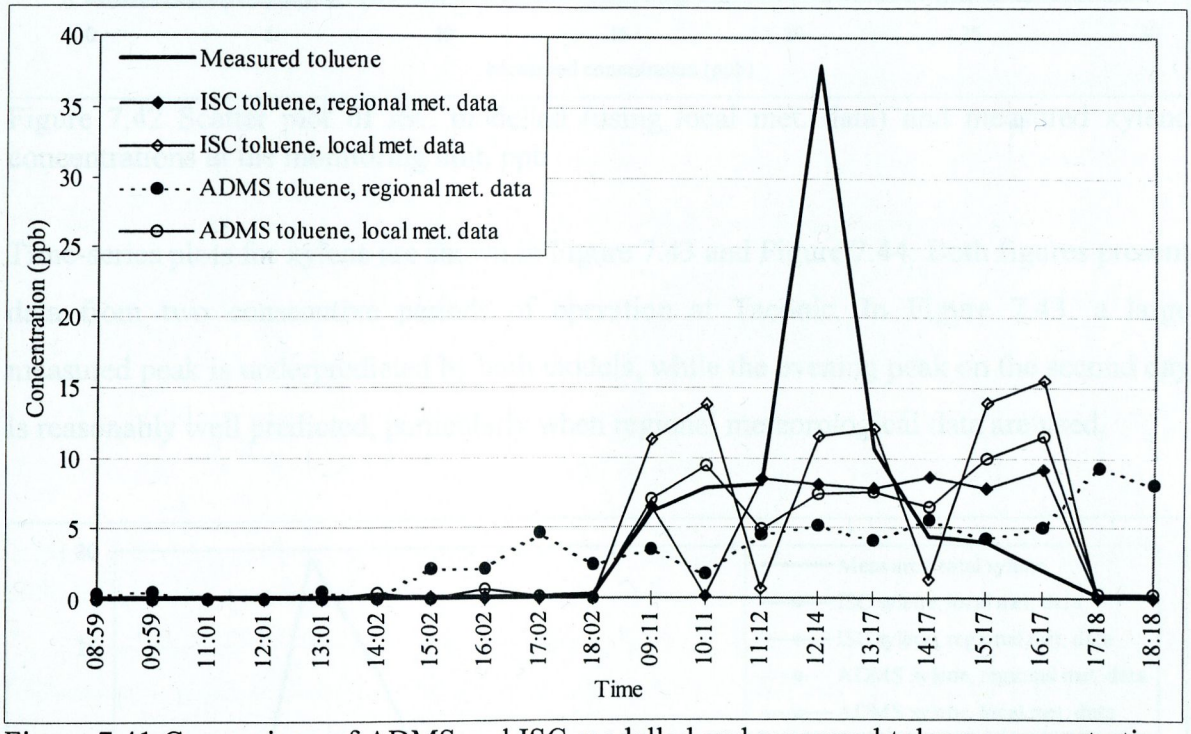


Figure 7.41 Comparison of ADMS and ISC modelled and measured toluene concentrations at the monitoring unit, ppb (2/12 - 3/12/99)

Short-Term Xylene Concentrations

Scatter plots of modelled and measured xylene indicate a poor relationship between the two parameters. An example for measured and ISC modelled xylene is given in Figure 7.42. As with toluene, a large number of measured concentrations are paired with zero predicted concentrations, indicating contributions from other sources. The model also predicts the highest measured concentrations of xylene poorly, indicating an underestimation of the xylene emissions from the Taconic facility.

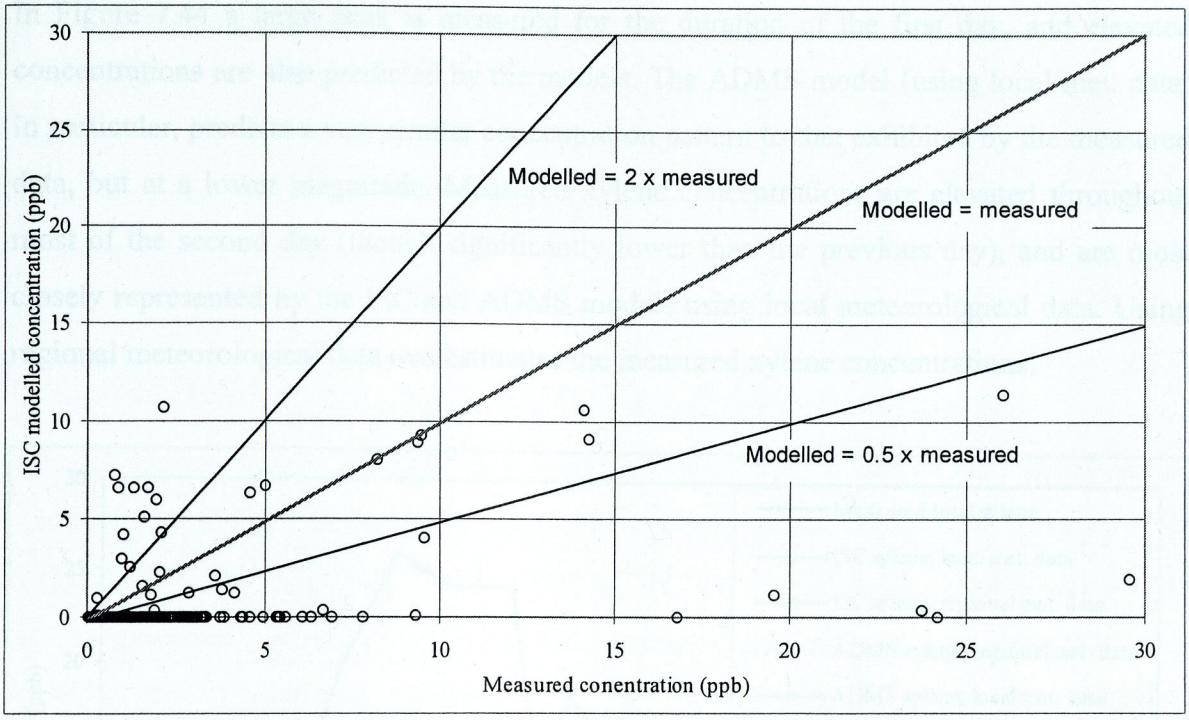


Figure 7.42 Scatter plot of ISC modelled (using local met. data) and measured xylene concentrations at the monitoring unit, ppb

Time-series plots for xylene are shown in Figure 7.43 and Figure 7.44. Both figures present data from two consecutive periods of operation at Taconic. In Figure 7.43, a large measured peak is underpredicted by both models, while the evening peak on the second day is reasonably well predicted, particularly when regional meteorological data are used.

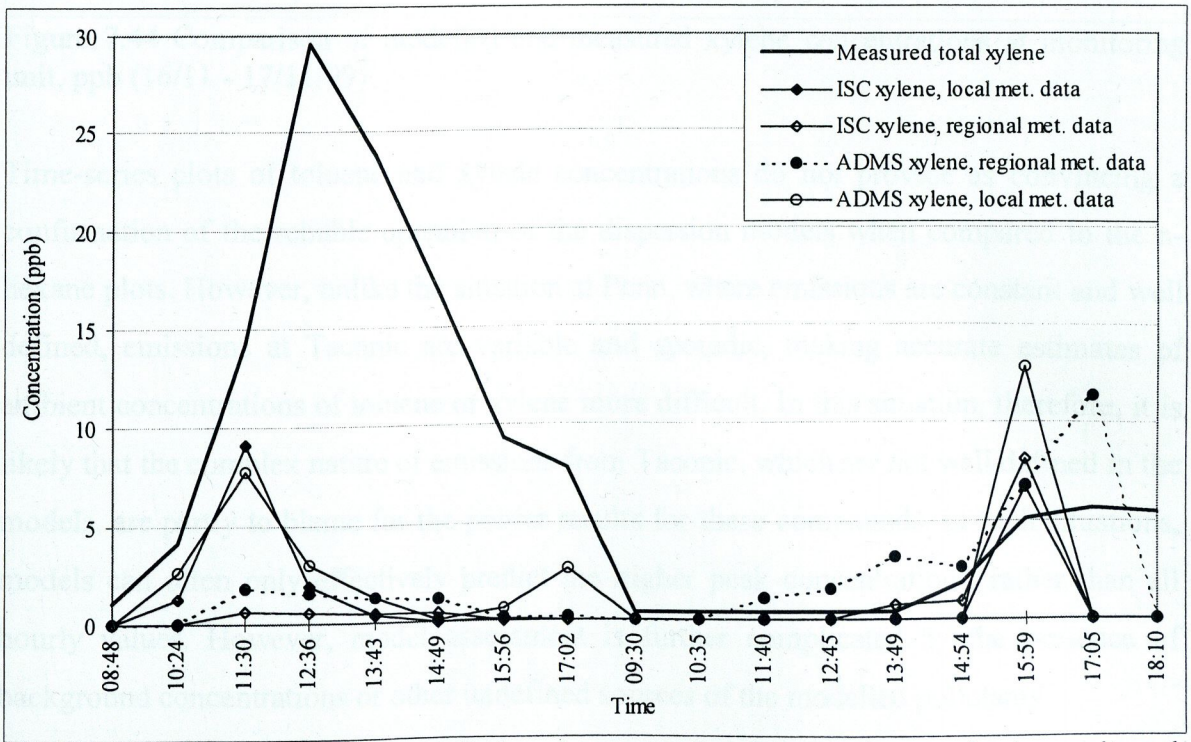


Figure 7.43 Comparison of modelled and measured xylene at the monitoring unit, ppb (5/11/99 and 8/11/99)

In Figure 7.44 a large peak is measured for the duration of the first day, and elevated concentrations are also predicted by the models. The ADMS model (using local met. data) in particular, predicts a very similar concentration pattern to that exhibited by the measured data, but at a lower magnitude. Measured xylene concentrations are elevated throughout most of the second day (though significantly lower than the previous day), and are most closely represented by the ISC and ADMS models using local meteorological data. Using regional meteorological data overestimates the measured xylene concentrations.

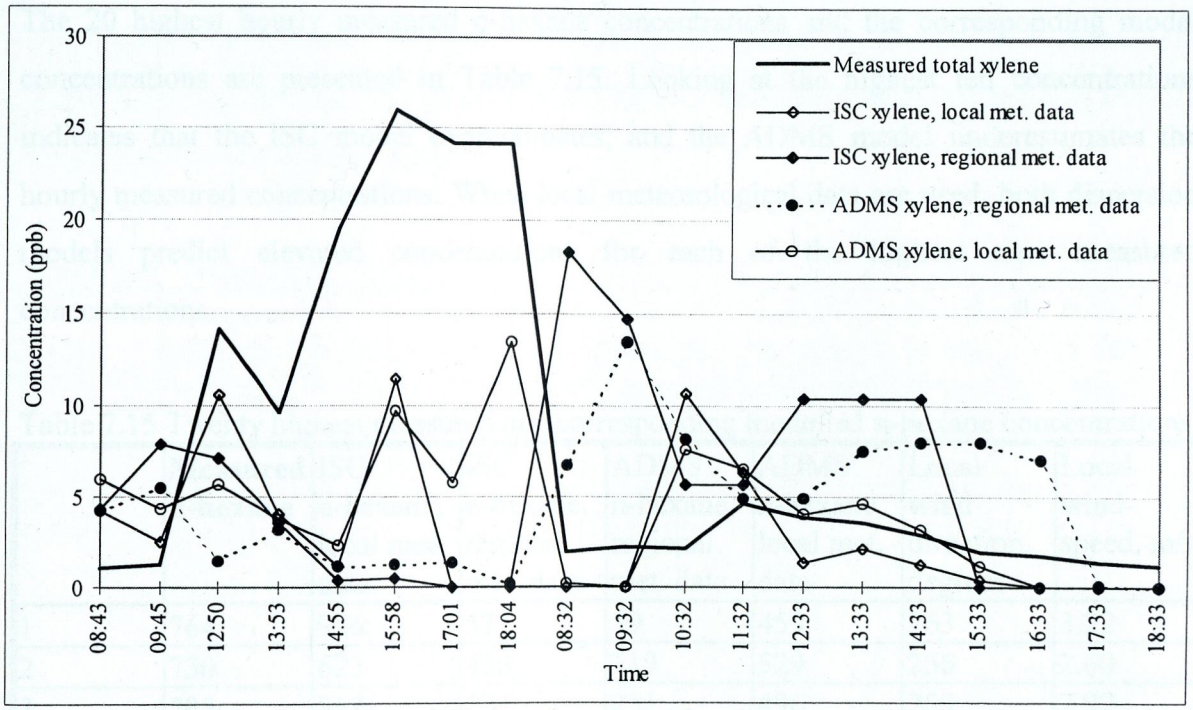


Figure 7.44 Comparison of modelled and measured xylene concentrations at monitoring unit, ppb (16/11 - 17/11/99)

Time-series plots of toluene and xylene concentrations do not provide as convincing a confirmation of the reliable operation of the dispersion models when compared to the n-hexane plots. However, unlike the situation at Penn, where emissions are constant and well defined, emissions at Taconic are variable and sporadic, making accurate estimates of ambient concentrations of toluene or xylene more difficult. In this situation, therefore, it is likely that the complex nature of emissions from Taconic, which are not well defined in the models, are partly to blame for the poorer results for these compounds. In such situations, models can often only effectively predict the higher peak concentrations, rather than all hourly values. However, model assessment is further complicated by the presence of background concentrations or other undefined sources of the modelled pollutants.

7.6.3 Statistical Methods of Model Comparison

A number of methods are used in this section to compare the performance of the two models. These focus mainly their abilities to accurately predict the most elevated concentrations, as these have the greatest impact on the surrounding environment, and will be most accurately measured.

Model Prediction of Elevated n-Hexane, Toluene and Xylene Concentrations

The 20 highest hourly measured n-hexane concentrations and the corresponding model concentrations are presented in Table 7.15. Looking at the highest ten concentrations indicates that the ISC model overestimates, and the ADMS model underestimates the hourly measured concentrations. When local meteorological data are used, both dispersion models predict elevated concentrations for each of the highest nine measured concentrations.

Table 7.15 Twenty highest measured and corresponding modelled n-hexane concentrations

	Measured n-hexane	ISC n-hexane, local met. data	ISC n-hexane, regional met. data	ADMS n-hexane, regional met. data	ADMS n-hexane, local met. data	Local wind direction, degrees	Local wind-speed, m/s
1	**764**	926	53	59	459	263	3.22
2	**730**	623	420	219	529	256	2.60
3	**705**	867	574	231	496	259	2.97
4	**682**	956	896	530	428	268	3.17
5	**653**	219	863	231	489	254	3.64
6	**621**	924	53	26	367	265	2.42
7	**606**	970	409	223	348	267	3.15
8	**589**	674	420	198	308	275	2.79
9	**561**	604	811	671	499	257	3.94
10	**559**	5	0	0	22	259	1.66
11	**541**	0	2	600	0	245	1.66
12	**529**	171	53	47	97	284	3.01
13	**512**	139	1	2	43	285	3.52
14	**508**	482	377	32	11	239	2.02
15	**476**	37	642	460	104	240	4.54
16	**472**	0	3	650	0	245	1.71
17	**467**	960	55	29	393	266	2.35
18	**462**	152	140	172	172	245	5.34
19	**461**	7	0	0	22	255	1.25
20	**459**	901	395	218	300	269	2.60
Average	**568**	481	308	230	254		

For the remainder of the highest measured concentrations a significant number of very low concentrations are predicted by the models. Because the ISC model tends to overestimate the measured concentrations, the average predicted concentration for all 20 elevated measurements is closest to the actual value. Both models perform well in predicting elevated concentrations at a specific location and time. Comparison of the highest measured and modelled concentrations for unpaired data (data not paired in time) is also assessed later in this section.

The highest 20 measured and modelled hourly toluene concentrations are presented in Table 7.16. On the majority of occasions the measured concentrations are significantly larger than those predicted by the models.

Table 7.16 Twenty highest measured and corresponding modelled toluene concentrations

	Measured toluene	ISC toluene, regional met. data	ISC toluene, local met. data	ADMS toluene, regional met. data	ADMS toluene, local met. data	Local wind direction, degrees	Local wind-speed, m/s
1	**38.06**	8.10	11.50	5.15	7.45	287	4.91
2	**27.76**	0.00	0.00	0.00	2.66	268	1.15
3	**26.58**	10.96	12.28	5.45	6.52	300	4.13
4	**24.47**	13.41	20.21	2.60	9.53	292	3.23
5	**20.98**	0.00	0.00	0.00	0.00	111	0.15
6	**20.33**	0.00	0.00	0.00	0.00	193	3.62
7	**17.53**	0.00	0.00	19.22	13.70	303	1.40
8	**17.21**	0.22	0.49	1.99	4.05	308	3.65
9	**17.15**	0.01	0.00	0.27	0.05	323	1.96
10	**14.48**	0.26	21.99	2.23	16.26	288	2.56
11	**14.34**	0.00	0.00	0.00	0.00	40	1.48
12	**14.30**	0.00	0.00	0.00	0.00	49	1.33
13	**13.67**	0.33	0.85	2.83	5.30	305	3.60
14	**11.92**	0.00	0.00	0.00	0.00	100	0.29
15	**11.81**	0.00	0.00	0.00	0.00	41	1.59
16	**11.31**	0.00	0.00	0.00	0.00	38	0.99
17	**10.62**	7.85	12.06	4.17	7.61	291	4.74
18	**10.43**	0.00	0.00	2.37	10.16	300	2.57
19	**10.29**	27.05	2.98	11.99	18.79	277	1.23
20	**10.21**	0.00	0.00	19.18	0.01	319	0.77
Average	**17.17**	3.41	4.12	3.87	5.67		

On several occasions the ADMS and ISC models using local meteorological data accurately predict the measured concentrations, however, on many occasions zero

concentrations are predicted. This is to be expected as the wind directions for these measurements are not from Taconic. Of the top ten measured concentrations, ADMS using local meteorological data predicts elevated concentrations on seven occasions, though the magnitude is underestimated. The ISC model only predicts elevated concentrations (above 1 ppb) on four of these occasions. The average for the highest 20 measured toluene concentrations is three times higher than the ADMS model estimate, which predicts the highest average of all the model results. Of the highest 20 measured toluene concentrations, seven are outside the expected influence of Taconic (300 ± 40 degrees). The average measured concentration for the remainder is 18.34 ppb, compared to 7.35 ppb and 6.33 ppb for ADMS and ISC, respectively (using local meteorological data). Though this is an improvement, there still appears to be some underestimation of Taconic emissions.

The highest 20 measured and modelled xylene concentrations are presented in Table 7.17. As with toluene, the measured xylene concentrations are higher than the corresponding model predictions, indicating an underprediction of hydrocarbon emissions from Taconic.

Table 7.17 Twenty highest measured and corresponding modelled xylene concentrations

	Measured total xylene	ISC xylene, local met. data	ISC xylene, regional met. data	ADMS xylene, regional met. data	ADMS xylene, local met. data	Local wind direction, degrees	Local wind-speed, m/s
1	**29.55**	1.90	0.56	1.57	2.99	305	3.60
2	**25.99**	11.36	0.46	1.24	9.71	288	2.56
3	**24.15**	0.00	0.00	0.17	13.43	291	2.18
4	**24.14**	0.00	0.00	1.31	5.75	300	2.57
5	**23.72**	0.32	0.46	1.30	1.25	312	3.77
6	**19.56**	1.11	0.38	1.11	2.27	308	3.65
7	**16.78**	0.00	0.42	1.20	0.13	322	4.09
8	**14.28**	9.13	0.64	1.77	7.74	296	2.68
9	**14.13**	10.54	7.09	1.46	5.63	292	3.23
10	**9.54**	4.03	3.52	3.14	3.76	300	4.13
11	**9.45**	9.24	0.51	1.41	5.96	292	3.27
12	**9.34**	8.91	3.90	3.77	6.27	296	2.76
13	**9.30**	0.08	0.01	0.21	0.65	315	4.47
14	**8.17**	8.00	7.13	4.48	5.71	284	3.01
15	**7.78**	0.00	0.00	0.16	2.60	306	3.68
16	**6.93**	0.00	0.00	0.00	0.00	100	0.29
17	**6.68**	0.33	0.48	2.14	2.30	268	3.17
18	**6.32**	0.00	0.00	0.00	0.00	111	0.15
19	**6.10**	0.00	0.00	11.38	7.62	303	1.40
20	**5.60**	0.00	0.00	11.38	0.02	319	0.77
Average	**13.88**	3.25	1.28	2.46	4.19		

Of the ten highest measured xylene concentrations, the ADMS model using local meteorological data predicts elevated concentrations on nine of these occasions, compared to six occasions for the ISC model using local meteorological data. In fact, the ADMS model predicts elevated concentrations for 15 of the 20 highest measured concentrations. Compared to the analysis for toluene, many more of the xylene highest concentrations are associated with winds from the direction of Taconic, resulting in improved performance of the models in terms of identifying high concentrations, even though the magnitude of the concentrations are underestimated. The average concentration for the highest 20 measurements is over three times larger than the highest average predicted by the models, again suggesting underprediction of the Taconic emissions.

The above analyses of the paired measured and modelled data suggest that the models perform well in predicting the occurrence of elevated concentrations, though the magnitude of these predicted concentrations appears more difficult to predict. The poor prediction of the magnitude of the concentrations, particularly for toluene and xylene, may be the result of poor emissions data used in the models. The following section uses percentile analysis to assess the agreement between unpaired measured and modelled data.

Percentile Analysis

The individual percentile values (1 to 100) for all measured and modelled n-hexane, toluene and xylene are presented below in Figure 7.45 to Figure 7.51. These plots do not compare paired hourly data, but rather the ability of the model to predict the range of measured hourly concentrations.

The percentile plot for all measured and modelled n-hexane concentrations is presented in Figure 7.45. All values up to the 60th percentile are very close to zero. Between the 60th and 85th percentile the models tend to underpredict the measured percentiles, except for ADMS using regional meteorological data, which accurately estimates these percentiles. From the 85th percentile onwards, the ISC model tends to overpredict the measured percentiles by, on average, 100 ppb. ADMS using regional meteorological data also tends to slightly overpredict these percentiles. The best model performance is seen with the ADMS model using local meteorological data, which shows excellent agreement with the measured data from the 85th percentile onwards.

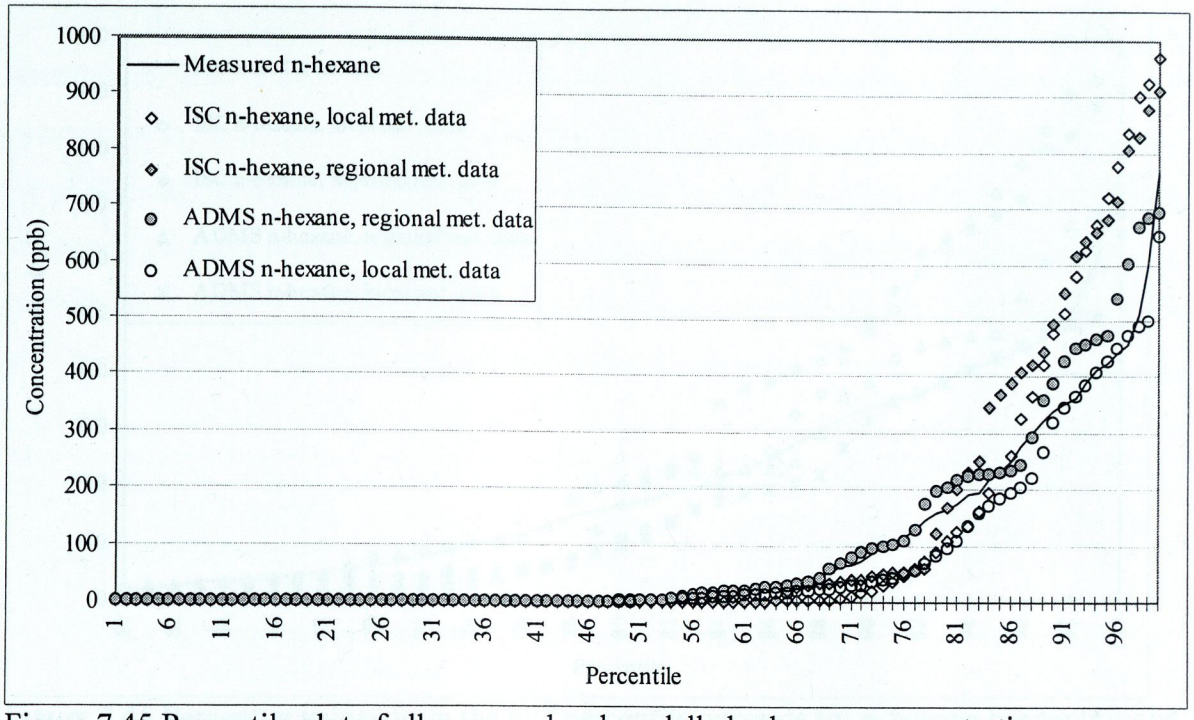


Figure 7.45 Percentile plot of all measured and modelled n-hexane concentrations

The percentile plot from the 60th percentile onwards is shown more clearly in Figure 7.46. The better performance of the ADMS model over this region is clear. It is important to remember that many of the latest air quality regulations specified under the air quality framework directive (CEC, 1996) define limit values which are not to be exceeded more than a specified number of times each year. For example, the 1-hour limit for SO_2 is 350 $\mu g/m^3$ which is not to be exceeded more than 24 times in one year. The use of models to predict possible exceedances is commonplace, and based on the above percentile analysis, the ADMS model would appear to be the more accurate, with ISC tending to overestimate the number of elevated concentrations. Other studies have also shown that the ISC model tends to overpredict the measured pollutant concentration (Kretzschmar and Cosemans, 1996).

Another means of graphically displaying the relative percentile values is to use a scatter plot of the measured and modelled percentile data, as shown for n-hexane in Figure 7.47. At lower concentrations the ADMS model, using regional meteorological data, provides the best agreement with the measured percentiles. However, from about 300 ppb onwards, the best agreement is shown for ADMS using local meteorological data, with other model results tending to overpredict the measured percentile values, particularly ISC, which overpredicts by 400 ppb on some occasions. Such plots provide a clear indication of the relative performance of the models.

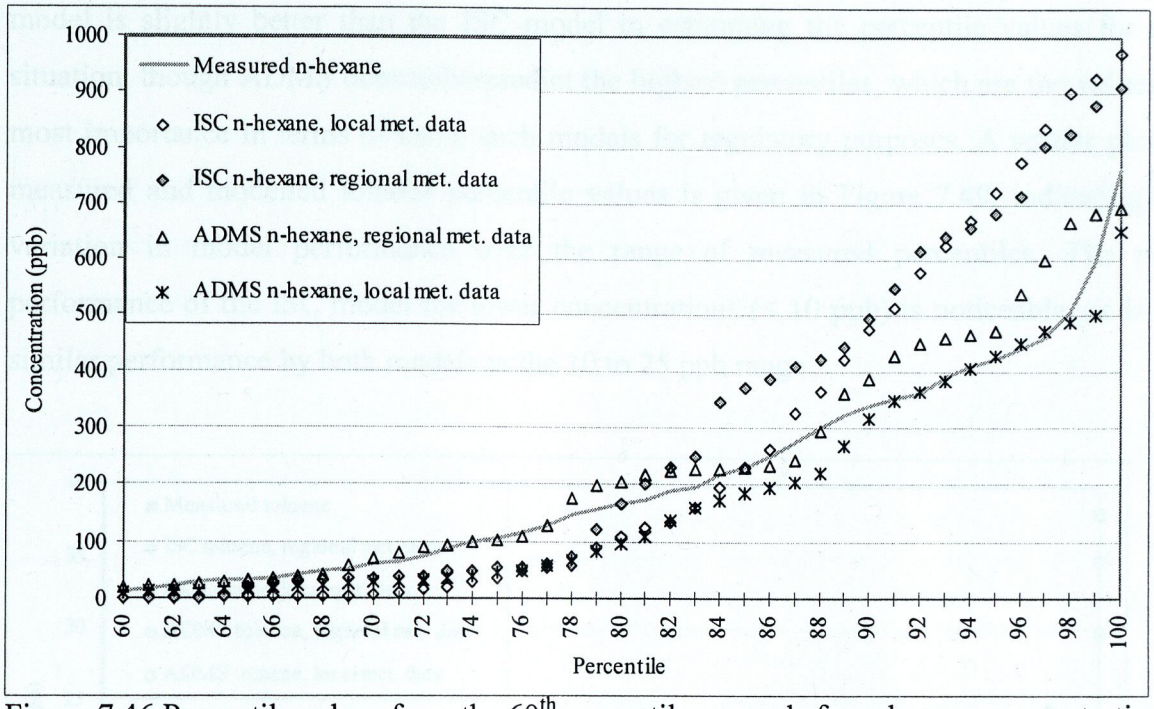


Figure 7.46 Percentile values from the 60th percentile onwards for n-hexane concentrations

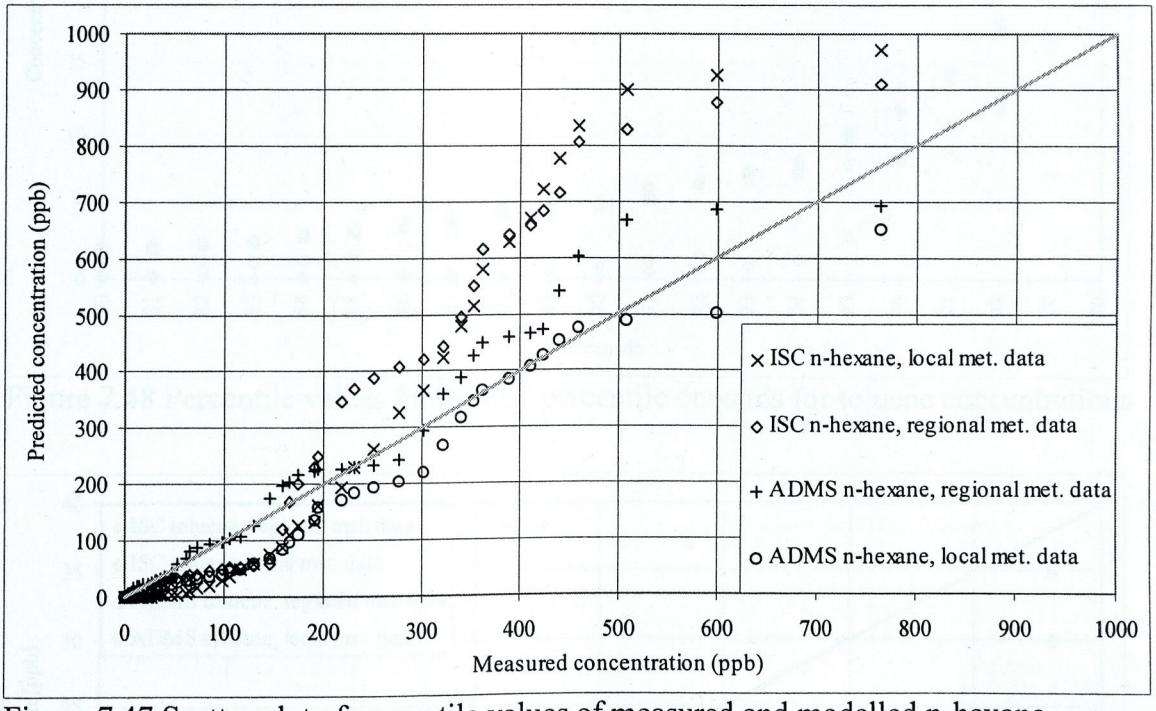


Figure 7.47 Scatter plot of percentile values of measured and modelled n-hexane

The percentile plot for toluene is presented in Figure 7.48, for percentiles above the 80th percentile, as all percentile values prior to this are close to zero. From the 80th to the 95th percentile good agreement is seen between the ADMS percentiles and the measured percentiles, while the ISC model underpredicts the measured concentrations by up to 10 ppb. From the 95th percentile onwards, the ISC model percentile values are in good agreement with the measured values, while the ADMS model slightly underpredicts the measured percentiles, though agreement is still good. Again, the performance of the ADMS

model is slightly better than the ISC model in estimating the percentile values for this situation, though ADMS does underpredict the highest percentiles, which are the values of most importance in terms of using such models for regulatory purposes. A scatter plot of measured and modelled toluene percentile values is given in Figure 7.49, indicating the variation in model performance over the range of measured percentiles. The poor performance of the ISC model for lower concentrations (< 10 ppb) is noticeable, as is the similar performance by both models in the 10 to 25 ppb range.

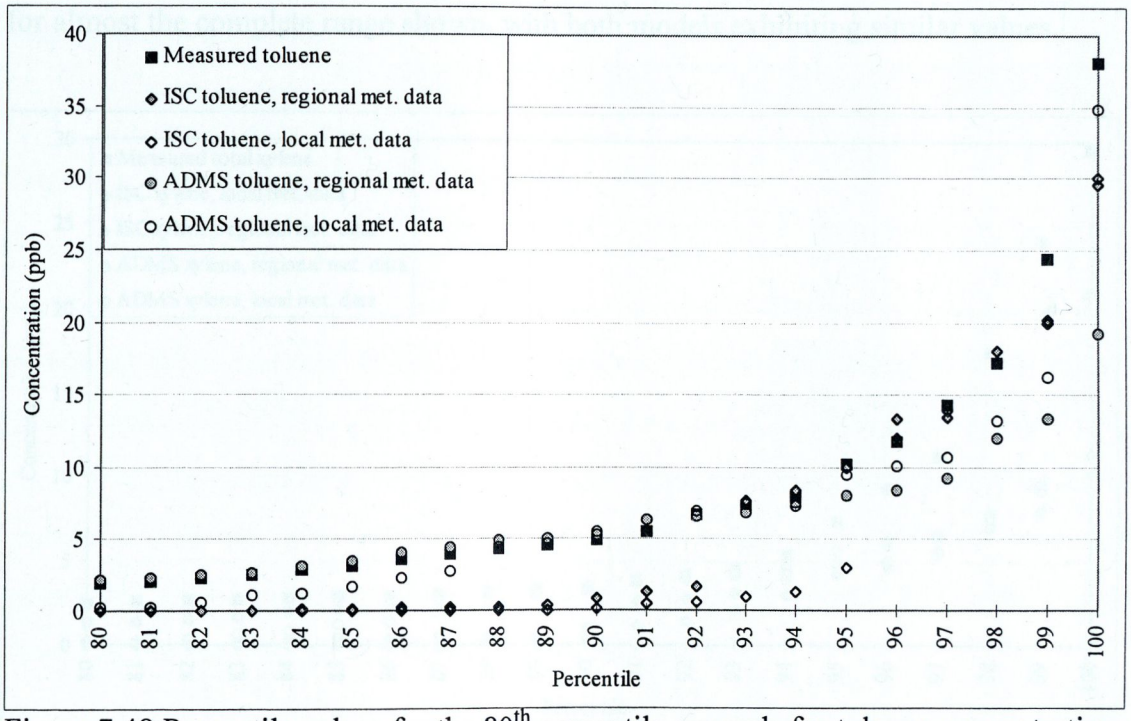


Figure 7.48 Percentile values for the 80th percentile onwards for toluene concentrations

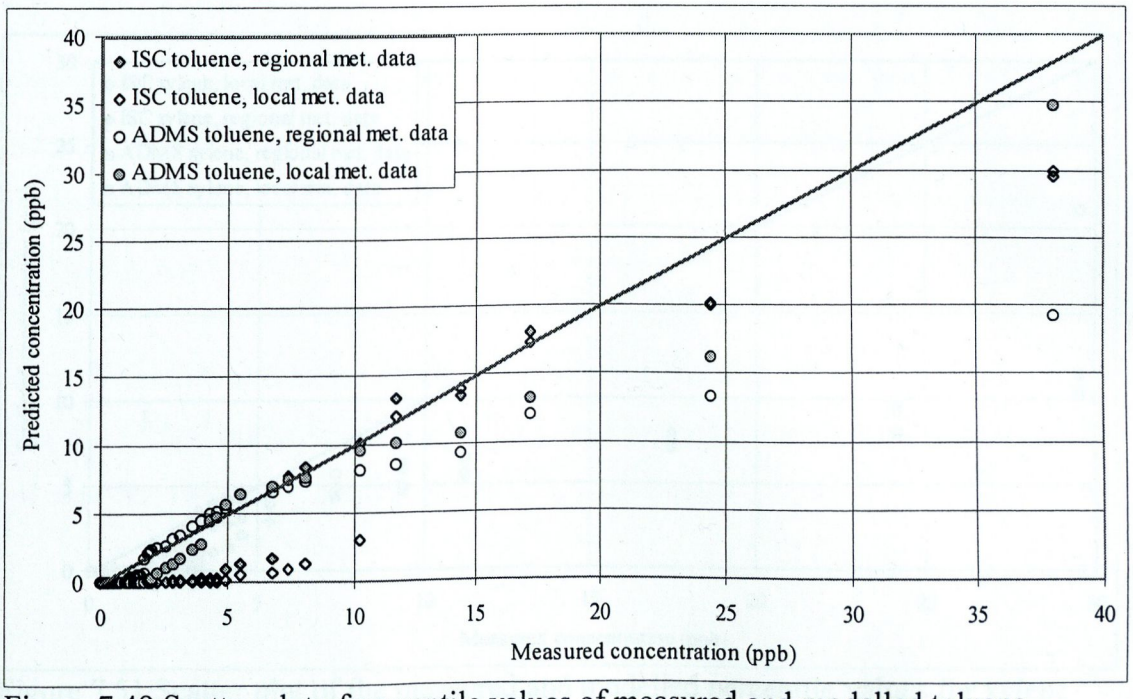


Figure 7.49 Scatter plot of percentile values of measured and modelled toluene

The percentile plots for measured and modelled xylene concentrations are presented in Figure 7.50, for the 80th percentile onwards. The percentile values for the measured concentrations are larger than the model percentile values on all occasions, again suggesting underestimation of the actual emissions from Taconic. ADMS results exhibit reasonable agreement with the measured data between the 80th and 95th percentiles, however, agreement is poor for the remaining values. Both models perform similarly from the 95th percentile onwards. A scatter plot of the measured and modelled percentile values is given in Figure 7.51. Agreement between the measured and modelled percentiles is poor for almost the complete range shown, with both models exhibiting similar values.

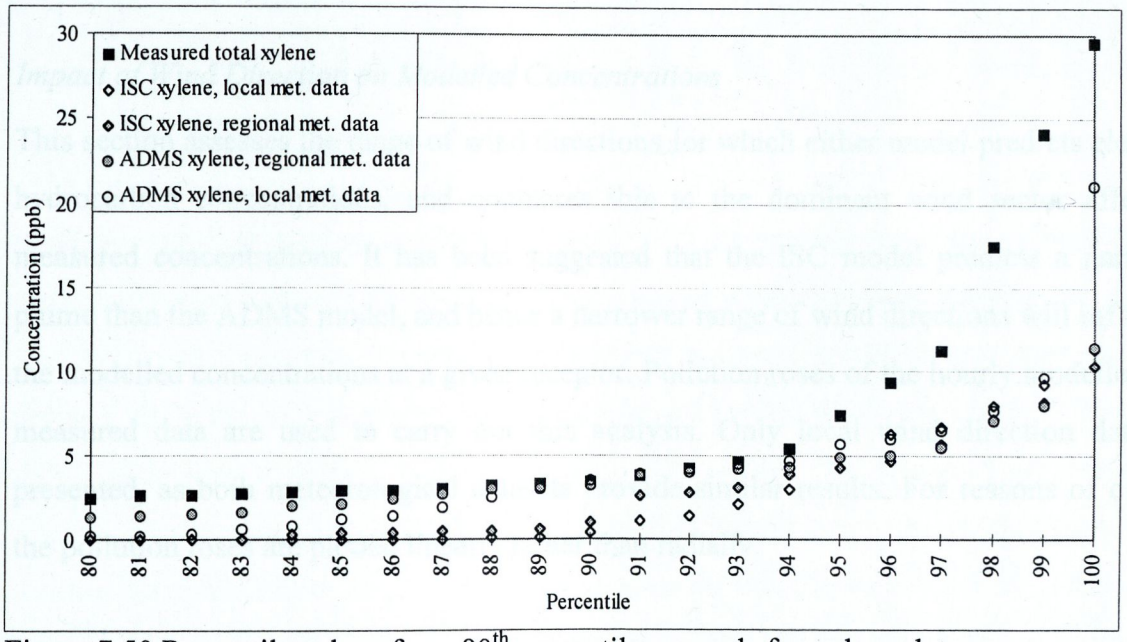


Figure 7.50 Percentile values from 80th percentile onwards for xylene data

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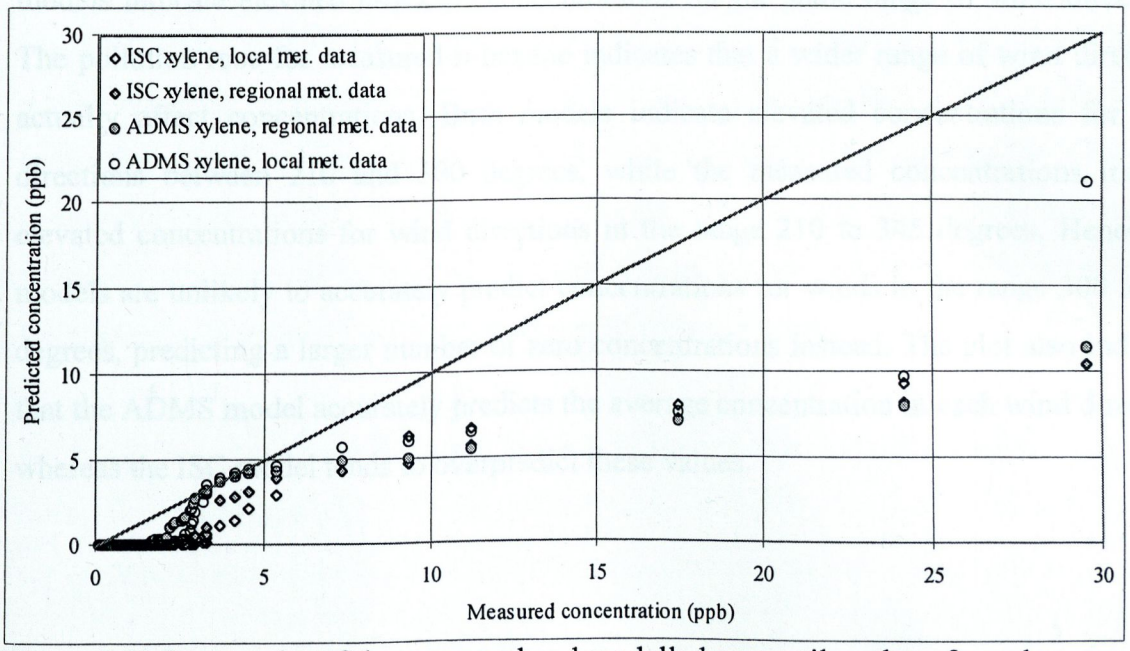

Figure 7.51 Scatter plot of the measured and modelled percentile values for xylene

The above percentile analyses indicate good performance of the models for n-hexane and toluene and poorer performance for xylene, though emissions are from the same location as toluene. This indicates underestimation of xylene emissions from Taconic. As mentioned previously, this method of model comparison is particularly valid if the models are intended to be used for regulatory purposes, in which the number of likely exceedances of a particular air quality limit must be estimated. Moreover, in the UK, limit values are sometimes specified in terms of percentiles. For PM_{10}, for example, the objective for 2005 is a 24 hour running average concentration of 50 $\mu g/m^3$, measured as a 99th percentile (Carruthers *et al.,* 1998).

Impact of Wind Direction on Modelled Concentrations

This section assesses the range of wind directions for which either model predicts elevated hydrocarbon concentrations, and compares this to the dominant wind sector affecting measured concentrations. It has been suggested that the ISC model predicts a narrower plume than the ADMS model, and hence a narrower range of wind directions will influence the modelled concentrations at a given receptor. Pollution roses of the hourly modelled and measured data are used to carry out this analysis. Only local wind direction data are presented, as both meteorological datasets provide similar results. For reasons of clarity, the pollution roses are plotted linearly rather than radially.

The n-hexane pollution rose for each 15 degree wind sector is given in Figure 7.52. Both models indicate elevated n-hexane concentrations for the same range of wind directions. The pollution rose for measured n-hexane indicates that a wider range of wind directions actually affect concentrations. Both models indicate elevated concentrations for wind directions between 210 and 300 degrees, while the measured concentrations indicate elevated concentrations for wind directions in the range 210 to 345 degrees. Hence, the models are unlikely to accurately predict concentrations for winds in the range 300 to 345 degrees, predicting a larger number of zero concentrations instead. The plot also indicates that the ADMS model accurately predicts the average concentration in each wind direction, whereas the ISC model tends to overpredict these values.

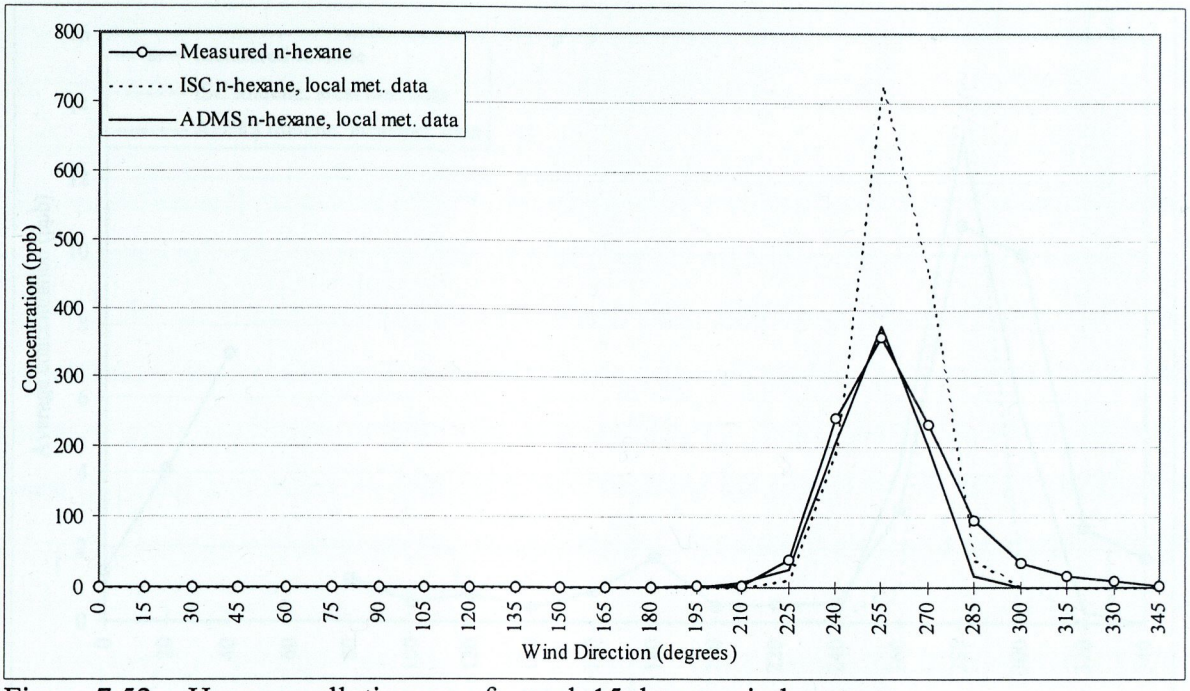

Figure 7.52 n-Hexane pollution rose for each 15 degree wind sector

A similar plot for toluene is given in Figure 7.53. In this situation, the ADMS model predicts elevated concentrations over a wider range of wind directions than the ISC model. The ISC model predicts elevated concentrations between approximately 240 and 320 degrees, while the ADMS model predicts elevated concentrations in the 220 to 340 degrees sector, estimating a slightly wider plume than ISC. Again, the measured concentrations cover a greater range of wind directions, which is partly due to emissions from other sources. Emissions from other sources can be seen for wind sectors which are outside the influence of emissions from Taconic, but which still exhibit elevated concentrations. Taking these values as a baseline concentration, the impact of Taconic can be estimated to occur between 220 and 340 degrees, or approximately the same as that for the ADMS model. However, agreement with the wind sector of influence for the ISC model is also good. The ADMS model exhibits a slightly higher average concentration for most wind sectors compared to ISC, however, both models provide good estimates of the average measured concentration for each wind sector, except between 300 and 340 degrees, where the models underestimate the average measured concentrations.

As xylene is emitted from the same location as toluene (i.e. Taconic), the impact of wind direction on measured and modelled concentrations is identical to that for toluene, however the models underestimate the average xylene concentration for each wind sector.

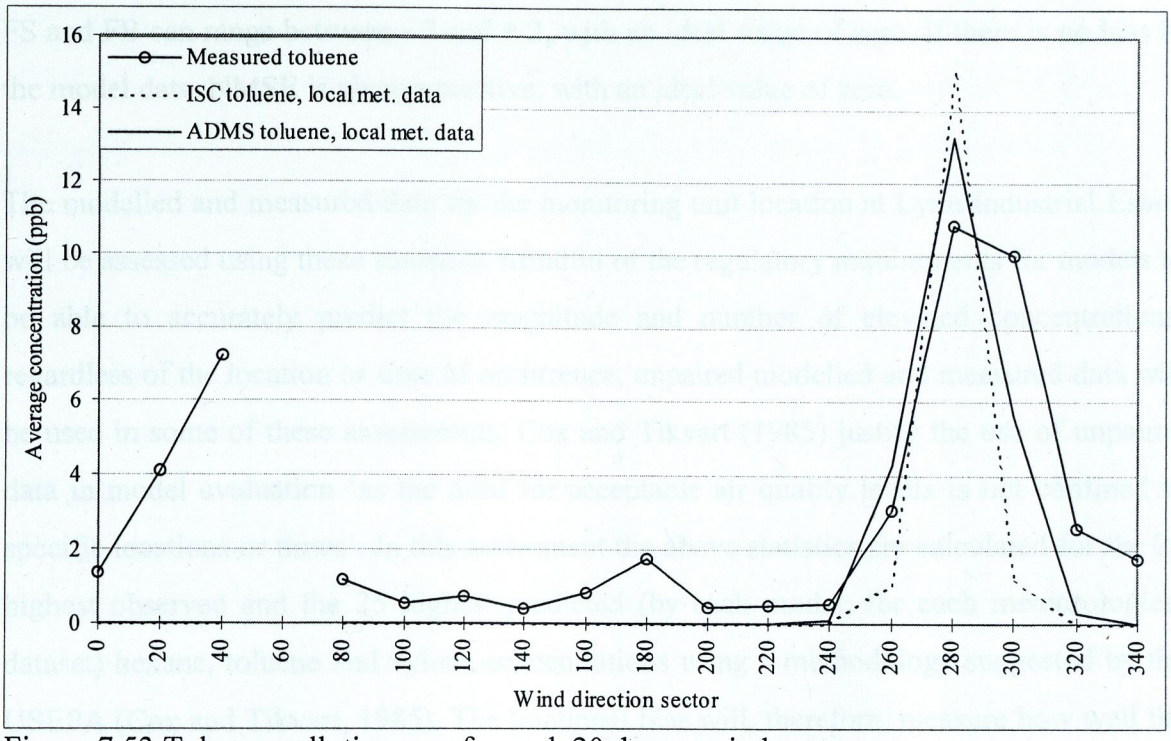

Figure 7.53 Toluene pollution rose for each 20 degree wind sector

Fractional Statistics of Modelled Data

A number of statistical methods are regularly used for the assessment of model performance and model comparison. The parameters which are most often used in model evaluations are the Fractional Bias (FB), the Fractional Standard Deviation (FS) and the Normalised Mean Square Error (NMSE) (Cox and Tikvart, 1985; Hanna, 1989; Cox and Tikvart, 1990; Thrall, 1992; Riswadkar and Kumar, 1994). These parameters are calculated as follows:

$$FB = 2*\frac{C_o - C_p}{C_o + C_p} \qquad 7.2$$

$$FS = 2*\frac{S_o - S_p}{S_o + S_p} \qquad 7.3$$

$$NMSE = \frac{(C_p - C_o)^2}{C_p C_o} \qquad 7.4$$

C_o, C_p are the observed and predicted mean pollutant concentrations, respectively

S_o, S_p are the standard deviations of the observed and predicted datasets, respectively

FS and FB can range between - 2 and + 2, with an ideal value of zero, if there is no bias in the model data. NMSE is always positive, with an ideal value of zero.

The modelled and measured data for the monitoring unit location at Lynn Industrial Estate will be assessed using these statistics. Mindful of the regulatory requirements for models to be able to accurately predict the magnitude and number of elevated concentrations, regardless of the location or time of occurrence, unpaired modelled and measured data will be used in some of these assessments. Cox and Tikvart (1985) justify the use of unpaired data in model evaluation 'as the need for acceptable air quality levels is not confined to specific locations or times'. In this assessment the above statistics are calculated for the 25 highest observed and the 25 highest predicted (by each model, for each meteorological dataset) hexane, toluene and xylene concentrations using a methodology suggested by the USEPA (Cox and Tikvart, 1985). The fractional bias will, therefore, measure how well the models estimate the highest observed concentrations. The fractional standard deviation measures how well the model results reflect the spread of the observed concentrations. The normalised mean square error is another measure of the model performance which assesses the scatter between the modelled and measured data, giving an overall assessment of the relative model performance for the given dataset. The values of each of these parameters for the above dataset are given in Table 7.18. The ideal value for these parameters is zero. The fractional bias and standard deviation can be presented graphically giving a useful indication of the relative performance of each model. The FB / FS plot for modelled n-hexane is given in Figure 7.54.

Table 7.18 Statistical parameters for evaluation

	Fractional bias	Fractional standard deviation	Normalised mean square error
ISC n-hexane, local met. data	-0.48	0.64	0.25
ISC n-hexane, regional met. data	-0.43	0.76	0.20
ADMS n-hexane, local met. data	0.08	0.66	0.02
ADMS n-hexane, regional met. data	-0.17	0.74	0.04
ISC toluene, local met. data	0.29	-0.09	0.16
ISC toluene, regional met. data	0.09	0.15	0.04
ADMS toluene, local met. data	0.19	0.25	0.07
ADMS toluene, regional met. data	0.38	0.86	0.31
ISC xylene, local met. data	0.68	0.90	0.91
ISC xylene, regional met. data	0.71	1.09	1.07
ADMS xylene, local met. data	0.49	0.73	0.55
ADMS xylene, regional met. data	0.68	1.25	1.08

In Figure 7.54, the scatter plot of FB and FS for each model and meteorological dataset reveals the relative performance of each model in predicting the highest 25 n-hexane concentrations. The closer the model is to the origin, the better its performance. Positive values indicate underprediction, implying that for all model analyses carried out, both models tend to underpredict the scatter in the observed highest concentrations. In terms of the fractional bias, three of the model analyses indicate negative values, implying overprediction of the highest measured concentrations, while ADMS using local meteorological data predicts the average concentration well. A value of FB or FS between -0.67 and + 0.67 indicates an accuracy of prediction to within a factor of two; such lines are included in the FB / FS plots. Both models, using both meteorological datasets are within or very close to FB and FS values of ± 0.67, indicating satisfactory model performance. In this regard the ADMS model performs better than the ISC model. Use of local meteorological data in the models leads to slightly improved performance, particularly for the ADMS model.

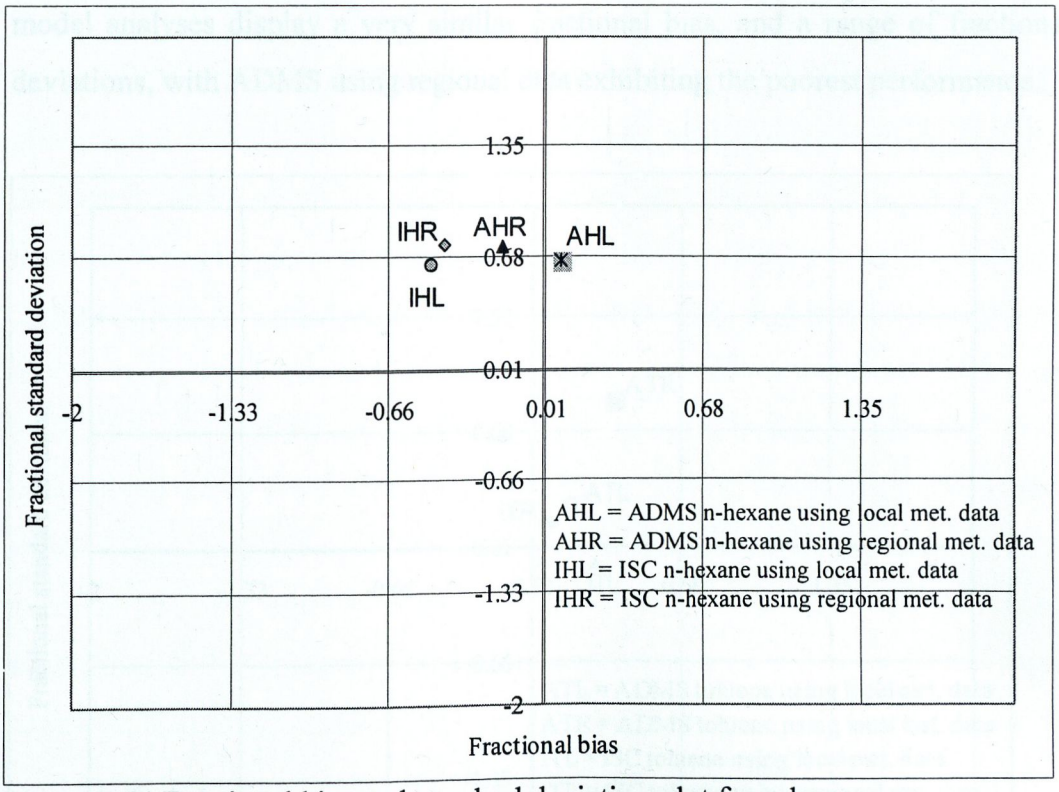

Figure 7.54 Fractional bias and standard deviation plot for n-hexane

The FB / FS scatter plot for toluene is given in Figure 7.55. Very good performance is exhibited by all model analyses (easily within a factor of two accuracy), with the exception of ADMS using regional meteorological data, which underpredicts the fractional standard deviation by over a factor of two, though still performs well in terms of the prediction of

the average concentrations. All other analyses indicate excellent performance in terms of the prediction of the highest concentrations, and in the scatter of these concentrations. The best performance is exhibited by the ADMS and ISC models, using local and regional meteorological data, respectively. ISC using local meteorological data underpredicts the average concentration (as do all the analyses, to a greater or lesser extent), though the performance of the model is still good. Earlier analyses of measured and modelled toluene concentrations indicated poor performance of the models at lower concentrations, however, for unpaired data, the model predicts elevated toluene concentrations well, as indicated by this analysis, and by the percentile analysis in the previous section.

The FB / FS plot for xylene is shown in Figure 7.56. All model results are distant from the origin indicating poor model performance, with all model analyses underestimating both the average concentration and the scatter. The best performing model is ADMS using local meteorological data, which displays an accuracy for the scatter of just over a factor of two, with improved performance in prediction of the average concentration. The other three model analyses display a very similar fractional bias, and a range of fractional standard deviations, with ADMS using regional data exhibiting the poorest performance.

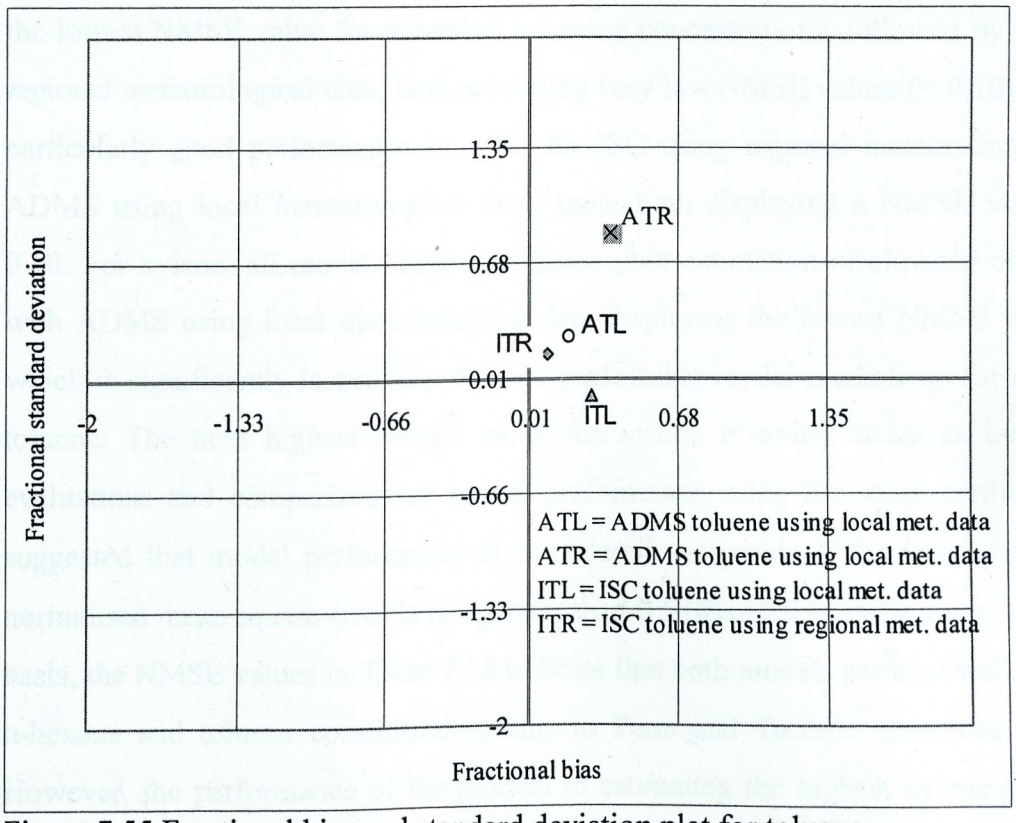

Figure 7.55 Fractional bias and standard deviation plot for toluene

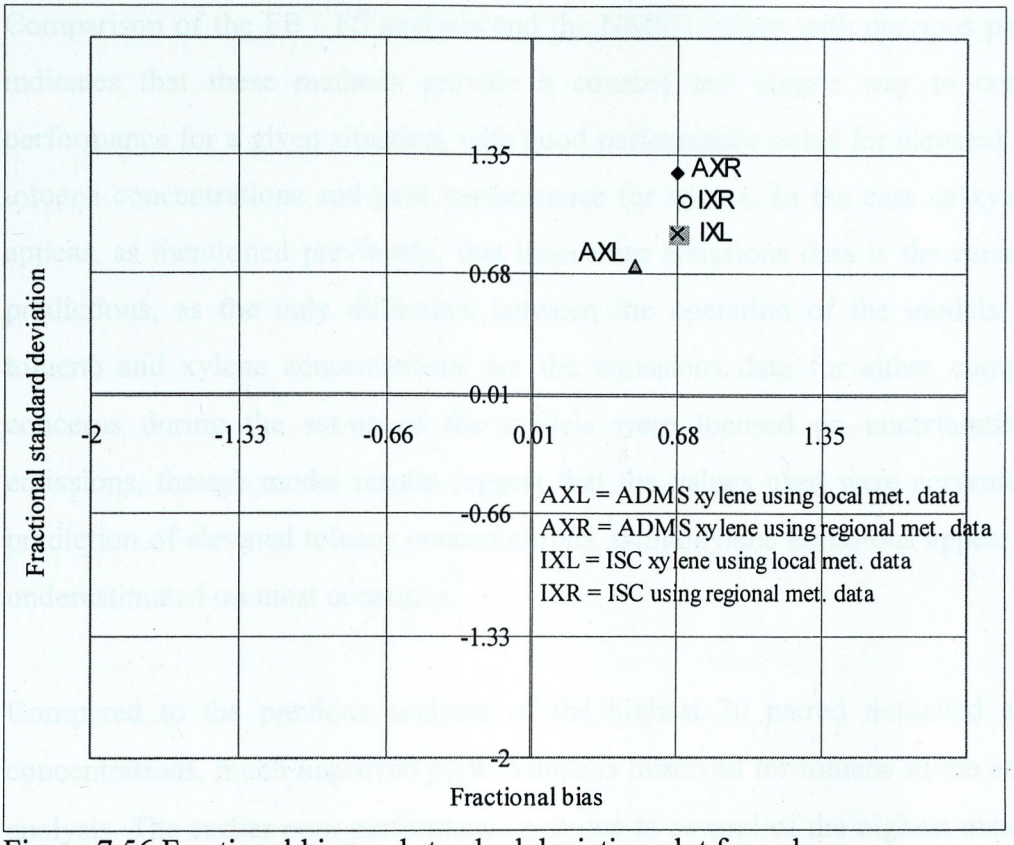

Figure 7.56 Fractional bias and standard deviation plot for xylene

The normalised mean square error values, given in Table 7.18, agree with the above observations on the FB / FS scatter plots. ADMS, using local meteorological data, exhibits the lowest NMSE value for modelled n-hexane concentrations, followed by ADMS using regional meteorological data, both exhibiting very low NMSE values (< 0.10). For toluene, particularly good performance is noted for ISC using regional meteorological data and ADMS using local meteorological data, again both displaying a NMSE value less than 0.10. For xylene, all model analyses indicate poor estimation of elevated concentrations, with ADMS using local meteorological data displaying the lowest NMSE value of 0.55, which is significantly larger than the best performing model predictions for n-hexane and toluene. The next highest NMSE value for xylene is nearly twice as large. Previous evaluations and comparisons of model performance using the same methodology have suggested that model performance is considered acceptable if the fractional bias or the normalised mean square error is not greater than 0.5 (Riswadkar and Kumar, 1994). On this basis, the NMSE values in Table 7.18 indicate that both models perform well in estimating n-hexane and toluene concentrations due to Penn and Taconic emissions, respectively. However, the performance of the models in estimating the highest xylene concentrations was unacceptable, though the NMSE value for ADMS using local meteorological data is close to 0.5.

Comparison of the FB / FS analysis and the NMSE values with previous percentile plots indicates that these methods provide a concise and simple way to compare model performance for a given situation, with good performance noted for elevated n-hexane and toluene concentrations and poor performance for xylene. In the case of xylene, it would appear, as mentioned previously, that inaccurate emissions data is the cause of the poor predictions, as the only difference between the operation of the models in predicting toluene and xylene concentrations are the emissions data for either compound. Initial concerns during the set-up of the models were focused on uncertainties in toluene emissions, though model results suggest that the values used were accurate, at least for prediction of elevated toluene concentrations, while xylene emissions appear to have been underestimated on most occasions.

Compared to the previous analyses of the highest 20 paired modelled and measured concentrations, much improved performance is observed for toluene in the above unpaired analysis. The earlier poor performance was due to several of the highest measured toluene concentrations being associated with wind directions outside the influence of Taconic emissions, resulting in zero model concentrations, while the above unpaired analysis allowed model results for winds from the direction of Taconic to be used in all cases, permitting more accurate assessment of the models ability to predict ambient concentrations due to emissions from Taconic.

Impact of Atmospheric Stability and Windspeed on Model Performance

It has been observed that model performance can vary significantly depending on the prevailing atmospheric stability and windspeed (Riswadkar and Kumar, 1994). It is, therefore, of particular interest to assess the relative performance of the models under different meteorological conditions, especially as the performance of the ADMS model under convective conditions has been modified to provide improved performance compared to traditional Gaussian models such as ISC (see Section 6.7.4 for further details).

The performance of each of the models in predicting elevated concentrations under unstable (stability classes A, B and C), neutral (class D) and stable atmospheric conditions (classes E and F) is assessed using the average measured and modelled concentrations and also the FB, FS and NMSE statistics, for the complete working hours dataset for Taconic

and Penn. The performance of each of the models for low and high windspeed is also assessed. The analysis is presented for n-hexane and toluene only, as the results for xylene are similar to those for toluene. Unlike the previous section, all analyses are carried out on paired data (measured and modelled results at the monitoring unit paired in time).

Measured and modelled n-hexane concentration results during unstable, neutral and stable conditions are presented in Table 7.19. For unstable conditions, ISC using local meteorological data predicts the measured concentration best, though ADMS also performs well under these atmospheric conditions. The NMSE values indicate the same findings with ISC and ADMS, using local meteorological data, both indicating a similar NMSE.

For neutral atmospheric conditions (which are dominant during this monitoring period), the ADMS predictions of the average concentration are closer to the measured value, with ISC significantly overpredicting the average measured concentration. The FS and FB values also indicate that the ADMS analyses provide the best results under these conditions, however, the ISC results are acceptable in this situation with FB and FS indicating accuracy within a factor of two of the measured concentrations.

The ISC model performs very poorly in stable atmospheric conditions, giving a very large NMSE. The ISC predicted average concentration for this period is very close to zero, compared to the measured concentration of 29.44 ppb. ISC predicts zero concentrations for the majority of hours during stability classes E and F. The ADMS performance under these conditions, particularly when regional meteorological data are used, is better than that of ISC. The NMSE values are an order of magnitude lower than those calculated for ISC n-hexane concentrations. As would be expected under stable conditions, windspeeds were often low. Under very low windspeed conditions, ADMS does not provide a concentration estimate, and these values were assumed to be zero in this analysis. This reduced the accuracy of the modelled average concentration, particularly for local meteorological data, where very low windspeeds were measured under stable conditions. The higher regional windspeed measurements (see Figure 6.13) resulted in less non-prediction hours and hence, improved agreement with the measured results, with FB and FS values very close to the ideal value of zero. The NMSE for each model analysis reflects the number of zero concentration predictions, which is highest for ISC, reasonably low for ADMS using local meteorological data, and very low for ADMS using regional meteorological data.

Table 7.19 Analysis of model performance for varying atmospheric stability, n-hexane

	Average	FB	FS	NMSE
Analysis for unstable conditions (measured average concentration = 50.82 ppb)				
ISC n-hexane, local met. data	48.47	0.05	-0.12	1.66
ISC n-hexane, regional met. data	66.31	-0.26	-0.19	4.67
ADMS n-hexane, local met. data	42.69	0.09	0.26	1.73
ADMS n-hexane, regional met. data	43.35	0.12	0.39	3.75
Analysis for neutral conditions (measured average concentration = 85.05 ppb)				
ISC n-hexane, local met. data	115.14	-0.30	-0.50	2.69
ISC n-hexane, regional met. data	124.35	-0.38	-0.49	4.26
ADMS n-hexane, local met. data	73.06	0.15	0.02	1.75
ADMS n-hexane, regional met. data	95.19	-0.11	-0.16	3.61
Analysis for stable conditions (measured average concentration = 29.44 ppb)				
ISC n-hexane, local met. data	0.32	1.96	1.94	927.63
ISC n-hexane, regional met. data	0.35	1.95	1.94	830.47
ADMS n-hexane, local met. data	8.50	1.10	0.72	27.95
ADMS n-hexane, regional met. data	24.95	0.16	-0.14	13.31

If the occasions mentioned above, where the ADMS model does not provide a concentration estimate due to low local windspeed, are ignored in the assessment of the ADMS model performance under stable conditions then FB, FS and NMSE improve slightly to 0.99, 0.70 and 12.69, respectively, for ADMS using local meteorological data. The average measured n-hexane concentration for this dataset is 63.7 ppb, compared to an ADMS predicted concentration of 21.4 ppb. The most significant improvement is for the NMSE, which reduces to half its value for ADMS predicted n-hexane under stable conditions (using local meteorological data) in Table 7.19. This is because the large number of zero concentrations used in calculating the NMSE presented in Table 7.19 has a more significant effect on the NMSE value than on FB or FS values. These results suggest that, in this analysis, ADMS performs similarly whether model predicted concentrations for very low windspeed hours are assumed to be zero or whether they are removed altogether.

Assessing the performance of the models separately for each stability class indicates that ISC performs best in unstable conditions, and also performs well under neutral conditions. However, in stable conditions ISC performs very poorly, with no agreement between measured and modelled data. This analysis agrees with previous evaluation studies of ISC, indicating best performance for unstable conditions followed by neutral conditions, with poor performance under stable conditions (Riswadkar and Kumar, 1994). ADMS performs

best in neutral conditions, and is also effective under unstable conditions. In this situation ADMS also performs well in stable conditions.

The results of the analysis of the toluene measured and modelled concentrations during unstable, neutral and stable conditions are presented in Table 7.20. In stark contrast to the n-hexane results above, the ISC model performs very poorly under unstable conditions, with FB and FS values at the upper limit of two. In fact, ISC does not predict any concentrations above zero during this period. The ADMS model also performs poorly in this situation, significantly underestimating the average concentration, though the FS, FB and NMSE values indicate better performance than ISC. Low toluene concentrations are measured for all hours exhibiting unstable conditions. Hence, the model performance is poor, as these measured concentrations are mainly due to sources other than Taconic.

Under neutral conditions both models perform well, with low FB and FS values for most of the model analyses. The best performance is exhibited by the models using regional meteorological data, with FB values below the suggested limit of 0.50. ISC exhibits an FS value close to zero, indicating a good representation of the scatter in the measured data. The ISC model using local meteorological data predicts the measured concentrations least well, with the accuracy of the prediction of the average concentrations being greater than a factor of two (i.e. an FB value > 0.67).

For stable conditions, the ISC model again performs poorly, with a predicted average concentration at or close to zero, compared to the measured concentration of 5.05 ppb. The ADMS model performs better than ISC under stable conditions, though the estimated average concentration for stable conditions is still less than half of the measured concentration. ADMS performs marginally better with local meteorological data than with regional meteorological data, though there is little difference between the two. Again, the low windspeeds measured during stable atmospheric conditions resulted in ADMS indicating that it could not predict concentrations for certain hours, due to calm conditions making the measured wind directions unreliable. The predicted concentrations for these hours were assumed to be zero. As with the n-hexane data, this assumption made little difference to the results, which were also similar if these hours were removed altogether. Despite this, the performance is much better than ISC, as indicated by a NMSE which is, at best, an order of magnitude greater.

Table 7.20 Analysis of model performance for varying atmospheric stability, toluene

	Average	FB	FS	NMSE
Analysis for unstable conditions (measured average concentration = 1.64 ppb)				
ISC toluene, local met. data	0.00	2.00	2.00	5375.81
ISC toluene, regional met. data	0.00	2.00	2.00	25091.09
ADMS toluene, local met. data	0.09	1.78	1.38	44.50
ADMS toluene, regional met. data	0.20	1.57	0.71	23.86
Analysis for neutral conditions (measured average concentration = 2.25 ppb)				
ISC toluene, local met. data	1.01	0.76	0.15	11.61
ISC toluene, regional met. data	1.51	0.39	-0.09	12.34
ADMS toluene, local met. data	1.35	0.50	0.23	8.68
ADMS toluene, regional met. data	1.62	0.33	0.32	8.52
Analysis for stable conditions (measured average concentration = 5.05 ppb)				
ISC toluene, local met. data	0.00	2.00	2.00	∞
ISC toluene, regional met. data	0.02	1.98	1.94	555.12
ADMS toluene, local met. data	2.15	0.80	-0.06	5.12
ADMS toluene, regional met. data	1.63	1.02	0.18	5.38

In this situation, the ISC model performs best under neutral conditions with poor performance for stable and unstable conditions. However, the large number of low measured concentrations during unstable conditions results in poor performance for both models, as the majority of the low measured concentrations are likely to be due to emissions from other sources, rather than from Taconic. The results of the n-hexane analysis are, therefore, likely to be more representative of the general behaviour of the ISC model under varying atmospheric conditions. For toluene, ADMS performs best under neutral conditions, with good performance also exhibited for stable conditions. ADMS performs poorly under unstable conditions in this situation, for the reasons outlined above.

To investigate the behaviour of the models under different windspeeds, a similar analysis to that detailed above was carried out for low (1 - 3 m/s) and high (> 3 m/s) windspeed situations. Roughly half of all hourly measured windspeed values fall within the low windspeed category, while the remainder are categorised as high windspeeds. The results for n-hexane are presented in Table 7.21. Only model results using local meteorological data are included as the measured and modelled data were split into low and high windspeed categories using local windspeed data. For the low windspeed situation, both models perform reasonably well, though the ISC model estimates an average concentration closer to the measured value. The FB and FS values indicate that ISC tends to overpredict

the measured concentrations, while ADMS tends to underpredict. The fractional bias for ADMS is slightly outside the recommended limit of 0.50. The NMSE value suggest that both models perform equally well, however, the FB and FS parameters suggest that ISC performs better for low windspeeds.

For high windspeed situations, both models perform well, with small FB values. The ADMS model performs particularly well, with FB and FS values very close to zero, and a NMSE value half that of ISC. The average concentration estimated by ADMS is very close to the measured concentration, while, as for the low windspeed situation, ISC overestimates the measured concentration, but to a slightly greater extent on this occasion.

Table 7.21 Analysis of model performance for varying windspeed situations, n-hexane

Windspeed	Average	FB	FS	NMSE
Analysis for low windspeed (1 to 3 m/s, average measured concentrations = 75.87 ppb)				
ISC n-hexane, local met. data	88.00	-0.15	-0.41	3.46
ADMS n-hexane, local met. data	43.55	0.54	0.24	3.63
Analysis for high windspeed (> 3 m/s, average measured concentration = 94.05 ppb)				
ISC n-hexane, local met. data	119.37	-0.24	-0.47	2.54
ADMS n-hexane, local met. data	97.38	-0.03	-0.02	1.21

The results for toluene are presented in Table 7.22. In this situation, ISC performs poorly in low windspeed situations, predicting an average concentration which is only 30 percent of the measured value. Although the modelled concentrations would not be expected to agree completely with the measured data, due to contributions from other sources, the ISC average concentration appears very low. The ADMS model performs well, with low FB and FS values, and a NMSE half that of the ISC estimates. For low windspeeds, the ISC model predicts a large number of zero hourly concentrations, compared to the ADMS model.

Table 7.22 Analysis of model performance for varying windspeed situations, toluene

	Average	FB	FS	NMSE
Analysis for low windspeed (1 to 3 m/s, average measured concentration = 2.34 ppb)				
ISC toluene, local met. data	0.78	1.00	0.01	15.30
ADMS toluene, local met. data	1.60	0.37	-0.18	7.62
Analysis for high windspeed (> 3 m/s, average measured concentration = 1.76 ppb)				
ISC toluene, local met. data	1.01	0.54	0.28	10.58
ADMS toluene, local met. data	1.05	0.51	0.65	9.74

For higher windspeeds, both models perform similarly, predicting average concentrations which are reasonably close to the measured concentration. The performance of the ISC model is better with high windspeeds than low windspeeds, while the performance of the ADMS model decreases slightly, though it is still comparable to that of ISC.

The strongest observation from the above analyses of model performance under different weather conditions is the superior performance of the ADMS model under stable atmospheric conditions. The performance of the ISC model under such conditions is particularly poor, with zero concentrations being predicted on the vast majority of occasions. The ADMS performance under stable conditions is not as good as that displayed under unstable and neutral conditions, but this is also due to the low windspeeds encountered during stable conditions, in which situation the ADMS model will not estimate the ambient concentration.

Under neutral conditions (the dominant stability encountered in Ireland) both models perform well, while based on the results of the n-hexane analysis, both models also perform well in unstable conditions, particularly when local meteorological data are used.

Analysis of model performance at low and high windspeeds indicates that both models perform better at higher windspeeds (> 3.0 m/s). Analysis of the n-hexane results suggests that ISC performs best at lower windspeeds, while analysis of the toluene results shows that ADMS performs best at lower windspeeds. This apparent contradiction may be due to different source distances, as Taconic is nearly three times further from the monitoring unit compared to Penn. It is possible that the more complex terrain (building effects) between Taconic and the monitoring unit is modelled more accurately by the ADMS building module compared to ISC, or that the dispersion coefficients used by ADMS are more accurate at this longer distance, resulting in a more accurate description of the plume behaviour, as indicated earlier in this section.

7.7 ANALYSIS OF RESULTS FROM RURAL MONITORING

Hydrocarbon monitoring at Rhode was only carried out for a short period of time before monitoring began at the industrial site in Mullingar. There is some uncertainty regarding

the validity of the results from Rhode, due to equipment problems, however, some brief analysis of the hydrocarbon data from Rhode is carried out in this section.

Measured hydrocarbon concentrations were generally low at the school monitoring site, with many zero readings being recorded. This is reflected in the zero median value for many of the compounds. Little useful analysis can be carried out on these data, other than an examination of the short periods in which non-zero readings occurred. As can be seen from Table 6.15, ethane and isoprene were the only compounds of those measured which exhibited high concentrations during the monitoring period. Higher ethane concentrations may be expected due to agricultural activity, while isoprene is emitted from plants and trees. In Table 7.23, the mean concentrations for the measured hydrocarbons at Ballybryan National School are compared with ambient data for other locations. The high ethane concentration measured is consistent with UK rural ethane concentrations. The n-pentane concentration is high compared to values measured in Dublin and rural UK sites. There is some concern regarding the magnitude of the higher concentrations measured during monitoring at Rhode (see maximum concentrations, Table 6.15) due to malfunctions which were experienced with the zero air generator used during this monitoring period. During monitoring at Mullingar, cylinders of zero air were employed to prevent this problem.

Table 7.23 Ambient hydrocarbon data for various sites (UK data from Appendix B)

Compound	Ballybryan NS	Dublin Period 1	UK rural average	London
Ethane	7.21	4.34	7.45	7.40
Ethylene	2.02	5.10	0.80	10.80
Propane	0.20	2.14	3.43	3.50
Propylene	0.06	1.58	1.37	5.80
Isobutane	0.11	1.57	0.20	6.38
n-Butane	0.07	3.85	0.28	12.13
Acetylene	0.09	2.81	0.30	19.30
Trans-2-butene	0.01	0.21	0.40	2.06
Cis-2-butene	0.02	0.19	< 0.1	0.83
1-Butene	0.12	0.07	< 0.1	0.70
Isopentane	0.21	2.62	not measured	7.45
n-Pentane	1.64	0.90	1.02	2.58
1,3-butadiene	0.17	0.38	not measured	0.80
2-methylpentane	0.19	0.40	< 0.1	0.90
3-methylpentane	0.07	0.37	< 0.1	0.80
Isoprene	18.60	0.13	not measured	0.20

Contamination roses cannot be plotted for the hydrocarbon data due to the limited dataset. Acetylene, which is generally accepted to be an indicator of vehicle emissions, was only identified on a small number of occasions. A sample plot showing an episode of elevated acetylene concentrations is shown in Figure 7.57. The first section of the plot has the highest concentrations and these correspond approximately to wind directions from the 90 to 130 degree sector. However, the measured acetylene concentrations are still relatively low. A plot of the thirty highest ethylene concentrations and corresponding wind directions (Figure 7.58) reveals a significant number of occurrences of high concentrations in the 90 to 130 degree sector, as noted for elevated acetylene concentrations in Figure 7.57. The 90 to 130 degree sector is consistent with emissions from the town of Edenderry located approximately seven kilometres from the monitoring site, in a direction of approximately 113 degrees. As both acetylene and ethylene are significant emissions from vehicles, it is expected that vehicle emissions from the Edenderry direction are responsible for the measured concentrations. A similar plot for 1,3-butadiene (Figure 7.59) shows the highest concentrations for winds from the 220 to 290 degrees sector, which suggests Rhode power station as a possible source (see Figure 6.7), although no other hydrocarbons displayed elevated concentrations for this (or any) particular wind direction.

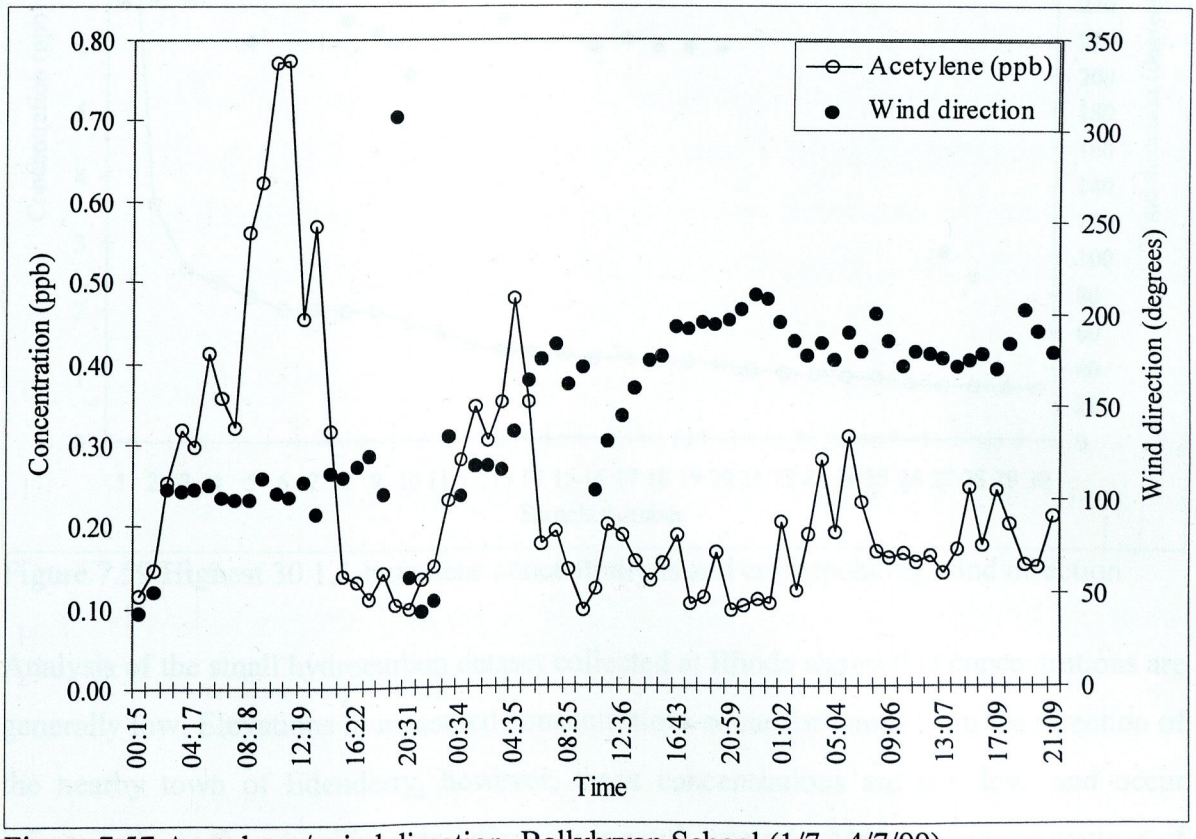

Figure 7.57 Acetylene / wind direction, Ballybryan School (1/7 - 4/7/99)

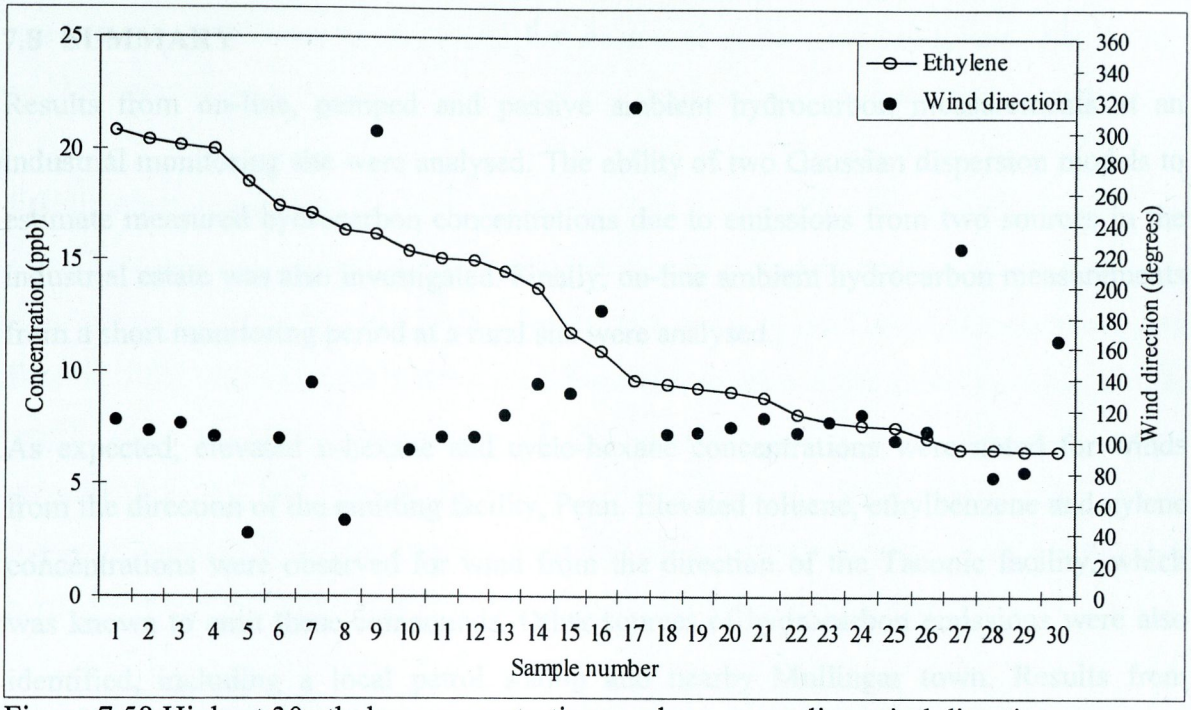

Figure 7.58 Highest 30 ethylene concentrations and corresponding wind direction

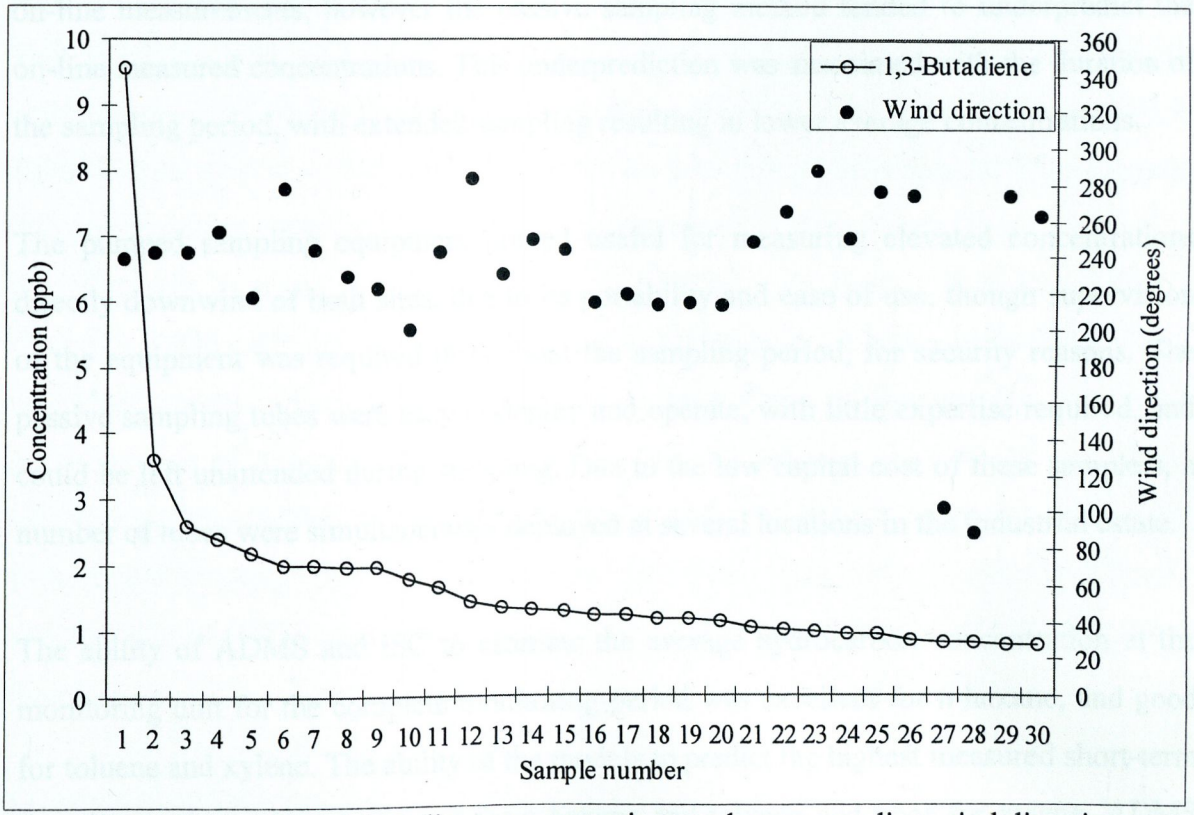

Figure 7.59 Highest 30 1,3-butadiene concentrations and corresponding wind direction

Analysis of the small hydrocarbon dataset collected at Rhode shows that concentrations are generally low. Elevations in measured concentrations occur for winds from the direction of the nearby town of Edenderry, however, these concentrations are still low, and occur infrequently, as the prevailing wind direction is south-westerly. Measured concentrations of ethane and isoprene are high, suggesting an influence from natural sources.

7.8 SUMMARY

Results from on-line, pumped and passive ambient hydrocarbon measurements at an industrial monitoring site were analysed. The ability of two Gaussian dispersion models to estimate measured hydrocarbon concentrations due to emissions from two sources in the industrial estate was also investigated. Finally, on-line ambient hydrocarbon measurements from a short monitoring period at a rural site were analysed.

As expected, elevated n-hexane and cyclo-hexane concentrations were noted for winds from the direction of the emitting facility, Penn. Elevated toluene, ethylbenzene and xylene concentrations were observed for wind from the direction of the Taconic facility, which was known to emit these compounds. Other sources of hydrocarbon emissions were also identified, including a local petrol station and nearby Mullingar town. Results from analyses of pumped samples collected at the monitoring unit were in good agreement with on-line measurements, however the passive sampling method tended to underpredict the on-line measured concentrations. This underprediction was associated with the duration of the sampling period, with extended sampling resulting in lower average concentrations.

The pumped sampling equipment proved useful for measuring elevated concentrations directly downwind of both sites, due to its portability and ease of use, though supervision of the equipment was required throughout the sampling period, for security reasons. The passive sampling tubes were easy to deploy and operate, with little expertise required, and could be left unattended during sampling. Due to the low capital cost of these samplers, a number of tubes were simultaneously deployed at several locations in the industrial estate.

The ability of ADMS and ISC to estimate the average hydrocarbon concentration at the monitoring unit for the complete monitoring period was excellent for n-hexane, and good for toluene and xylene. The ability of the models to predict the highest measured short-term (hourly) concentrations was good for n-hexane and toluene and poor for xylene. ADMS performed better than ISC over the range of measured hourly concentrations. The model results were in good agreement with most of the pumped tube samples taken in the industrial estate, though agreement with passive tube results was poor. Comparison of model and measured results with wind direction data indicated that the measured results exhibit a wider plume than the model results. ISC performs very poorly under stable

atmospheric conditions, while ADMS performs well under such conditions. The ADMS and ISC models perform best in neutral and unstable atmospheric conditions, respectively.

Initial concerns regarding the emissions data used in dispersion modelling of emissions from Taconic were focused on estimating the toluene emissions, due to the variability of these emissions from the plant, while xylene emissions were considered more constant (see Section 6.7.5). However, the toluene emission estimate used in the model produced results which were in good agreement with the measured data, while modelled xylene concentrations suggest that emissions of this compound were underestimated. The models tended to underestimate the highest measured xylene concentrations, while performing particularly well in estimating the highest measured toluene concentrations.

The ISC model performs better than ADMS in estimating n-hexane concentrations at lower windspeeds, though ADMS still performs well, while ADMS performs excellently at higher windspeeds, with good performance from ISC. However, modelling toluene emissions from Taconic indicates poor performance of ISC at low windspeeds compared to ADMS, with similar performance from both models at high windspeeds. This suggests differences in model performance over this longer source - receptor distance.

Overall, ADMS performs consistently better than ISC in predicting average and short-term n-hexane concentrations due to emissions from Penn. However, in predicting concentrations of toluene and xylene, ADMS does not perform consistently better than ISC, as can be seen from several of the analyses in Section 7.6. Comparison of measured and modelled hydrocarbon concentrations indicated that both models performed satisfactorily in most circumstances, though overall, the performance of ADMS was better than ISC.

Monitoring results from the rural monitoring site at Rhode indicate generally low concentrations. High concentrations of ethane and isoprene were noted at this site. High ethane concentrations would be expected in rural farming areas, while isoprene is a known emission from plants and trees. Emissions from the nearby town of Edenderry were observed to have a small impact on the concentrations of vehicle-related hydrocarbons at the monitoring site, when winds were blowing from this direction.

8. CLOSURE

8.1 SUMMARY

Ambient hydrocarbon measurements were carried out at three different sites types: urban roadside, rural and industrial. Hourly on-line measurements were collected at all sites, while pumped and passive tube sampling methods were also employed at the industrial site. A detailed hydrocarbon analysis of typical Irish fuels was also carried out, for comparison with the roadside ambient measurements. Dispersion modelling of emissions was performed for the industrial site using two Gaussian dispersion models. Meteorological data were collected at all sites to assess the influence of these parameters on measured hydrocarbon concentrations.

The measured hydrocarbon concentrations at each of the sites were interpreted using a range of graphical and statistical techniques. The performance of the monitoring equipment and models used was also assessed. A summary based on these analyses is presented below.

- Public concern regarding air quality is increasing, and more information on ambient air quality in our cities is required. The most recent EU 'air quality framework directive' requires that such characterisation of air quality be carried out on a widespread basis.

- Compared to pollutants such as smoke and SO_2, contamination of ambient air due to anthropogenic hydrocarbon emissions has only recently become an area of concern, both as primary pollutants, and in the formation of secondary pollutants. Therefore, few detailed measurements of these compounds have been performed in Ireland.

- The performance of the chromatographic system used in this project, in terms of qualitative and quantitative precision, is excellent for the measured hydrocarbons.

- In Dublin, the average concentrations measured between March and April 1998 were larger than those measured between May and August, due to reduced emissions and improved atmospheric mixing during the summer months (as a result of increased

temperatures), which resulted in lower average concentrations for most compounds, with the exception of isoprene, propylene and 1-butene. The compounds with the highest average concentrations were ethylene, ethane and n-butane with average concentrations of 5.1, 4.3 and 3.85 ppb, respectively, between March and April, and 3.4, 2.7 and 2.4 ppb, respectively, between May and August.

- Comparison of the average measured benzene concentration with existing EU and UK limit values indicated an average concentration above the EU limit value during Period 1. Comparison of 1,3-butadiene concentrations with UK limit values indicated that the average concentration during both periods was less than 50 percent of the limit value. Although the duration and location of monitoring did not meet the specific criteria for comparison with these limit values, monitoring at such a heavily-trafficked location gives an indication of the worst case ambient concentrations which can be expected due to vehicle emissions.

- The average hydrocarbon concentrations measured in Dublin compare well with those measured in other similar locations world-wide, particularly in the UK monitoring network. BTX measurements made by the EPA, at the same monitoring site, indicated similar results for toluene and o-xylene, though benzene concentrations were lower.

- Assessment of the frequency distribution which best fits the urban hydrocarbon measurements indicated that both the lognormal and gamma distributions fit the data successfully. The distributions are complementary, in that any occasions where the data are not lognormally distributed they tend towards the gamma distribution, and vice versa.

- A comparison of meteorological data collected on site and at Dublin airport indicated good agreement for temperature and windspeed. There are significant differences between the wind direction measurements, due to the impact of local buildings and other obstacles surrounding the monitoring site.

- The double-peaked diurnal pattern exhibited by the majority of the measured hydrocarbons suggests a common source. This diurnal pattern is similar to that exhibited

by traffic flow, confirming vehicle emissions as the dominant source. The main exceptions to this pattern are ethane and propane, which displayed a relatively constant concentration, with only small increases during the early part of the day.

- The concept of the representative day is a useful method for identifying the actual day which is closest to the average day. However, it is possibly even more useful for identifying days in a given dataset which are furthest from typical behaviour, without having to examine in detail the diurnal plots for each individual day. Unusual days are normally of most interest, in that individual factors affecting measured concentrations can be identified. The representative day methodology, if applied to a number of different compounds, can also be used to assess whether pollutants come from the same source, as they would be expected to share the same representative day, or range of most representative days. For the Dublin hydrocarbon data, most compounds share similar representative days, indicating a common source, the main exceptions being toluene and n-hexane.

- Correlation between the measured hydrocarbon concentrations at the roadside monitoring site is strong, with the exception of ethane and propane which exhibit a significantly weaker correlation with all of the other measured compounds. The correlation analysis for Monitoring Period 2 also indicates weaker correlations for propylene and the methylpentanes, indicating possible alternate sources of these compounds.

- Results from analysis of measured concentrations of ethane and propane indicate that these compounds experience a significant contribution from natural gas leakage. Ethane and propane have been identified as the most abundant hydrocarbon components, after methane, present in natural gas used in Dublin.

- Hydrocarbon concentration and wind direction comparisons indicate that, for local wind direction data, the highest concentrations are measured for winds from the north-west and north (the direction of the city centre and the junction itself, respectively), while for airport wind direction data, the highest concentrations are measured for winds from the south-east (from the direction of Pearse Street Lower), and from the north-west (from the city centre). Most compounds display similar pollution roses. Ethane and propane,

using airport wind direction, display a constant concentration for winds from all directions, supporting previous conclusions that these compounds are related to emissions from an area source, such as natural gas leakage. Toluene also exhibits a slightly different pollution rose to that noted for most hydrocarbons, displaying a large peak for airport wind directions between 300 and 330 degrees. Investigation of this direction identified a printing press in the city centre, with large toluene emissions, as the most likely source of these high concentrations.

- Windspeed was also observed to have a moderate negative impact on measured hydrocarbon concentrations. Although the daily peak hydrocarbon concentration tended to occur in the evening, it was noted that on days where the daily peak occurs in the morning, the morning average windspeed was significantly lower than on days when the peak occurs during the evening.

- During Monitoring Period 1, temperature was observed to have a weak positive correlation with several compounds known to be vehicle evaporative emissions. For Period 2, however, negative correlations are noted for most of the measured compounds. This is likely to be related to reduced vehicle emissions and improved mixing noted during the summer, which are related to ambient temperature increases. Consequently, no impact on evaporative emissions is immediately apparent during this period, as the effects of improved mixing and reduced emissions tend to be greater than any evaporative emissions. However, comparison of individual hydrocarbon : acetylene ratios with temperature revealed evaporative effects for a range of alkenes and alkanes. However, the mass evaporative emissions depend on the mass of these compounds present in the fuel, and most of the alkenes are not major constituents of vehicle fuels.

- Stable atmospheric conditions, which occur at night-time, were seen to have a significant impact on off-peak hydrocarbon concentrations, with average concentrations measured during stable conditions nearly twice those measured during neutral atmospheric conditions.

- Principal component analysis carried out on the roadside hydrocarbon data indicated that vehicle emissions accounted for over 80 percent of the variance in the measured data. Small percentages of variance in the data were also accounted for by natural gas

emissions (ethane and propane), emissions from non-vehicle sources (toluene) and ambient temperature variations.

- Comparison of the hydrocarbon concentrations measured in Dublin with results from exhaust and tunnel studies elsewhere, revealed good agreement between the data, particularly for exhaust studies on non-catalyst vehicles. This suggests that the current ambient hydrocarbon concentrations measured in Dublin are dominated by emissions from non-catalyst vehicles, or vehicles in which the catalysts are not functioning efficiently.

- Analysis of several petrol fuels used in Ireland indicated that most share similar properties and hydrocarbon contents. Comparison of the properties of these 1998 fuels with the most recent fuel specifications, introduced in early 2000, indicates that most fuels were already close to complying with the latest limits values for fuel properties such as vapour pressure and benzene content.

- Comparison of the relative ratios of the ambient measured hydrocarbon species in the fuel and in the ambient air indicated the best correlation for aromatic hydrocarbons. Several of the alkanes measured in the air were not present in the fuel, instead arising as partial oxidation products of the fuel reactions. Removing these compounds from the alkane analysis revealed good correlation for the other alkanes, which are unburned fuel components. Good agreement was noted between the fuel and ambient air alkene content, taking into account that light alkenes are partial oxidation products of heavy alkenes.

- High concentrations of n-hexane, toluene, ethylbenzene and xylene were measured by the on-line hydrocarbon monitoring system at Lynn Industrial Estate, due to emissions of these compounds from the Penn and Taconic facilities. Pumped tube sampling methods also identified elevated concentrations of these compounds, and pumped samples collected at the on-line monitoring unit were in good agreement with the on-line results. Passive tube sampling methods also indicated measurable concentrations of n-hexane, toluene and xylene, though samples collected at the monitoring unit tended to underestimate the concentrations measured by the on-line system.

- The pumped and passive sampling methods proved extremely easy to use and were ideally suited to taking measurements at a range of locations around the industrial estate, which could not have been carried out by the mobile monitoring unit due to issues such as power supply and security. These methods are particularly suited to point source monitoring, where good spatial definition (using passive tube sampling) and equipment portability (pumped sampling unit) are particularly important.

- The on-line hydrocarbon data collected at Lynn Industrial Estate proved difficult to fit to a particular frequency distribution function. At a 95 percent confidence interval, the Kolmogorov-Smirnov test indicated that the data were rarely either lognormally or gamma distributed, which are the distributions most associated with air quality data. Analysis of the results did show, however, that the majority of the measured data tended more towards lognormal behaviour, rather than gamma or normal behaviour.

- Comparison of meteorological data collected on-site, with data from the regional meteorological station, north of Mullingar, indicates excellent agreement between temperature measurements at both sites. The regional windspeed tended to be greater than that measured locally, probably due to local obstructions. Agreement between local and regional wind direction data is good (significantly better than in Dublin), with a slightly larger spread of directions noted for the local data.

- The diurnal pattern of compounds measured at Lynn Industrial Estate varies substantially from day to day, due to variations in wind directions and emissions. For n-hexane, concentrations can range from zero to 700 ppb over the course of a day. It is, therefore, meaningless to calculate an average day from such data.

- The strongest correlation between hourly data measurements was, as expected, for n-hexane and cyclo-hexane. A strong correlation was also found between the xylenes and ethylbenzene. The correlation between toluene and xylene / ethylbenzene, was weak, reflecting the variability of toluene emissions (in both duration and magnitude) from Taconic.

- The pollution roses for n-hexane and cyclo-hexane identified Penn as the only significant source of these compounds. Taconic was confirmed as a significant source of toluene, however, a stronger source was also noted to the north-east of the monitoring unit, suspected to be the local petrol station. This source is also significant for o-xylene, m+p-xylene and ethylbenzene, however, Taconic is the dominant source for these compounds. The highest benzene concentrations were measured during winds from the direction of the industrial estate and from Mullingar town, however, average concentrations are low. For 1,3,5-trimethylbenzene, the highest concentrations are measured for winds from the north-east, suggesting the petrol station as a probable source. The pollution rose for 1,2,4-trimethylbenzene is similar to that noted for ethane in Dublin, with constant concentrations in all directions, indicating an area source, though no definite source was identified.

- Stable atmospheric conditions have a measurable impact on night-time measured hydrocarbon concentrations in Lynn Industrial Estate, with the vast majority of measured night-time peaks being associated with stable atmospheric conditions. However, stable atmospheric conditions occur infrequently.

- Pumped sampling methods proved successful in measuring elevated concentrations of n-hexane, benzene, toluene and xylene, but less successful at measuring lower ambient concentrations. This was partly due to the sensitivity of the analytical method used, though low concentrations were generally also measured by the on-line system when pumped sampling was carried out at the monitoring unit. Good agreement was observed between the on-line n-hexane measurements and pumped samples collected at the monitoring unit, all such samples being collected when winds were blowing from Penn. Pumped sampling carried out downwind of Taconic measured higher average xylene concentrations than were detected by the on-line unit throughout monitoring, as the pumped sampling location was closer to Taconic. Elevated toluene concentrations were also detected at this location.

- Analysis of the passive tubes revealed measurable quantities of n-hexane, toluene, xylene and benzene. Average measured benzene concentrations were low (< 1 ppb), while average measured concentrations of n-hexane, toluene and xylene above 5 ppb were measured at several monitoring locations. Passive sampling carried out at the

monitoring unit indicated concentrations lower than those measured by the on-line equipment. Analysis of all passive tube results showed that the relative concentrations of the measured compounds appeared correct for different sampling locations, though the magnitude of the measured concentrations was lower than expected. This agrees with previous studies using Radiello sampling tubes, which indicated that longer sampling periods could actually result in a lower sample mass being retained on the tubes. This suggests that the sampling duration of two to three weeks employed at Lynn Industrial Estate was too long, resulting in loss of hydrocarbon mass collected on the tube. This effect was most noticeable in the case of n-hexane.

- Summary results from dispersion modelling of n-hexane, toluene and xylene concentrations using the ISC and ADMS models indicated that both models performed well in predicting the average and maximum measured concentrations of these compounds at the monitoring unit. Both models predicted a larger number of zero concentrations, compared to the measured data. A comparison of pumped tube sampling results and ADMS predicted concentrations indicated good agreement between the two datasets. However, ADMS predicted higher concentrations than were measured using passive sampling tubes. This is in agreement with the above analyses, which confirmed the good performance of the pumped sampling method and the tendency of the passive method to underpredict ambient concentrations.

- A strong correlation was observed between hourly measured and modelled n-hexane concentrations at the monitoring unit, particularly when local meteorological data were used in the models. A weaker correlation was observed for measured and modelled toluene and xylene concentrations. As for n-hexane, the strongest correlation for these compounds was observed when local meteorological data were employed in the models. Scatter plots of modelled and measured data indicated that ISC tended to overestimate hourly measured n-hexane concentrations. Both models tended to underpredict measured hourly xylene concentrations and, to a lesser extent, toluene concentrations. This is attributable to an underestimation of toluene and xylene emissions from Taconic, particularly for the highest measured xylene concentrations.

- Percentile analysis of the measured and modelled data indicated that the ADMS model most closely predicted the measured ranges of n-hexane, toluene and xylene

concentrations. Both models significantly underestimated the highest percentiles of measured xylene, again due to underestimated emissions.

- Analysis of the variation of modelled n-hexane concentrations with wind direction showed that both models estimated non-zero concentrations for a similar range of local wind directions. However, the measured data displayed elevated concentrations over a wider range of wind directions. For the further source from the monitoring unit (Taconic), both models behaved differently, with ADMS predicting elevated concentrations over a wider range of wind directions than ISC. However, as with n-hexane, the measured concentrations displayed elevated concentrations over a wider range of directions.

- On almost all occasions, a positive fractional standard deviation was observed for the 25 highest measured and modelled concentrations, indicating that the models tended to underestimate the scatter in these elevated concentrations. For n-hexane, based on the fractional bias and standard deviation, the ADMS model performed best, particularly when local meteorological data were used. For toluene, both models performed very well at predicting the 25 highest elevated concentrations. The best performance was observed for ISC using local meteorological data, while the performance of ADMS using local meteorological data was only marginally lower. For xylene data, both models indicated a large positive fractional standard deviation; however, the fractional bias values were closer to the ideal value of zero. The best performance was observed for ADMS using local meteorological data, which performed substantially better than ISC using local meteorological data. The normalised mean square errors for the highest 25 modelled and measured concentrations indicated that both models performed acceptably at predicting elevated n-hexane and toluene concentrations, though the performance for xylene was marginal for ADMS using local meteorological data, and unacceptable for the rest of the model analyses. This is due to the underestimation of xylene emissions from Taconic.

- The performance of ISC under stable atmospheric conditions was very poor, while ADMS performed well under such conditions, particularly when regional meteorological data were used, as higher windspeed values were observed in these data.

ISC performed better in unstable conditions, while ADMS performed better in neutral conditions (which dominate in Ireland).

- Assessment of model performance in low and high windspeed situations indicated that both models performed consistently better at higher windspeeds. ISC displayed a significantly poorer performance in estimating toluene concentrations at low windspeeds, than in estimating n-hexane concentrations at low windspeeds, suggesting that differences in model performance are apparent for different source-receptor distances.

- Overall, the performance of the ADMS model was better than that of ISC, though the performance of both models was observed to be acceptable, particularly in predicting the highest measured concentrations, which are often of most importance. The performance of ADMS under stable atmospheric conditions was significantly better than that of ISC. ADMS consistently performed better than ISC in estimating n-hexane concentrations, though model performance was closer for modelling toluene and xylene concentrations, with ADMS performing marginally better than ISC.

- Problems with regard to estimating the emissions from Taconic caused the greatest uncertainty in assessing the accuracy of the model estimates of ambient concentrations. Other model inputs, such as meteorological data, building dimensions and receptor locations were known to be accurate, while the emissions estimates used were based on a small number of samples collected during monitoring. Model results suggest that the largest error in the estimation of emissions was for xylene emissions from Taconic, particularly with regard to the model's ability to predict the highest measured concentrations. Estimation of emissions data is the factor which is most likely to lead to uncertainty in future modelling studies carried out in Ireland, as continuous emission measurements are not available for most point sources. This implies that employing highly complex models would be of limited use in such situations, particularly as this study has shown that, if accurate emissions data are used in Gaussian models, their performance is satisfactory.

- Average measured hydrocarbon concentrations at the rural monitoring site in Rhode were low, with the exception of ethane and isoprene, which were suspected of having a

natural emissions source. Elevated concentrations of ethylene and acetylene were noted for winds from the direction of the nearby town of Edenderry, though the magnitude of the measured concentrations was low compared to roadside concentrations measured in Dublin. Elevated 1,3-butadiene concentrations were noted for wind from the 220 to 290 degree wind sector, indicating a possible contribution from Rhode power station, though no other hydrocarbons exhibited similar behaviour.

8.2 CONCLUSIONS

Many of the measurements and analyses carried out during this study were novel, particularly in an Irish context, providing substantial original information on the sources and typical short-term ambient concentrations of hydrocarbons in Ireland. Such an extensive dataset of short-term ambient hydrocarbon concentrations under Irish conditions was not previously available. In particular, short-term continuous measurements of ambient hydrocarbon concentrations and comparison of these data with vehicle fuel hydrocarbon composition provided important information on the dominant source of urban hydrocarbon concentrations. The possible impact of evaporative emissions was also investigated using a new technique developed during this study, while many of the other analytical techniques used had not previously been applied to air quality data collected in Ireland. Several measurement methods, in conjunction with dispersion modelling, also allowed assessment of the impact of emissions from low level point sources on ambient hydrocarbon concentrations in an industrial context, where vehicle emissions were generally a minor source of ambient hydrocarbons. No data on ambient pollutant concentrations due to emissions from low level stacks were previously available in Ireland.

Several methods have been employed in this work to measure and analyse hydrocarbon concentrations. Continuous short-term (hourly) hydrocarbon measurements proved particularly useful in characterising short-term ambient hydrocarbon variations and, in conjunction with meteorological data, identifying possible sources of hydrocarbon emissions, and also the impact of variations in meteorological data on ambient hydrocarbon concentrations. Pumped sampling methods proved very easy to use, and were easily portable, which allowed down-wind short-term hydrocarbon concentrations to be readily assessed. Passive sampling methods do not have the portability of pumped sampling techniques, and cannot provide the short-term resolution offered by continuous monitoring

techniques. However, the low capital cost of these samplers means that sampling can be carried out at several locations at the same time, and are therefore an ideal method of assessing longer term average concentrations over a wide area.

The results of the dispersion model assessment indicate that these models (ISC3 and ADMS) can be used to provide a tentative estimate of ground level pollutant concentration due to emissions from a given source, though the level of confidence in the model input parameters must be considered in assessing the likely accuracy of the model results. In particular, the importance of accurate emissions data to model performance was illustrated. It is considered that pollutant mass emission rate is the model input parameter which is most likely to lead to poor prediction of ground level pollutant concentration, as emissions data for most sources are normally only available from infrequent grab samples and are therefore unlikely to be representative of all emissions scenarios at a given source.

Several different graphical and statistical methods were employed to analyse the measured and modelled hydrocarbon data. Statistical analyses allowed single datasets to be represented in terms of a small number of parameters. However, to compare a number of different datasets, graphical methods were found to be more useful in providing an indication of the relationships between the data. Correlation analysis was also found to be a useful statistical technique in summarising the relationship between two sets of data. In terms of comparing modelled and measured concentrations, statistical and graphical techniques were both found to be effective. Indeed, graphical methods were used to illustrate results from statistical comparisons of the various modelled and measured datasets. Overall, graphical methods were generally preferred as they provided a clearer illustration of the relationship between datasets, compared to statistical techniques.

Significantly more data is now available relating to ambient hydrocarbon concentrations and their sources in Ireland. Also, more importantly, several methods have also been demonstrated for analysing and characterising these data, and identifying possible emissions sources. The utility of several measurement and modelling techniques have also been demonstrated. This work provides a substantial basis for future research. Some suggestions for such work are provided in the following section.

8.3 RECOMMENDATIONS FOR FURTHER RESEARCH

- The on-line hydrocarbon monitoring system should be deployed at different site types where significant hydrocarbon concentrations are likely to be measured, or population exposure is likely to be high. Suggestions for monitoring sites include sub-urban, airport, motorway, multi-storey car park, vehicle tunnel (Lee tunnel in Cork), sea port and remote (such as Mace Head) monitoring sites. All of these sites exhibit different hydrocarbon characteristics and would aid in the preparation of a detailed hydrocarbon emissions inventory for Ireland.

- Results from a number of short-term (several weeks) roadside and urban monitoring studies should be employed to validate and assess available dispersion models for traffic sources, as hydrocarbon emissions from vehicle are known to be significant.

- Pumped and passive sampling methods should also be evaluated further and compared with on-line measurements. In particular, the Radiello passive sampling method should be evaluated for shorter sampling periods (less than one week) to re-assess its performance. Analysis of pumped and passive tubes using highly sensitive analytical equipment would allow assessment of the performance of these sampling methods at low ambient concentrations.

- The on-line hydrocarbon monitoring system should also be employed for the analysis of pumped and passive tube samples, allowing more confidence in comparisons made between on-line and passive or pumped tube measurements. This would require little alteration of the current analytical methods used and could significantly increase the spatial coverage of measurements at a given site.

- Detailed hydrocarbon exhaust analysis of a selection of current fleet Irish vehicles would allow a representative comparison of roadside hydrocarbon concentrations and exhaust emissions in Ireland, as opposed to comparisons with European studies. This would complement the tunnel study proposed above.

- Comparison of the fuel samples collected (in 1998) during this project, with current retail fuels composition would allow the impact of the latest EU fuel specifications to be assessed.

- The ISC dispersion model has recently been replaced with a more advanced model, AERMOD, which shares many of the features of the ADMS dispersion model. Evaluation of this model is now required to assess if AERMOD is an improvement over ISC and if its performance is comparable to ADMS.

- Further evaluation of available dispersion models should be performed, using measurements at a larger selection of sites around a carefully selected point source, or group of sources. An intensive campaign of on-line, passive and pumped tube monitoring would provide a large dataset for comparison, providing a significant range of spatial and temporal measurements for comparison with model results. Ideally, continuous emissions data would be available for the source, to ensure that all model inputs were as accurate as possible.

- Rather than running the dispersion models using a single emissions value, several modelling scenarios should be investigated for a given emitter. This would involve running the model three times, under a low emissions, typical emissions and high emissions scenario, based on measurements of emissions and on knowledge of the operation of the facility. This would, in effect, provide error bars for the model performance comparison with ambient measured data. Under the majority of emissions scenarios, the ambient measurements would be expected to be within the range of concentrations calculated by the model, if the model operation is satisfactory.

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APPENDIX A: SAMPLE DIURNAL HYDROCARBON PLOTS FROM PHASE 1

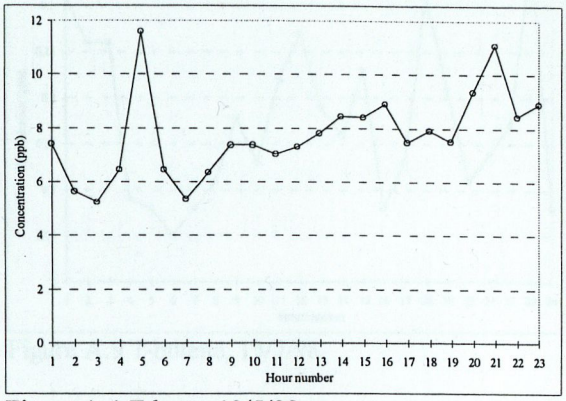


Figure A.1 Ethane, 13/5/98

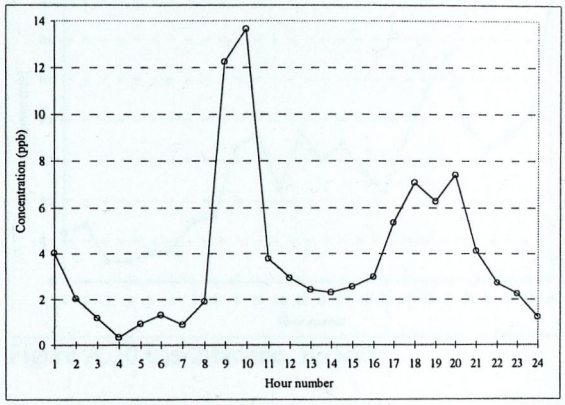


Figure A.2 Ethylene, 10/3/98

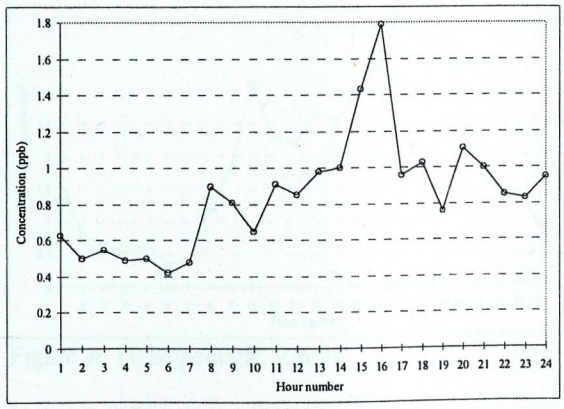
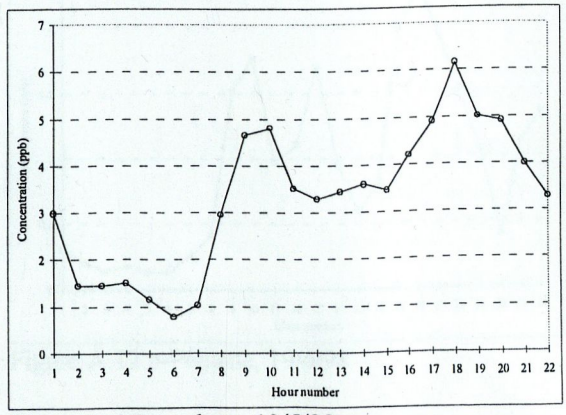


Figure A.3 Propane, 11/6/98



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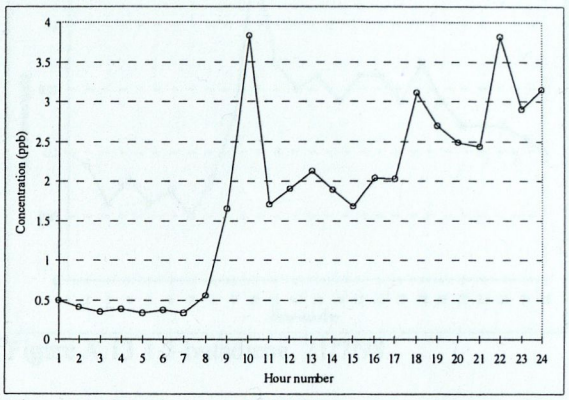

Figure A.5 Isobutane, 18/3/98

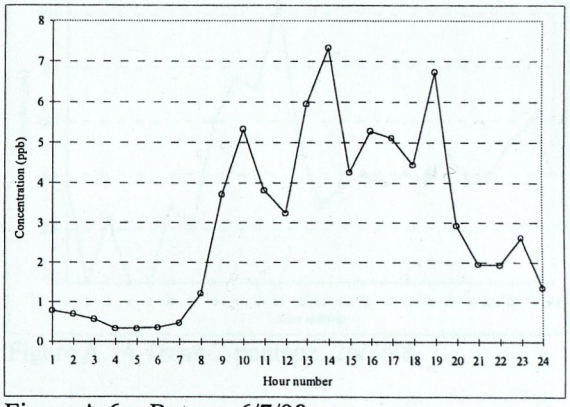

Figure A.6 n-Butane, 6/7/98

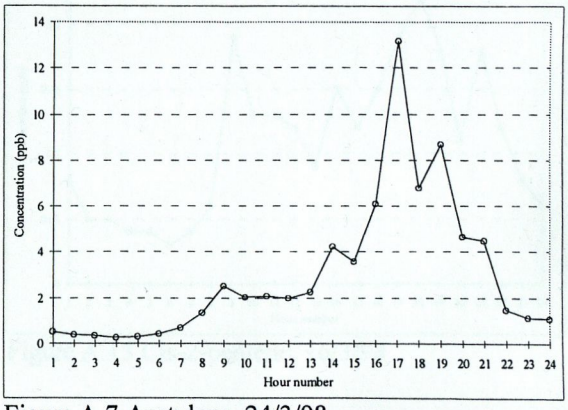

Figure A.7 Acetylene, 24/3/98

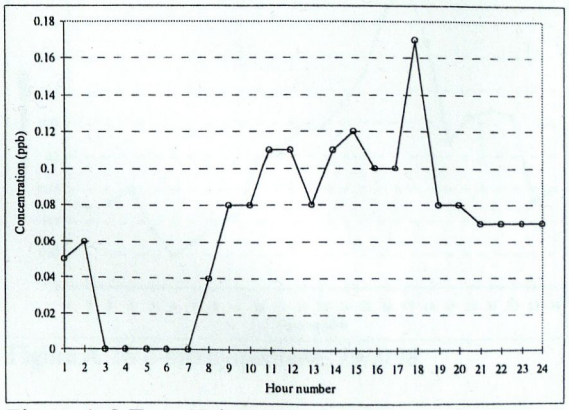

Figure A.8 Trans-2-butene, 10/6/98

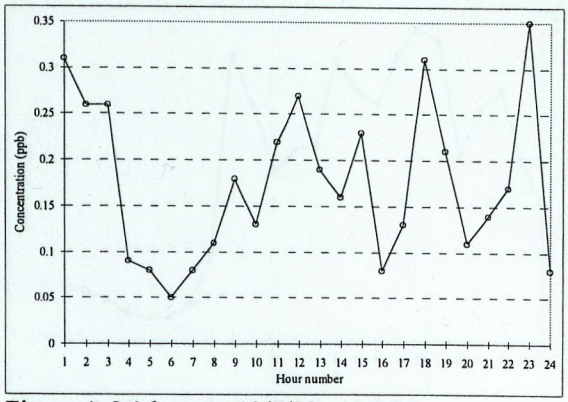

Figure A.9 1-butene, 13/7/98

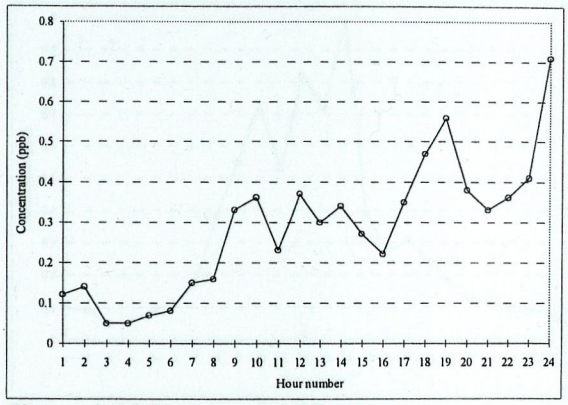

Figure A.10 Cis-2-butene, 12/5/98

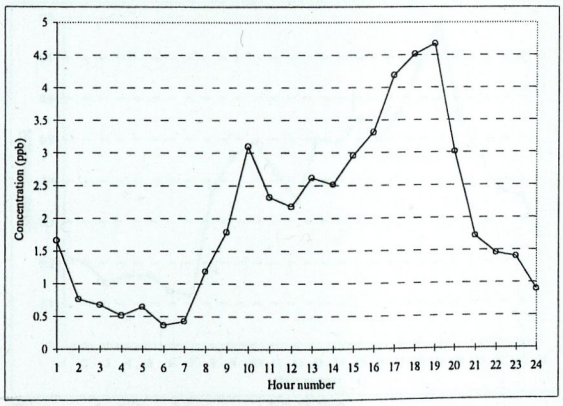

Figure A.11 Isopentane, 2/6/98

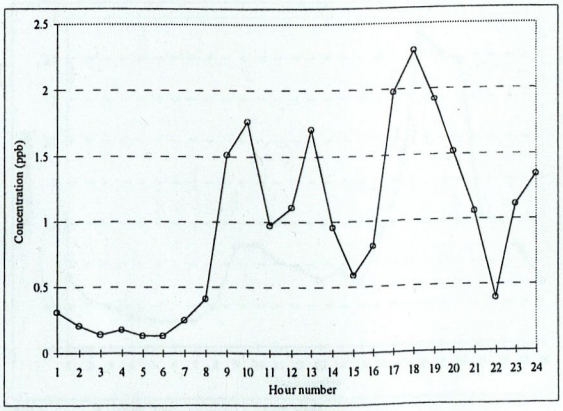

Figure A.12 n-Pentane, 19/6/98

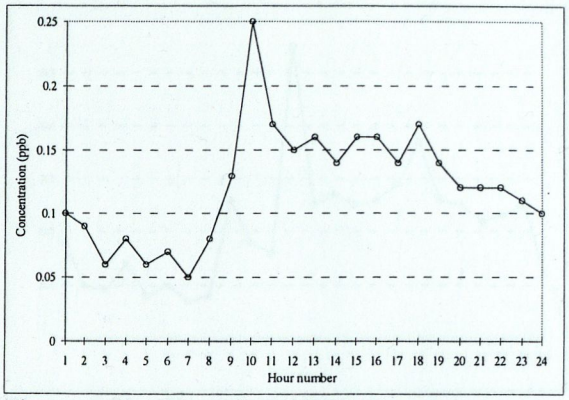

Figure A.13 1,3-butadiene, 21/7/98

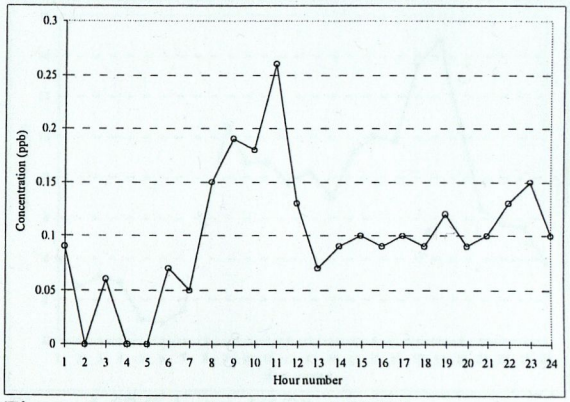

Figure A.14 Trans-2-pentene, 26/7/98

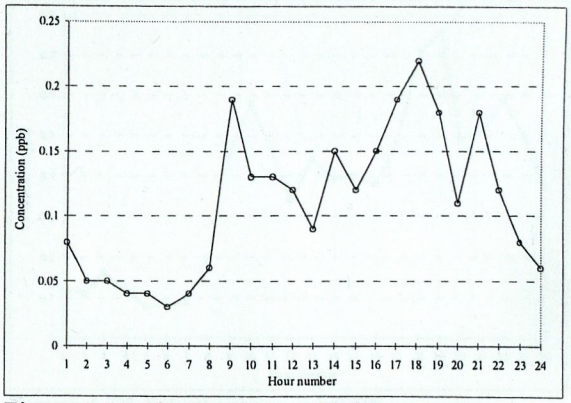

Figure A.15 Cis-2-pentene, 16/3/98

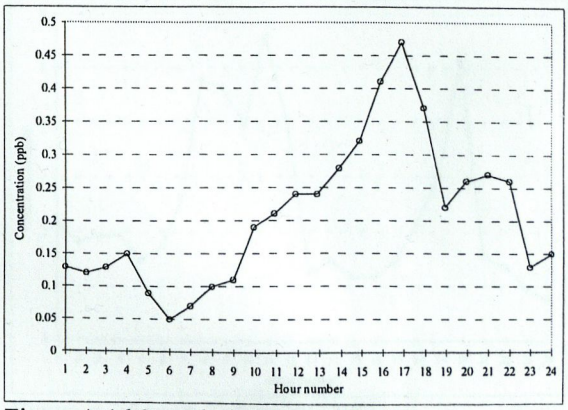

Figure A.16 2-methylpentane, 29/3/98

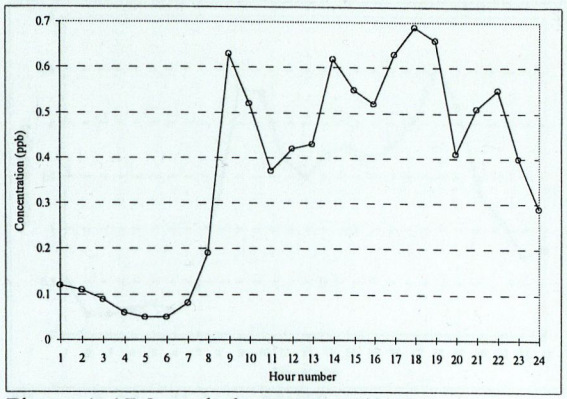

Figure A.17 3-methylpentane, 13/3/98

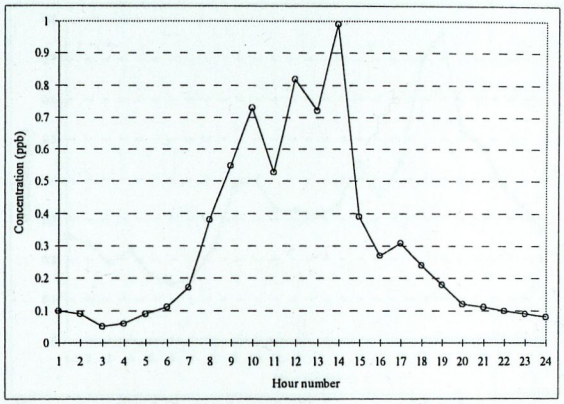

Figure A.18 Isoprene, 8/6/98

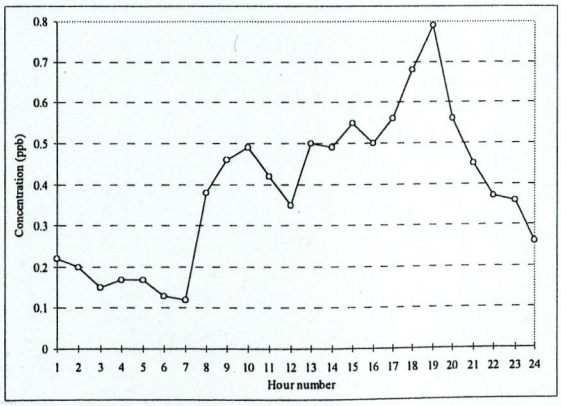

Figure A.19 n-Hexane, 23/3/98

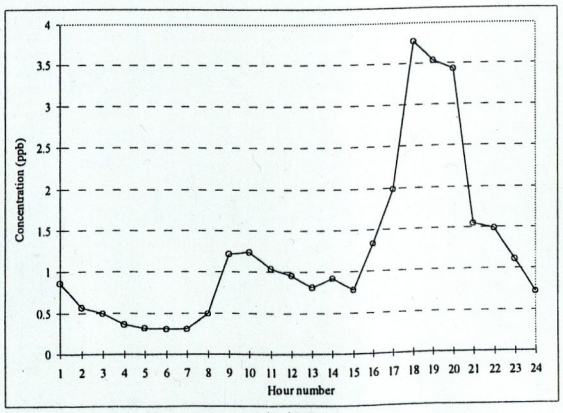

Figure A.20 Benzene, 4/3/98

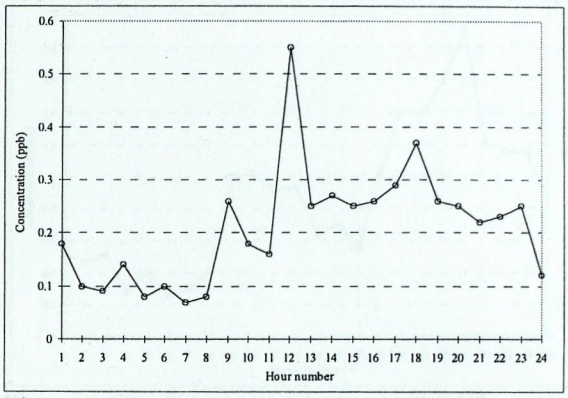

Figure A.21 n-Heptane, 2/4/98

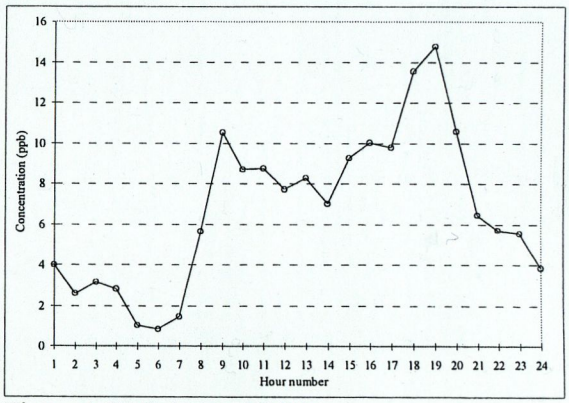

Figure A.22 Toluene, 1/4/98

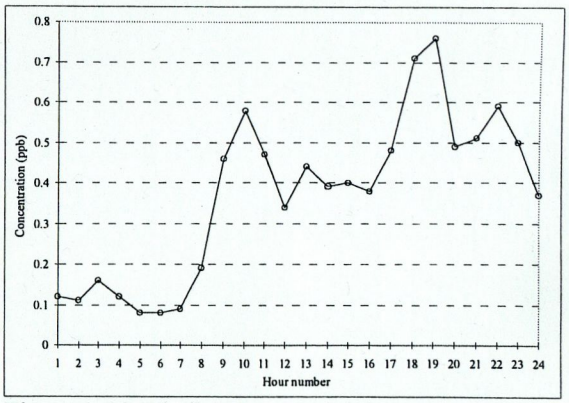

Figure A.23 Ethylbenzene, 11/3/98

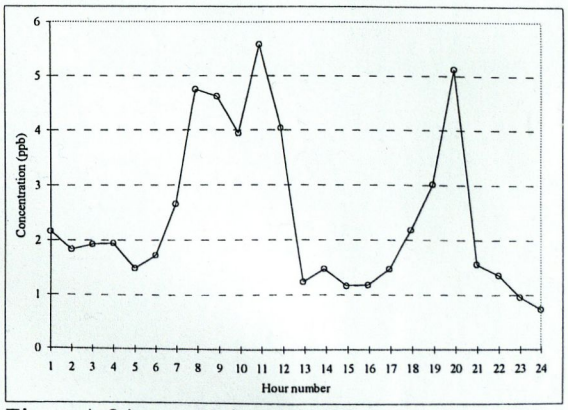

Figure A.24 m+p-Xylene, 9/3/98

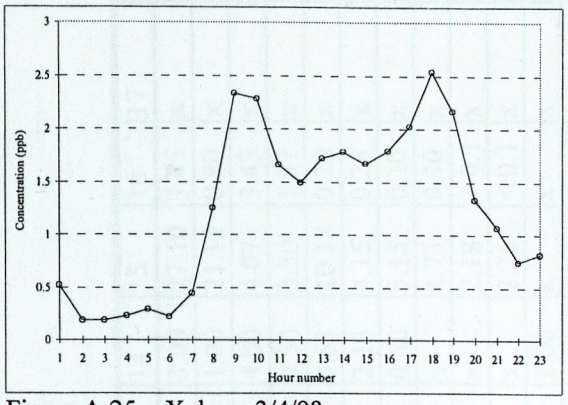

Figure A.25 o-Xylene, 3/4/98

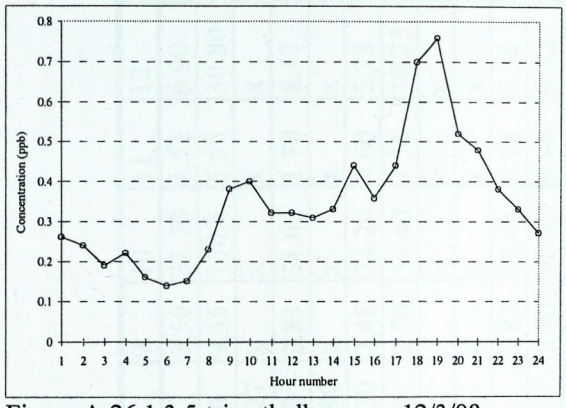

Figure A.26 1,3,5-trimethylbenzene, 12/3/98

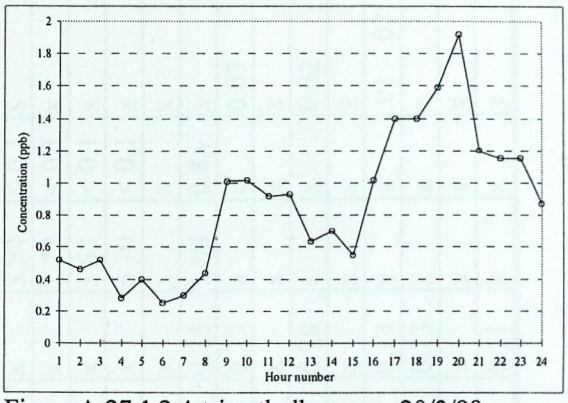

Figure A.27 1,2,4-trimethylbenzene, 20/3/98

APPENDIX B: WORLD-WIDE HYDROCARBON MONITORING DATA

Table B.1 Results from world-wide hydrocarbon monitoring, ppb

Site number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ethane	5.50	95.50	x	x	x	x	9.94	x	3.50	32.70	1.55	6.90	4.00	3.00	27.10	7.45	x
Ethylene	3.50	75.50	x	x	x	x	19.24	9.10	9.35	130.5	5.55	30.80	x	1.00	21.15	0.80	x
Propane	4.00	46.67	x	x	x	x	13.01	35.27	x	x	x	x	3.00	4.00	4.07	3.43	x
Propylene	1.33	20.00	x	x	x	x	10.54	6.20	2.83	31.03	1.70	8.47	1.33	0.50	3.30	1.37	x
isobutane	1.75	16.25	x	x	x	x	12.81	15.90	x	x	x	x	3.00	0.63	10.18	0.20	x
n-Butane	4.00	71.50	x	x	x	12.11	14.72	24.30	2.48	24.20	0.60	5.28	7.25	2.13	4.15	0.28	x
Acetylene	x	x	x	x	x	x	28.86	3.60	2.70	39.40	1.35	10.25	4.50	0.50	5.15	0.30	x
Trans-2-butene	Trans +	Trans +	x	x	x	x	3.69	x	x	x	x	x	0.50	x	4.73	0.40	x
Cis-2-butene	Cis < 1	Cis = 5	x	x	x	x	1.68	x	x	x	x	x	x	x	2.18	< 0.1	x
1-butene	x	x	x	x	x	x	1.76	x	1.83	18.48	0.98	7.38	x	x	2.75	< 0.1	x
Isopentane	x	x	x	x	x	17.64	24.86	x	5.90	68.32	0.86	9.72	7.00	1.00	x	x	x
n-Pentane	2.00	34.20	10.49	13.20	0.22	14.03	7.78	x	2.26	24.40	0.42	3.70	3.20	0.70	2.24	1.02	x
1,3-butadiene	x	2.75	x	x	x	x	2.05	x	x	x	x	x	x	x	x	x	x
Trans-2-pentene	Trans +	Trans +	2.54	1.41	0.01	x	2.06	x	x	x	x	x	x	x	3.94	< 0.1	x
Cis-2-pentene	Cis < 0.2	Cis =6.4	1.27	0.58	0.01	x	1.03	x	x	x	x	x	x	x	2.72	< 0.1	x
2-methylpentane	1.17	23.00	11.34	7.82	0.13	x	7.63	x	1.57	18.73	0.42	2.95	2.00	x	3.53	< 0.1	x
3-methylpentane	0.67	11.33	6.85	4.72	0.08	x	5.39	x	0.92	11.48	0.23	1.70	1.33	x	6.70	< 0.1	x
Isoprene	x	x	0.11	0.11	0.05	x	x	x	x	x	x	x	x	x	x	x	x
n-Hexane	0.67	13.67	4.69	4.64	0.12	x	4.41	x	0.75	9.60	0.18	1.47	1.50	0.25	1.68	0.85	x
Benzene	x	15.00	12.17	12.20	0.57	16.01	11.08	x	x	x	x	x	1.33	0.25	x	x	0.07
n-Heptane	0.29	5.71	2.04	1.47	0.04	x	2.31	x	x	x	x	x	x	x	x	x	x
Toluene	3.29	37.00	25.33	22.07	0.27	26.67	26.07	x	5.07	48.63	1.09	7.60	4.00	0.29	x	x	0.02
Ethylbenzene	0.63	6.00	3.83	3.24	0.05	x	3.99	x	0.79	11.15	0.15	1.39	0.50	x	x	x	x
m+p-Xylene	0.75	22.00	13.37	10.37	0.10	11.98	12.39	x	2.68	38.23	0.65	5.29	1.38	0.13	x	x	.01 - .02
o-Xylene	0.75	8.00	5.49	4.18	0.07	x	5.70	x	1.09	13.46	0.21	2.01	0.63	0.13	x	x	x
1,3,5-trimethylbenzene	0.22	3.00	1.08	0.74	0.01	x	4.53	x	0.33	5.50	0.11	0.74	x	x	x	x	x
1,2,4-trimethylbenzene	1.00	9.00	2.81	1.20	0.03	x	4.21	x	1.03	22.38	0.34	2.42	0.56	0.11	x	x	x

Table B.1 continued

Site number	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Ethane	5.37	3.18	4.26	7.40	3.21	x	x	x	x	x	x	x	x	x
Ethylene	3.99	3.06	3.86	10.80	27.15	x	x	x	x	x	x	x	x	x
Propane	2.74	3.87	2.83	3.50	12.62	x	x	x	x	x	x	x	x	x
Propylene	0.58	x	2.10	5.80	6.93	x	x	x	x	x	x	x	x	x
Isobutane	1.18	1.69	2.82	6.38	2.65	x	x	x	x	x	x	x	x	x
n-Butane	2.75	4.66	4.60	12.13	4.93	x	x	x	x	x	x	x	x	x
Acetylene	1.06	5.73	7.88	19.30	37.19	x	x	x	x	x	x	x	x	x
Trans-2-butene	x	x	0.26	2.06	1.37	x	x	x	x	x	x	x	x	x
Cis-2-butene	x	0.18	0.19	0.83	0.99	x	x	x	x	x	x	x	x	x
1-butene	x	0.27	0.28	0.70	1.63	x	x	x	x	x	x	x	x	x
Isopentane	2.85	3.16	3.69	7.45	6.11	26.30	215.80	3.20	x	x	x	x	x	x
n-Pentane	1.44	1.01	0.80	2.58	3.54	x	x	x	x	x	x	x	x	x
1,3-butadiene	x	0.34	0.36	0.80	1.20	x	x	x	x	x	x	x	x	x
Trans-2-pentene	x	0.23	0.23	0.57	1.89	x	x	x	x	x	x	x	x	x
Cis-2-pentene	x	0.13	0.13	0.30	0.93	x	x	x	x	x	x	x	x	x
2-methylpentane	x	Sum=	Sum=	0.90	2.68	x	x	x	x	1.2	x	x	x	x
3-methylpentane	x	1.40	1.48	0.80	1.40	4.70	32.20	0.60	x	0.5	x	x	x	x
Isoprene	x	x	x	0.20	0.53	x	x	x	x	x	x	x	x	x
n-Hexane	x	0.38	0.35	0.60	2.26	4.10	25.00	0.60	0.45	0.6	x	x	x	x
Benzene	0.48	1.80	1.75	4.63	3.68	11.70	61.20	2.50	0.59	2.8	0.5	1.53	8.90	3.40
n-Heptane	x	0.18	0.20	x	1.23	1.30	7.10	0.20	0.12	0.3	x	x	x	x
Toluene	1.35	3.16	3.14	7.48	5.44	21.20	103.50	6.70	1.10	4.6	0.9	3.07	35.60	13.50
Ethylbenzene	0.25	0.63	0.58	1.18	1.32	4.00	19.20	1.30	0.18	0.6	0.3	x	3.50	2.60
m+p-Xylene	0.82	1.98	1.68	3.83	3.20	11.30	57.40	3.20	0.39	2.2	0.5	sum=	8.30	3.10
o-Xylene	0.31	0.69	0.62	1.45	1.25	5.50	27.40	1.50	0.14	0.8	0.3	6.07	3.00	1.20
1,3,5-trimethylbenzene	0.09	x	x	0.30	0.64	x	x	x	0.04	x	x	x	x	x
1,2,4-trimethylbenzene	0.28	x	x	1.08	x	x	x	x	0.12	x	x	x	x	x

Table B.1 continued

Site number	32	33	34	35	36	37	38	39	40	41	42	43	P 1	P 2	P 3
Ethane	4.80	1.69	2.22	1.35	x	5.70	14.4	2.22	2.12	4.78	3.67	22.35	4.34	2.71	x
Ethylene	x	1.84	1.31	1.63	x	6.32	135.6	2.36	1.71	4.57	2.83	16.10	5.10	3.43	x
Propane	5.77	1.05	0.91	0.61	0.41	2.50	3.10	12.35	7.31	3.05	2.27	6.34	2.14	1.37	x
Propylene	1.93	0.406	0.18	0.03	0.02	1.95	40.3	0.99	0.91	2.31	1.57	5.29	1.58	1.92	x
Isobutane	6.08	0.34	0.26	0.12	0.04	1.80	12.0	1.24	0.96	3.52	1.98	6.46	1.57	0.82	x
n-Butane	total	0.83	0.43	0.25	0.28	3.07	29.6	2.79	1.91	5.11	3.31	27.52	3.85	2.41	x
Acetylene	x	1.935	1.44	0.309	0.13	4.43	86.8	2.85	1.37	8.80	2.82	4.48	2.81	1.77	x
Trans-2-butene	x	x	x	x	0.01	0.06	3.82	x	x	x	x	0.88	0.21	0.12	x
Cis-2-butene	x	x	x	x	0.03	0.05	2.78	0.11	0.08	0.24	0.18	0.70	0.07	0.19	x
1-butene	x	x	x	x	x	x	5.45	0.17	0.12	0.33	0.21	0.93	0.19	0.12	x
Isopentane	1.58	0.77	0.30	0.09	0.04	5.96	65.3	1.45	0.90	4.31	2.51	10.62	2.62	1.97	x
n-Pentane	total	0.30	0.20	0.06	0.02	2.10	6.11	0.54	0.42	0.99	0.64	2.23	0.90	0.69	x
1,3-butadiene	x	x	x	x	x	x	x	0.16	0.10	0.38	0.23	1.05	0.38	0.24	x
Trans-2-pentene	x	x	x	x	x	0.19	2.46	0.11	0.05	0.28	0.17	0.76	0.27	0.13	x
Cis-2-pentene	x	x	x	x	x	0.10	1.28	0.05	0.02	0.15	0.09	0.44	0.16	0.09	x
2-methylpentane	x	x	x	x	x	1.63	10.1	0.45	0.33	1.62	1.36	2.87	0.40	0.32	x
3-methylpentane	x	x	x	x	x	0.83	5.47	total	total	total	total	1.70	0.37	0.24	x
Isoprene	x	x	x	x	0.04	0.12	x	0.15	0.08	0.37	0.16	1.46	0.13	0.16	x
n-Hexane	0.58	x	x	x	0.01	0.62	1.78	0.15	0.11	0.43	0.31	1.33	0.48	x	x
Benzene	1.77	0.57	0.30	0.11	0.03	1.49	x	0.91	0.69	1.75	1.20	3.94	1.80	x	0.50
n-Heptane	0.26	x	x	x	0.01	0.29	x	0.11	0.10	0.20	0.16	0.66	0.17	x	x
Toluene	3.10	0.93	0.19	x	0.04	4.43	x	1.67	1.25	3.54	2.40	8.61	3.30	x	2.82
Ethylbenzene	0.51	x	x	x	0.01	0.69	x	0.35	0.24	0.69	0.43	1.39	0.48	x	x
m+p-Xylene	1.69	x	x	x	0.02	2.09	x	0.99	0.75	1.97	1.26	4.55	1.56	x	x
o-Xylene	0.64	x	x	x	0.01	0.73	x	0.43	0.31	0.78	0.48	1.64	0.59	x	0.53
1,3,5-trimethylbenzene	x	x	x	x	0.04	1.01	x	x	x	x	x	x	0.42	x	x
1,2,4-trimethylbenzene	0.56	x	x	x	0.01	x	x	x	x	x	x	x	0.74	x	x

Legend for Table B.1

1: St. Louis Missouri (urban), Morning Peak Time, Legge and Krupa, 1986	23: Athens, Greece (city centre roadside), Rappengluck *et al.,* 1998
2: Los Angeles California (urban), Morning Peak, Legge and Krupa, 1986	24: Athens, Greece (city Centre max.), Rappengluck *et al.,* 1998
3: Rome (urban), Ciccioli, 1993	25: Athens, Greece (suburban average), Rappengluck *et al..,* 1998
4: Milan (urban), Ciccioli, 1993	26: Huijbergen, Netherlands (rural average), Thijsse *et al.,* 1999b
5: Italy, Montelibretti (forest), Ciccioli, 1993	27: Munich, Germany (city centre average), Rappengluck and Fabian, 1999
6: Berlin Intersection, De Wiest, 1978	28: Munich, Germany (suburban average), Rappengluck and Fabian, 1999
7: Rome (urban centre), Brocco *et al.,* 1997	29: Dublin average (range of site types), Henderson *et al.,* 1997
8: Bombay Centre, Pandit and Rao, 1990	30: Dublin city centre average (March/April 1996), Envirocon, 1997
9: McHenry Tunnel, USA, minimum values, cars only, Zielinska *et al.,* 1996	31: Dublin suburban average, Envirocon, 1997
10: McHenry Tunnel, USA, maximum values, cars only, Zielinska *et al.*, 1996	32: Sacramento, California (roadside), Hammond and Cook, 1993
11: Tuscarora Tunnel, USA, minimum values, Zielinska *et al.,* 1996	33: Switzerland, Tanikonen (rural), Solberg *et al.,* 1998
12: Tuscarora Tunnel, USA, maximum values, Zielinska *et al.,* 1996	34: Czech Republic, Kosetice (rural), Solberg *et al.,* 1998
13: Boston (urban), Sexton and Westberg, 1984	35: Finland, Pallas (rural), Solberg *et al.,* 1998
14: Illinois (rural), Sexton and Westberg, 1984	36: Greece (rural mountain), Moschonas and Glavas, 2000
15: Lancaster, UK (urban, junction), Colbeck and Harrison, 1985a	37: Berlin, Germany (roadside), Thijsse *et al.,* 1999a
16: NW England (rural), Colbeck and Harrison, 1985a	38: France, Paris (tunnel), Touaty and Bonsang, 2000
17: Atlantic air average, Singh *et al.,* 1985	39: Belfast (urban background), 1997 (from NETCEN air quality archive)
18: Colombus Ohio (urban/suburban average), Spicer *et al.,* 1995	40: Belfast (urban background), 1998 (from NETCEN air quality archive)
19: Southampton Centre (background 1998) (from NETCEN air quality archive)	41: London (roadside, UCL), 1997 (from NETCEN air quality archive)
20: London roadside, adapted from AEA Technology, 1998	42: London (roadside, UCL), 1998 (from NETCEN air quality archive)
21: London, Exhibition Road (roadside), Derwent *et al.,* 1995	43: London (roadside, Marylebone), 1998 (from NETCEN air quality archive)
22: Porto Alegre, Brazil (urban), Grosjean *et al.,* 1998a	