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MONITORING OF TRAFFIC RELATED 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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May 2005

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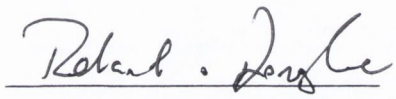

Roland O Donoghue

May 2005

SUMMARY

The research completed represents an experimental investigation of atmospheric hydrocarbon concentrations in the Dublin area, of which very little reported data were previously available. There was a notable lack of short-term measurements, which are useful in source apportioning and investigating the behaviour and trends of ambient hydrocarbon concentrations.

Approximately eight months of online sampling was carried out to investigate the road traffic source effect, emanating from the M4 motorway at a sub-urban / rural location. HC concentrations were compared with meteorological and traffic data obtained locally. HC compounds which showed a higher mean than median value were found to be associated with a greater local source effect. These compounds also showed the highest Pearson's correlation coefficients with acetylene and ethene, known traffic emission markers. Well defined diurnal profiles were obtained for most compounds, for wind directions associated with the M4, when periods of local atmospheric inversions and low wind speeds were filtered out. Various trends in HC ratios were investigated, which showed the youngest HC's were sampled during morning peak traffic times, when near parallel winds relative to the M4 were observed. The highest average ethene / acetylene ratios were also observed during these times. Using the HC / acetylene ratio, some evidence for evaporative emissions was also obtained.

Using the online system, ambient hydrocarbon concentrations were also monitored over a six-month period, at a heavily trafficked junction in Dublin City centre. When HC data associated with stable atmospheric conditions were filtered out, very pronounced diurnal profiles were obtained for almost all compounds. Clearly defined peaks associated with morning and evening traffic flow were observed. Concentrations were highest with wind directions associated with the junction. Evaporative emissions and the m+p xylene / ethylbenzene ratio were investigated for both wind direction sectors, where higher evaporative ratios and relatively older HC's were associated with wind sector 40-90°, most likely due to long range transport of pollutants. Concentrations of all compounds except ethane, propane and acetylene decreased substantially from values reported in 1998, mainly due to a lower percent of high emitting vehicles in the 2003 vehicle fleet relative to that of 1998. It was hypothesised that the

rise in acetylene concentrations was due to long range transport from Continental Europe and the UK, due to its relatively long atmospheric lifetime.

After completing the monitoring campaign at the M4, the limitations of the online system became apparent and a mobile sampling method was developed and validated to extend sampling flexibility. The method was validated under the following headings: specificity, linearity, method detection limits, precision, accuracy, robustness and sample stability. Acceptable method performance was documented for ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, ethene, propene, 1,3-butadiene, acetylene and benzene. The sampling method allowed for sampling times of between 5 and 40 minutes, and samples were stable for at least 24hours.The mobile sampling method was applied to several sampling campaigns, the first of which, a 2 week pilot study, assessed the HC concentrations to which bus and cycling commuters are exposed in Dublin City. Average HC concentrations were found to be 1.47 times higher for the bus commuter than the cyclist.

The second campaign involved measuring hydrocarbon concentrations on a daily basis over a 5 week period, during the morning peak traffic period at six different receptor locations, three on either side of a busy sub-urban Motorway (M50). A clear and well-defined M50 source effect was observed for n-pentane, iso-pentane, ethene, propene, 1,3 butadiene, benzene and acetylene. Background corrected concentrations compared very well for both main wind direction sectors, with greater dispersion observed for winds between 165° and 315°, due to the higher average wind speed observed for this sector. The measured results were compared on a day-to-day basis with the gaussian dispersion model, CALINE4. On a day-to-day basis, the model performance was acceptable, however, the model behaviour improved significantly for long term (5 week) average predictions, where the average modelled / measured concentration ratio varied from 0.90 to 1.05 for 25 to 250 metres from the source, respectively.

The third campaign involved a 5 week monitoring period in Dublin City centre, to establish which site gave a more accurate background city centre estimation: a roof-top or green field site. The lowest concentrations and relative standard deviations were observed at the green field site, regardless of wind direction. The ethene / acetylene ratio was consistently lowest at the green field site, however highest evaporative ratios were observed at the rooftop site.

ACKNOWLEDGEMENTS

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I would also like to thank my brother Albert and friend Paul "Fitz", for their continued support when others in the "club" questioned my reasoning and motivation for returning to University in pursuit of a higher degree.

Finally, my heart-felt and greatest appreciation is reserved for my parents, Marion and Leo, without whose support, both financial and moral, this research thesis would not have been written. Their good nature, hard working attitude and blind devotion to their children is inspiring.

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LIST OF ABBREVATIONS

AEAT	AEA technology
AIRS	Aerometric information retrieval system (US database)
AOAC-PVMP	Association of Official Analytical Chemists Peer Verified Methods Program
ATD	Automated thermal desorption
AutoGC	Automated Gas Chromatograph
BP	Bonded phase
BTEX	Benzene, toluene, ethylbenzene and xylene's
calEPA	California Environmental Protection Agency
CEC	Coucil of the European Communities
CO	Carbon monoxide
CRC	Co-ordinating Research Council
CSO	Central Statistics Office
DELG	Department of the Environment and Local Government
DETR	Department of the Environment, Transport and the Regions
DOE	Department of the Environment
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency (Ireland)
EU	European Union
FB	Fractional Bias
FDA	Food and Drugs Administration
FID	Flame Ionisation Detector
GC	Gas Chromatograph
HC	Hydrocarbon
HGV	Heavy Goods Vehicle
ICH	International Conference on Harmonisation
IPC	Integrated Pollution Control
ISO	International Organisation for Standardisation
LDV	Light Duty Vehicle
MS	Mass Spectrometer
NATA	National Association of Testing Authorities, Australia
NMHC	Non Methane Hydrocarbon
NMSE	Normalised mean square error
NPTBC	Neath Port Talbot Borough Council
NO_2	Nitrogen dioxide
NO_x	Oxides of Nitrogen
NPL	National Physical Laboratory (UK)
°C	Degree Celsius
OECD	Organisation for Economic Co-Operation and Development
PAMS	Photochemical assessment monitoring stations
PC	Personal computer
PLOT	Porous Layer Open Tubular (capillary column)
PM_{10}	Particulate matter with a diameter of less than 10 micrometers
PORG	Photochemical Oxidant Review Group
ppbC	Parts per billion Carbon

ppbv	Parts per billion volume
ppm	Parts per million
psi	Pounds per square inch
QUARG	Quality of Urbam Air Review Group
RVP	Reid vapour pressure
SO_2	Sulphur dioxide
T_{50}	50 percent distillation temperature (of an automotive fuel)
T_{90}	90 percent distillation temperature (of an automotive fuel)
UK	United Kingdom
USEPA	United States Environmental Protection Agency
VOC	Volatile organic Compound
WHO	World Health Organisation

1. INTRODUCTION

As a species, we have historically had a fascination with all things celestial, whether it reveals itself through mythology, religion or science. That we posses an innate desire to understand the atmosphere in which we live and beyond is undeniable.

1.1 BRIEF HISTORY OF AIR POLLUTION

The issue of air pollution is not solely a modern day phenomenon. Combustion in the earliest times was a cause of air pollution, with nomadic tribes polluting their indoor environment with the products of incomplete combustion from cooking fires, behaviour still observed today in more primitive areas of the world.

The first documented observations of urban air pollution were made by classical writers, where the poet Horace mentions the blackening of buildings in Rome. In addition, Emperor Nero's tutor, Seneca, was encouraged to leave Rome due to continued ill-health. After re-locating in approximately AD 61, he reported that as soon as he left Rome's "oppressive odours", his health improved (Brimblecombe, 1987).

The first documented air pollution incident in England involved Queen Eleanor of Provence, who, upon a visit to Nottingham castle in 1257, found the air so full of sea coal smoke, that she was forced to leave to preserve her health. In crowded, medieval cities, dominated by tall buildings, smoke would have been emitted at low level, where it had the potential to be trapped by the nowadays, common "canyon effect".

By 1661, the pollution of London had become so bad, that John Evelyn was prompted to write a letter to Charles II, in which he described the inconvenience of air pollution and possible measures to remedy the situation. Earlier in the same century, the topic of air pollution had pervaded into one of Shakespeare's great works; Hamlet.

" This most excellent canopy of air.....appears no other thing than a foul and pestilent congregation of vapours" (Act II, scene ii).

The predominant air pollution problem of the nineteenth century was smoke and ash from the burning of coal or oil in the boiler furnaces of stationary power plants, locomotives and marine vessels, and in home heating fireplaces and furnaces. In Great Britain, the abatement of such pollution was considered to be a health agency responsibility and was confirmed as such by the first Public health act of 1848 and the later ones of 1866 and 1875 (Boubel *et al*, 1994).

In conjunction with a growth in cities and hence greater emissions, the twentieth century saw the emergence of the automobile as the primary mode of transport. With this emergence of both stationary and mobile polluters, severe pollution episodes were experienced in many cities.

1930 saw a five day pollution episode effect Meuse in Belgium. 1943 saw the first major smog episode in Los Angeles. 1948 saw a four day episode effect Donora in Pennsylvania and 1952 saw the great smog in London which captured the attention of the public at large.

The Great London Smog of 1952, which resulted in around 4,000 extra deaths in the city, led to the introduction of the Clean Air Acts of 1956 and 1968 in the UK. These introduced smokeless zones in urban areas, with a tall chimney policy to help disperse industrial air pollutants away from built up areas into the atmosphere.

At the start of the 1990s the main air quality problem facing Ireland was the occurrence of "winter smog" (smoke and sulphur dioxide emissions) resulting from widespread use of bituminous coal in major urban areas, notably Dublin. In the mid to late 1980's, levels of smoke and sulphur dioxide were as much as seven times the EU and national limit values (OECD, 2000). To deal with the problem, regulations were made in 1990 to ban the marketing, sale and distribution of bituminous coal in the Dublin area. Smoke and SO_2 levels showed considerable improvement once the ban was introduced. The ban was extended to Cork in 1995 and in accordance with a commitment in "An Action Programme for the Millennium", the ban was extended to five additional areas in 1998 (Arklow, Drogheda, Dundalk, Limerick and Wexford). Regulations made in September, 2000 further extended the ban to five new areas (Celbridge, Galway, Leixlip, Naas and Waterford) with effect from 1st October, 2000.

With the control of bituminous coal burning and industrial emissions limited by the EPA under the IPPC licensing scheme, the major contributors to urban air pollution are now generally accepted to be mobile emissions from passenger cars.

Amongst the pollutants of concern emitted by mobile sources are a class of volatile organic compounds called hydrocarbons, several of which are carcinogenic at relatively low concentrations. In addition, these compounds play a significant role in the formation of tropospheric ozone and have the potential to act as greenhouse gases, contributing to global warming. Some hydrocarbons are often good tracers for road traffic emissions, which makes them useful in understanding processes that effect other, but less exclusively traffic related pollutants, such as NO_x and PM_{10}. This includes the development and validation of quantitative assessment and numerical modelling techniques.

From this we can see why it is necessary to monitor air quality on a continual basis with as much spatial variation as practical. From such monitoring we can estimate the prevalence and concentrations of such trace hydrocarbon species and in conjunction with establishing spatial variation, deduce their effect on atmospheric chemistry. With the aid of source apportioning techniques, we can ascertain the major contributors to pollution episodes and hence control the emissions from such polluters. In addition, air quality standards based on air quality criteria, which are cause-effect relationships, observed experimentally, epidemiologically, or in the field, of exposure to various ambient levels of specific pollutants (Boubel *et al*, 1994) can be established from ambient air quality monitoring. Once air quality standards have been ascertained and imposed, monitoring is also required to ensure compliance, and to establish the effect of implementation of the standards on ambient levels and the environment as a whole.

1.2 AIMS AND OBJECTIVES

- The primary aim of this project is to characterise ambient hydrocarbon concentrations at a variety of sites in the Dublin area. To facilitate this, the functionality of the online system shall be extended to enable greater flexibility in sampling time and location by developing a mobile sampling method, the analysis of which shall incorporate the existing online equipment.

- A complete analytical validation of the mobile sampling and analysis method shall be conducted, with the aim of assuring the reliability of method performance.

- A mobile sampling pilot study shall be carried out, investigating the levels of hydrocarbon exposure for various commuting modes in Dublin City.

- Using both online and mobile sampling methods, the contribution of local traffic sources to ambient hydrocarbon levels in the Dublin area shall be examined.

- Comparisons of background and roadside concentrations, at both urban and motorway sites shall be undertaken.

- The factors influencing hydrocarbon concentrations at both urban and motorway sites shall be assessed in detail.

- The applicability of using various HC ratios to yield information in regard to emissions sources shall be thoroughly investigated. An examination into whether certain ratios can reveal insights into the relative age of air samples and hence how far pollution has travelled shall be explored, along with a thorough investigation into the ethene / acetylene ratio determining whether this ratio is a true reflection of catalytic converter activity and if not its uses in determining traffic source effects.

- The ability of the CALINE4 dispersion model to predict the traffic source effect at a motorway site will be investigated and the factors affecting model performance assessed.

1.3 OVERVIEW OF RESEARCH PROGRAMME

The research programme centres around an online system for the measurement of hydrocarbons, previously used in a doctoral research programme (Marnane, 2000) and now extended and developed by the validation of a mobile sampling method incorporating the online system for analysis. With the aid of the validated mobile sampling method and the online system run as standard, separate monitoring campaigns were carried out at a number of different sites, both urban and sub-urban in nature.

The first site where monitoring was carried out was at a sub-urban motorway (M4) site in Leixlip, Co. Dublin. Monitoring was carried out using the online system run as standard, where hourly data was obtained over an eight month monitoring period. This work formed part of a larger monitoring study, in which concentrations of other pollutants (CO, NO_X, PM_{10}), were also measured, with a view to evaluating dispersion model performance.

The second site where the online system was employed to take hourly measurements was at a heavily trafficked Dublin city centre junction, where previous monitoring had been carried out in 1998.

The mobile sampling method was developed and validated over a six-month period under such headings as : Specificity, Linearity, Limits of Detection, Accuracy, Precision, Robustnesss and Concentration range.

A short pilot study was carried out using the mobile air sampling method over a two week period, monitoring the concentrations of hydrocarbons commuters were exposed to while commuting in and out of Dublin city, using two separate modes of transport; cycling or public transport bus.

A five-week mobile sampling study was carried out to establish which gave a truer representation of an urban city centre background, a green field site or a building rooftop site. Representative urban background concentrations of a number of hydrocarbons were obtained.

A five-week study was also carried out at a sub-urban motorway site (M50), using the mobile sampling method, where the spatial variation of HC concentrations was examined. This involved short term sampling on both sides of the motorway. The results obtained were compared with those predicted with the CALINE 4 dispersion model.

1.4 THESIS OUTLINE

Chapter two contains a detailed discussion on the sources, effects and fates of hydrocarbons in the troposphere. Included in this are the effects of hydrocarbons on the formation of the secondary pollutant ozone, and the negative effect this compound can have at ground level. Section 2.6 deals with the effect meteorology has on air pollution, outlined in this section are also specific air pollution episodes, relating to meteorological conditions which were conducive to high ambient concentrations of pollutants. Common sampling and analysis techniques for hydrocarbon monitoring are discussed in section 2.7, along with a brief discussion on bio-monitoring. Section 2.8 outlines some of the various emission control techniques available, both regulatory and engineering. Section 2.9 presents a selection of recent monitoring studies carried out in Ireland, Europe the United States and elsewhere.

Chapter 3 describes the online monitoring system in some detail. Also included is a discussion on Quality Control and calibration procedures.

Chapter 4 incorporates the mobile sampling method development and validation procedures. Section 4.1 covers the method development while section 4.2 outlines the procedures carried out to validate the proposed mobile sampling method. The validation was carried out under the following headings; specificity, linearity, limits of detection, accuracy, precision, robustness and concentration range. Section 4.3 deals with sample stability while section 4.5 deals with the quality control procedures necessary to ensure reliable results. Section 4.6 outlines the results obtained for the pilot study using the mobile sampling method. The HC concentrations obtained for two separate modes of transport are compared and contrasted, with comparisons to similar studies carried out in different cities also outlined.

Chapter 5 is the first chapter which outlines results obtained for a long term online monitoring campaign, carried out at the M4 Motorway, at Leixlip, County Dublin. Section 5.1 outlines the

site details along with monitoring details. Sections 5.2 and 5.3 outline local and regional meteorological conditions encountered, respectively, while 5.4 presents the traffic data associated with the monitoring period. Sections 5.6 to 5.8 present detailed analysis of the data obtained. Section 5.9 compares the results obtained at Leixlip to those reported in separate world-wide studies.

Chapter 6 outlines the M50 motorway monitoring campaign at the Dublin sub-urban Tallaght location, where spatial and temporal variations in concentrations were investigated. Sections 6.1 and 6.2 describe the receptor locations and monitoring details. Section 6.3 presents the traffic data associated with the monitoring period. Sections 6.4 to 6.6 presents detailed analysis of the data obtained. Section 6.7 outlines the dispersion modelling approach used to estimate the road traffic emissions from M50. This section includes 2003 vehicle fleet estimations, composite emission factors derived from COPERT3 and daily modelling of emissions from the M50 using the CALINE4 line source dispersion model.

Chapter 7 presents data obtained from a Dublin City centre online monitoring campaign. Section 7.1 illustrates the site location and monitoring details, while section 7.2 presents the meteorological and traffic data for the period of interest. Sections 7.3 to 7.7 present detailed analysis of the data obtained and comparisons to separate world-wide studies. Section 7.8 compares the concentrations observed in 2003 to those obtained for a similar study at the same location in 1998.

Chapter 8 presents data obtained for two Dublin City centre background locations. Results obtained for a roof-top and green field location were compared and contrasted. Section 8.1 presents the site locations and sampling details. Sections 8.2 to 8.6 outline results obtained after detailed analysis. Section 8.7 compares the results obtained to those observed at each monitoring site within this research project.

Conclusions are drawn in chapter 8 based on the data obtained during each phase of research.

2. BACKGROUND TO HYDROCARBON MONITORING

2.1 INTRODUCTION

The earth's atmosphere is composed roughly of 79% nitrogen, 21% oxygen, varying amounts of water vapour, 0.95% argon, 0.036% carbon dioxide and a host of minor trace substances. Those substances we deem to have an adverse effect we call "pollution" after the Latin word for "dirt" (Lipfert, 1994).

Due to recent advances in measurement science and technology, our ability to study the composition of the atmosphere in ever-greater detail is increasing (Lewis, 2000), giving scientists the capacity to analyse and investigate the composition of these trace substances in the atmosphere. This is particularly true of the organic chemical composition of the atmosphere (Hewitt and Sturges, 1993).

The most studied compounds in this group are volatile organic compounds (VOCs). These substances are a topic of interest in many disciplines, such as food, flavour and fragrance, medical and forensic sciences. The main area dealing with VOCs is environmental chemistry, due to their contribution to stratospheric ozone depletion, tropospheric ozone formation, toxic and carcinogenic human health effects and their potential to act as greenhouse gases (Dewulf *et al.*, 2002). Frequently used definitions are based on vapour pressure. In the USA, VOCs are defined as organic compounds that have a vapour pressure more than 13.3 Pa at 25 °C (ASTN test method D3960–90). The USEPA defines VOCs as having a vapour pressure of 0.13 Kpa at 20°C and 1 atm (Derwent, 1995). In the European Union, a common definition is that VOCs are organic compounds with a vapour pressure above 10 Pa at 20 °C (CEC, 1999a). The Australian National Pollutant Inventory defines a VOC as a chemical compound based on carbon chains or rings (and also containing hydrogen) with a vapour pressure greater than 2 mm of mercury (0.27kPa) at 25 °C, excluding methane.

Hydrocarbons are a group of VOCs, defined as "organic compounds composed entirely of hydrogen and carbon", and as raw materials are derived primarily from petroleum, coal tar and plant sources (Lewis, 1993).

These are probably the most widely studied and ubiquitous class of organic compounds in the troposphere. While methane is the single most abundant hydrocarbon in the atmosphere (1.7 parts per million volume), there is a whole range of hydrocarbon species with a carbon skeleton containing 2 or more carbons which are present as parts per billion by volume (ppbv) or lower concentration (Hewitt and Sturges,1994). Though the abundance of these compounds are orders of magnitude lower than methane, their atmospheric reactivity in terms of carbon conversion can exceed that of methane (Erhalt and Rudolph, 1984).

2.2 HYDROCARBON SPECIES

Compounds containing only carbon and hydrogen are termed hydrocarbons. If a hydrocarbon consists of only single bonds, it is called a saturated hydrocarbon. Included in this classification are alkanes and cyclo-alkanes. Unsaturated hydrocarbons contain one or more carbon double or triple bonds. There are three classes of unsaturated hydrocarbons: alkenes, alkynes and aromatic hydrocarbons.

2.2.1 Saturated hydrocarbons

These are the simplest class of organic compounds with a general formula C_nH_{2n+2}. Thus, from the number of carbon atoms in a molecule, it is a simple process to determine the number of hydrogens and hence the molecular formula. For alkanes of size C_4 or greater, structural isomerism, or compounds having the same molecular formula but different orders of attachment of atoms, is displayed. For the molecular formula C_4H_{10}, two orders of attachment of atoms are possible. In one, the 4 carbon atoms are attached in a chain, in the second they are attached three in a chain and the fourth as a branch on the three chain carbon.

The isomeric alkanes shown in Figure 2.1 are named butane and iso-butane. They are different compounds and have different physical and chemical properties. For example, the boiling points of the two compounds differ by greater than 10°C (Zuhmdahl, 1989).

(butane) (iso-butane)

CH3-CH2-CH2-CH3 CH3-CH-CH3

CH3

Figure 2.1 Isomeric structures of butane and iso-butane

The number of structural isomers increases with an increase in carbon number. In addition to the branched and un-branched hydrocarbons shown above, an additional form of alkane exists. A molecule that contains carbon atoms joined in a closed ring structure is termed a cyclic hydrocarbon, when all the carbons of this ring are saturated, we obtain a molecule termed a cycloalkane.

Cycloalkanes of ring size 3 to 30 are found in nature. Cyclopentanes and cyclohexanes are especially abundant in nature and have therefore received the most attention (Brown, 1988). The use of carbon bonds to close the ring structure means that cycloalkanes contain 2 fewer hydrogens than an alkane of similar carbon number. A general formula of C_nH_{2n} is obtained.

Alkanes and cycloalkanes can be either solid (paraffin wax), liquid (petrol, diesel) or gas (natural gas) at room temperature. As boiling points generally increase with an increase in carbon number, the lighter, lower molecular weight alkanes are gasses at room temperature and the heavier waxes are solid. This increase in boiling point, with increased carbon number, is due to an increase in dispersion forces as molecular weight increases.

Alkanes and cycloalkanes are generally unreactive to most reagants, a behaviour consistent with the fact that they are non-polar compounds and are composed entirely of strong *sigma* (single) bonds (Brown, 1988).

2.2.2 Unsaturated hydrocarbons

Alkenes, alkynes and aromatics are the three classes of unsaturated hydrocarbons.

Hydrocarbons that contain a carbon-carbon double bond are termed alkenes (sometimes named olefins), and have a general formula C_nH_{2n}. The simplest alkene C_2H_4, ethylene (ethene) has the structure :

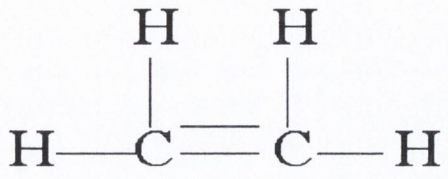


Fig 2.2 Ethene (ethylene) structure

The double bond consists of a strong C-C sigma bond and a weaker C-C π bond formed between the *p* orbitals. The π bond formation prevents rotation of the two CH2 groups around the double bond. This restricted rotation about the double bond results in alkenes exhibiting *cis-trans* isomerism. For example, there are two stereo-isomers of 2-butene (Figure 2.3). Identical substituents on the same side of the double bond are designated *cis* and on the opposite side are labelled *trans*. Similar to alkanes, alkenes can exist as cycloalkenes.

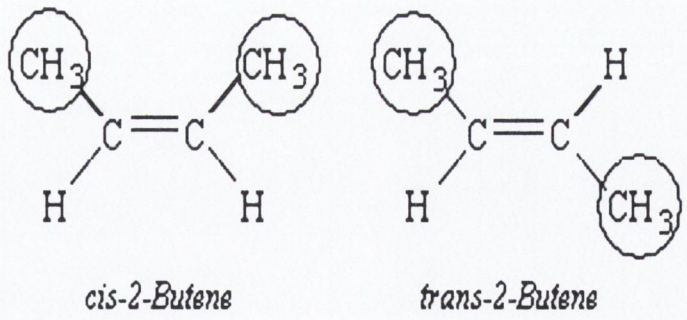


Figure 2.3 Stereo-isomers of 2-butene

Alkynes are unsaturated hydrocarbons containing a triple carbon-carbon bond. The simplest alkyne is ethyne (acetylene) shown in Figure 2.4. The triple bond can best be described as one sigma bond and two π bonds involving two 2p orbitals on each carbon atom.

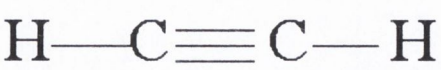


Figure 2.4 Structure of ethyne (acetylene)

Because both alkenes and alkynes are non-polar, and the only interactions between molecules are dispersion forces, their physical properties are similar to those of alkanes. However, in contrast to alkanes, the alkenes and alkynes react with a variety of compounds (Brown, 1988). Because they are unsaturated, their most important reactions are addition reactions across the double or triple bond.

A special class of cyclic unsaturated hydrocarbons is known as aromatic hydrocarbons. The simplest of these is Benzene (C_6H_6) with a planar structure illustrated in Figure 2.5.
In general these compounds are hexagonal ring compounds with three double bonds. They are by definition, cyclic, planar, and conjugated systems with 4n+2 electrons (Brown, 1988). The hexagonal ring can have substituent groups attached, for example toluene, which has a methyl group attached (Figure 2.5).

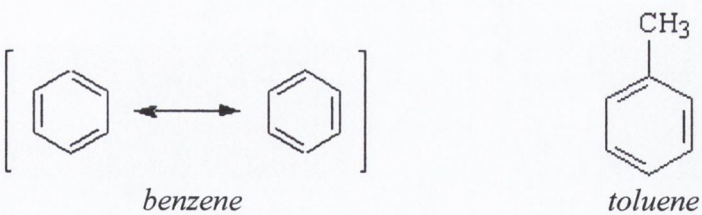


Figure 2.5 Structures of benzene and toluene

The delocalization of the π electrons makes the benzene ring behave quite differently from typical unsaturated hydrocarbons. As stated earlier, unsaturated hydrocarbons normally undergo rapid addition reactions, aromatics do not. Rather, substitution reactions take place where hydrogen atoms are replaced by other atoms (i.e, toluene, Figure 2.5). Substitution

reactions are more characteristic of saturated hydrocarbons and indicates the greater stability of the delocalized π electron system associated with aromatic compounds (Zuhmdahl, 1989).

Benzene is the simplest aromatic compound. More complex aromatic systems can be viewed as consisting of "fused" benzene rings. These compounds are termed poly-aromatic hydrocarbons of which napthalene and anthracene are examples.

2.3 SOURCES OF HYDROCARBONS

Air pollution emitted directly into the atmosphere is termed primary, for example, stack emissions from an industrial plant, or HC emissions from the exhaust of a vehicle. In contrast secondary pollutants are not emitted directly, but are formed within the atmosphere itself, the most widely studied of which is ozone (O_3).

The major sources for HCs are more diverse than most primary pollutants and encompass both anthropogenic and biogenic sources, many of which emit a range of individual compounds of which some 200 HC species have been analysed and measured in some ambient air samples (Harrison, 2001).

There are two major reasons for interest in the HC concentrations in the atmosphere. The first is due to the toxicity of such pollutants as benzene and 1,3 butadiene, the second results from the ozone formation potential of the emitted HC pollutants.

2.3.1 Anthropogenic sources

Anthropogenic (man-made) sources can be grouped into two main sectors based on mobility, and categorised as mobile and stationary sources.

Mobile sources

A mobile source of air pollution is one which is capable of moving from one place to another under its own power (Boubel *et al.*, 1994). The chemical process on which propulsion of the mobile source relies is known as combustion. The balanced chemical equation 2.1 for the combustion of methane is shown as an example.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_20\,(g) + \text{energy} \qquad (2.1)$$

Within an internal combustion engine, the ideal combustion process would follow that seen above and would complete as indicated in equation 2.2:

$$\text{Fuel (HC)} + \text{air } (O_2 + N_2) \rightarrow CO_2 + H_20 + \text{unaffected } N_2 \qquad (2.2)$$

In reality the process is represented by equation 2.3:

$$\text{Fuel} + \text{air} \rightarrow \text{unburned / partially burned HC} + NO_X + CO + CO_2 + H_20 \qquad (2.3)$$

The more incomplete the reaction the greater the amount of unburned or partially burned hydrocarbons (Friedrich and Obermeier,1999).

The internal combustion engine, which relies on the above process can be classified as reciprocating or rotary, spark ignition or compression ignition, and two-stroke or four-stroke; the most familiar combination, used from automobiles to lawn mowers, is the reciprocating, spark-ignited, four-stroke petrol engine.

Vehicle emissions are dependant upon many variables, of which vehicle condition, vehicle speed (engine load), driving behaviour, fuel type and quality, and ambient temperature are the more important factors.

Vehicle condition

There is a definite relationship between vehicle age, condition and associated emissions (Anilovich and Hakkert, 1996). Newer, well maintained vehicles emit less pollutants than older vehicles or relatively new, yet poorly maintained vehicles. However, emission differences between well maintained and badly maintained vehicles is larger than the age-dependent deterioration of emissions (Revitt *et al.*, 1999).

Vehicle emission control systems begin to function improperly while the vehicles are in use. As a result, used and ageing vehicles have become a major problem of air pollution in many urban areas. It has been frequently reported that the majority of vehicle emissions come from

roughly 10% to 30% of used vehicles which are poorly maintained or have malfunctioning emission control systems (Bishop *et al.*, 1997;Calvert *et al.*,1993).

In a bid to control these polluters, the department of transport initiated regulatory testing on vehicles of five years of age or greater, to ensure all cars being driven on Irish roads had a certificate of road worthiness. The National Car Test (NCT) was introduced on the 4th of January 2000. Ireland is one of the last countries to comply with the EU Directive (CEC, 1996a), which makes car testing compulsory in EU member states and is aimed primarily at improving road safety and enhancing environmental protection.

The cost effectiveness of this scheme has not yet been evaluated. Such schemes have recently been called into question as a tool to identify highly polluting vehicles, as actual vehicle emissions on the road have been discovered to be, on average, one and a half to two times higher than the design values to which the vehicles were certified, with some vehicles having emissions 50 times higher (Ramsden, 1997). As most test procedures do not account for the real world driving conditions such as acceleration and deceleration cycles, the vehicles passing the emission tests may still be gross polluters in real world driving conditions (Washburn *et al.*, 2001).

Vehicle speed

It is generally admitted that pollutant emissions are dependant on the speed level (Andre and Hammerstrom, 2000). Indeed, the specific emissions which are currently measured as a function of the average speed of a driving cycle, show a clear speed dependency.

The specific driving mode will have an extreme effect on the emissions as discussed by Friedrich and Obermeier (1999) and illustrated in Table 2.1.

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 3-way catalyst	0.04	0.03	0.06	0.48
Passenger car	Diesel	0.04	0.05	0.12	0.23

Table 2.1 Exhaust hydrocarbon emissions from different vehicle types due to different driving modes, g / Km (Friedrich and Obermeier, 1999)

Lower average speeds relate to more "stop-go" driving conditions frequently observed in urban conditions. Urban driving modes are associated with an increase in periods of acceleration and deceleration, leading to the higher emissions observed.

In addition to vehicle speed, driver behaviour can have a significant effect on emissions. "Driver variability" describes the differences in vehicle operating behaviour between drivers. These differences may include variations in the duration, frequency or intensity of different driving modes such as cruise, acceleration and deceleration (Holmen and Niemeier,1998). Since the operation of a vehicle directly affects its exhaust gas concentrations, it is readily apparent how individual driving habits and behaviour can effect exhaust emissions. This was investigated by Holmen and Niemer (1998), who found that the variability in driving styles may also have important implications on how vehicle fleet emissions testing is performed. For example, a well-moderated driver will produce different emission levels when driving the FTP dynamometer exhaust emission testing cycle than a less-experienced driver.

Fuel type and quality

The two main fuels used in Europe are petrol and diesel and are likely to dominate for the foreseeable future (Harrison, 2001). Due to the different physical characteristics of both fuels, different forms of internal combustion engines are required for each fuel type. Petrol consists mainly of HC compounds in the C_5-C_{10} range whereas diesel fuel consists of C_{15}-C_{25} (Zuhmdahl, 1989). As petrol requires a spark to ignite the fuel, such engines are termed spark

ignition engines. Diesel fuel is ignited by compression, hence the term compression ignition engines for the combustion of diesel fuel.

The majority of vehicles (82%) in Ireland rely on petrol as their primary fuel (Marnane., 2000). The majority of diesel engines are installed in heavy goods vehicles, light goods vehicles and buses. As a result the vast majority of HC emissions are anticipated to emanate from petrol engines.

Three important petrol fuel characteristics are the T_{50}, T_{90} and RVP values. T_{50} and T_{90} values are the 50% and 90% distillation temperatures. Lower T_{90} can lead to increased evaporative emissions but reduced total non-methane hydrocarbon emissions (Rutherford *et al.*, 1995). The Reid Vapour Pressure (RVP) is an indicator of the volatility of the fuel, lower RVP values giving reduced evaporative emissions.

In 2000, in accordance with EU directive 98/70/EC (CEC, 1998b), relating to the quality of petrol and diesel fuels, limit values were set as to the quality of fuels in the market amongst the EU. In addition to these limits shown in Table 2.2, the aromatic content must be reduced to 35% by 2005.

Parameter	Limit	
	minimum	maximum
Research octane number (RON)	95.00	-
Reid Vapour pressure (Summer only)	60.00 kPa	-
Distillation		
Evaporated at 100°C	46 % v/v	-
Evaporated at 150°C	75 % v/v	-
Hydrocarbon analysis		
Olefins (alkenes)	-	18 % v/v
Aromatics	-	42 % v/v
Benzene	-	1 % v/v
Oxygen content	-	2.7 % m/m

Table 2.2 Selected specifications for market fuels to be used for vehicles equipped with positive-ignition engines (CEC, 1998b)

Results of analysis of 1998 Irish fuels by Broderick and Marnane (2002), indicated that fuels in the Irish market were already close to meeting EU fuel specifications and a comparison between the fuel and ambient HC components indicated good agreement.

While effects of fuel quality changes alone on emissions from fixed technology engines are relatively small compared to reductions achievable from changes to engine technology, real benefits from changes to fuel quality arise when they are used to enable new technologies. The introduction of Unleaded Gasoline for catalyst cars, low sulphur diesel fuels for Euro 2 diesel engines and development of detergent additives to prevent problems in fuel injected engines show where fuel properties are effective as an enabling tool (CONCAWE, 2003).

The conventional wisdom is that there is no relationship between fuel economy and motor vehicle emissions, at least for new cars (Harrington, 1997). As cars age, however, the emission control equipment tends to break down, providing reason to think that the conventional wisdom might do the same. After linking EPA fuel economy certification data to a large database of motor vehicle emission measurements collected by remote sensing Harrington (1997), found that better fuel economy is strongly associated with lower emissions of CO and HC and that the effect gets stronger as vehicles age.

Ambient temperature

The two extremes of ambient temperature can have a significant effect on vehicle emissions. At low ambient temperatures, the increased time taken for catalytic converters to reach their optimum working temperature leads to an increase in exhaust emissions. Emissions associated with such conditions are termed cold start emissions. At higher ambient temperatures, evaporative emissions can be significant (Field *et al.*, 1994). These can take the form of diurnal, running or hot soak losses.

Cold start emissions

Most journeys are of short duration (AEAT, 1999) and take place in urban areas. These journeys will start (and most of them end) with the vehicle significantly below its normal operating temperature. This situation is exacerbated with low ambient temperatures, inhibiting a rapid rise in engine temperature. Under these conditions the emission of most pollutants will

be higher than if the catalyst was working at optimum. Thus, nowadays, cold start emissions are the most important source for traffic related HC emissions in most European countries (Heeb *et al.*, 2003).

For 15 petrol engines examined by the DETR in 1999 (AEAT, 1999), a cold start at a -7°C ambient approximately doubled the emissions relative to a hot start at 20°C ambient. Heeb *et al.* (2001), examined the cold start emissions of five EURO-0, twenty EURO-1, eighteen EURO-2 and six EURO-3 passenger cars. At room temperature a clear reduction of 94%, 81% and 85% was found for the methane, benzene and alkyl benzene cold start emissions from EURO-0 to EURO-3 technology, respectively.

Evaporative emissions

Evaporative emissions of petrol fuel vapour from the tank and fuel delivery system in vehicles constitute a significant fraction of total HC emissions from road transport (www.aeat.co.uk/netcen/airqual/naei/roadproj).

Evaporative emissions are dependent on ambient temperature and the volatility of the fuel and, in the case of diurnal losses, on the daily rise in ambient temperature. Fuel volatility is usually expressed by the empirical fuel parameter known as Reid vapour pressure (RVP).

There are three different mechanisms by which gasoline fuel evaporates from vehicles:

i) Diurnal loss

By definition (USEPA, 1998b), diurnal losses are those emissions associated with daily temperature change, its effect on vaporization of a vehicle's fuel, and the expansion of fuel vapor. Evaporation through "tank breathing" will occur each day for all vehicles with petrol fuel in the tank, even when stationary.

ii) Hot soak losses

Hot soak losses are, by definition, the evaporative hydrocarbon emissions which escape from a vehicle during the first hour after the engine is stopped. They arise from the transfer of heat from the engine and hot exhaust, to the fuel system, where fuel is no longer flowing.

Carburettor float bowls contribute significantly to hot soak losses. The limited data in this area suggests that the emissions are not distributed evenly throughout the hour, but decline as the hour passes (USEPA, 1998a). This is likely due to the cooling of the vehicle and its evaporative system.

iii) Running loss

Running losses are evaporative losses that occur while the vehicle is in motion and are defined as the non-tailpipe hydrocarbon emissions produced, or given off, by a vehicle while it is "in operation." In operation means that the engine is running, even if the vehicle is at rest (CRC, 1999). There are two components to running losses; i.e. fuel, and non-fuel. Fuel related emissions come from many places; i.e. joints, vents, leaks, and permeation through the rubber-like components of the fuel system. Non-fuel emissions result from the out-gassing of the paint, adhesives, vinyl, tires, and others, such as windshield washer solvent, and air conditioning refrigerant. Running losses are difficult to distinguish from tail-pipe emissions in normal ambient air monitoring and additional analysis is usually needed to distinguish the two.

Diurnal evaporative emissions were observed in studies on ambient HC concentrations by Na *et al.* (2003); Gou *et al.* (2004);Ho *et al.* (2004) and Bourbon *et al.* (2002). Each showed a rise in HC concentrations with temperature for those compounds associated with evaporative emissions.

Running losses were examined in detail by the CRC (1999). Running loss emissions were measured in a Running Loss SHED (RL-SHED). The major causes of high running loss emissions were liquid leaks on carburetor equipped models. Speciation analysis of the end-of-test data indicated that approximately 50% of the emissions come from vapor sources and 50% come from liquid sources (leaks in the fuel line etc.). The program identified 30 vehicles as candidates for repair and retest. The result showed a very high (>90%) effectiveness for the repairs. This shows that vehicle age and hence condition is the major contributing factor for vehicles with associated high levels of running loss evaporative emissions.

A report by Pierson *et al.* (1999), for the air and waste management association evaluated evaporative HC emissions from light-duty spark-ignition vehicles. Emissions from volunteer

fleets of in-use vehicles were assessed in chassis dynamometer and sealed housing for evaporative determination (SHED) tests. Running-loss emission rates were seen to be critically dependent on driving cycle and conditioning, decreasing steeply with increasing vehicle speed. They increased with ambient temperature and fuel Reid vapour pressure (RVP) at rates of ~7%/°F and 46%/psi. Hot soak and diurnal loss emission rates all increased with increasing ambient temperatures, at rates in the range of 2.2-4.6%/°F. Hot soak and diurnal emission rates increased with increasing fuel RVP, at rates between 34% and 47%/psi increase in RVP (at 95 °F ambient temperature). Vehicle-to-vehicle variation in HC emission rates was very large in all vehicle categories examined.

Anthropogenic Stationary sources

Stationary or point source emissions can emanate from a variety of sources linked to various processes as diverse as pharmaceutical production to solvent and paint manufacture to waste disposal in landfill sites. A common denominator amongst these sources is that they are controlled by the EPA under the Integrated Pollution Prevention and Control (IPPC) licensing, previously Integrated Pollution Control (IPC) licensing.

EU directive 96/61/EC (CEC,1996b), covering the implementation of IPPC licenses defines the basic obligations to be met by all the industrial installations concerned, whether new or existing. These basic obligations cover a list of measures for tackling discharges into water, air and soil and for tackling waste, wastage of water and energy, and environmental accidents. They serve as the basis for drawing up operating licences or permits for the installations concerned. Central to the system is the requirement of an operating license, the aim of which is to prevent the release of pre-scribed substances, to reduce them to a minimum or to render them harmless if they are released. The EPA continually monitors the level of adherence to the licensing requirements and takes action against companies seen to breach the terms of the license. The licensing is applied to 13 sectors of Industry outlined in Table 2.3. The majority of Class 5 facilities are located in Dublin or Cork.

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	

Table 2.3 Industrial sectors covered by IPPC licensing (EPA, 2002)

From the commencement of IPC licensing in 1994 to the end of 2002, a total of 663 IPC applications were received. During 2002, 34 new applications were received, of which five were for reviews of existing licences. The Intensive Agriculture sector had the highest number of applications in 2002 (11 applications).

The EU Council Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC) was transposed into Irish law in 2003 with the enactment of the Protection of the Environment Bill, 2003.

The changes imposed by this bill significantly strengthen the regulatory framework for the control of emissions and protection of the environment. Amongst the key changes from the IPC licensing system are a change in the technical basis of the licensing system from best available technology not entailing excessive costs (BATNEEC) to best available techniques (BAT), a greater emphasis on pollution prevention in the licensing system and on minimising environmental problems at source and the extension of the scope of licensing for the purpose of fully implementing the Directive, bringing more activities into the licensing system in areas such as intensive agriculture, the treatment and processing of milk, the slaughter of cattle, food production, and the production of paper, pulp or board (EPA, 2002a).

The EPA is obliged to keep a statutory Register of Licences. This Register is available for inspection at the headquarters and regional inspectorates of the Agency, and at relevant planning authorities.

In addition council directive 1999/13/EC was implemented in November 2002, which provided a means for controlling VOC emissions from the solvent industry where those per annum emissions were less than the 10 tonne / annum limit, above which an IPPC license is required.

The extent of VOC emissions from point sources has been documented to a considerable extent worldwide. Ho *et al.* (2004), investigated their prevalence along with mobile and evaporative emissions in Hong Kong, while Vrieling and Neustadt (2003), examined the effect turbulence has on multiple stack emissions, where stacks are located in close proximity. Saarinen (2003), investigated the comparability of Industrial emissions and concluded that any international comparisons made are seriously restricted by the fact that the coverage of the different emission sources and operating conditions is disparate.
In addition, Grodziska *et al.* (1997), concluded that the protection of Polish mountain forest health against deterioration requires reduction of industrial emissions, changing of the existing forests into genotypes that are less sensitive to air pollution and more compatible with local habitats, and recultivation of deteriorated forests. Finally, Yang *et al.* (1997), reported the results from an ongoing study of outdoor air pollution and the health of persons living in the communities in close proximity to petrochemical industrial complexes. It was concluded that exposure to petrochemical air emissions may be associated with increased rates of acute irritative symptoms.

2.3.2 Biogenic sources

It is now well known that reactive organic gases are emitted from vegetation, including urban landscapes, agricultural crops, and natural plant communities. The global budget of volatile organic compounds (VOC) is dominated by biogenic emissions (Guenther *et al.*, 1995) and biogenic volatile organic compound (BVOC) emissions play important roles in tropospheric ozone formation, global tropospheric chemistry, and balancing the global carbon cycle (Fesenfeld *et al.*,1992). Vegetative emissions are as reactive or more reactive than the VOC exhaust and evaporative emissions from motor vehicles, and can have higher ozone-forming potential (Carter, 1994:Benjamin and Winer, 1998).

Because biogenic VOCs are emitted into the atmosphere as a by-product of natural processes, their emissions are strongly affected by ecosystem-dependent factors. Human activities such as urbanization or agriculture can change land cover, impacting the magnitude, species, and spatial distribution of vegetation (Steiner *et al.*,2002).

The VOC emission rates for aspen, silver birch and tea-leafed willow were measured in the boreal vegetation zone in Finland by Hakola *et al.* (1998). During the growing season hydrocarbon emissions of isoprene, ethene, 1-butene and propene were all detected.

For the whole of Finland, containing a portion of the boreal vegetation zone which is one of world's largest forest areas, covering a land surface of 15.8×10^6 km^2 (Archibold, 1995), biogenic emissions were calculated to be 318 kiloton per annum, which exceeds the annual anthropogenic VOC emissions of 193 kiloton (Mroueh, 1994). The biogenic emissions are affected by a number of factors; temperature, light intensity, plant phenology, injury, stress, etc. (Kesselmeir and stoudt, 1999), making emission inventories difficult.

In addition to biogenic natural emissions, extreme natural events can also have an effect on HC emissions. Earthquakes, volcanic eruptions and subsequent bio-mass burning and wildfires can release significant emissions of hydrocarbons (Young *et al.*, 2003).

2.4 EFFECTS OF HYDROCARBONS

Human exposure to air pollutants may result in a variety of health effects depending on the type of pollutant; the magnitude, duration and frequency of exposure; and the associated toxicity of the specific pollutant (WHO, 1995). Mixtures of chemicals can have additive, synergistic or antagonistic effects. In general, our knowledge of these interactions is rudimentary. One exception can be found in a WHO publication on summer and winter smog (WHO, 1992), which deals with commonly recurring mixtures of air pollutants.

Individual organic compounds may have important impacts on human health through direct mechanisms in addition to their indirect impacts through photochemical ozone formation (Derwent,1995). Some organic compounds effect the human senses through their odour, others exert a narcotic effect, but most importantly, some are toxic (WHO,1995).

2.4.1 Individual Hydrocarbons

With the advent of such air quality monitoring networks as the Photochemical Air Monitoring System (PAMS) in the US and the National Hydrocarbon Monitoring Network in the UK, a better understanding of the makeup of the ambient atmosphere in regard to individual species and their ambient concentrations has been obtained. It has also facilitated better understanding of the ozone formation process and the particular HC species which contribute most to its formation (categorised as the ozone formation potential). From this form of network analysis we can determine which chemicals are present in the air, at what levels, and whether likely levels of exposure are hazardous to human health and the environment.

Although the majority of HC compounds in the C_2-C_{10} range are non-toxic or mildly toxic at typical ambient concentrations, several HC compounds are associated with serious health effects with long term exposure. The two main pollutants in this category are benzene and 1, 3 butadiene.

Benzene

Benzene is classified in Group 1 of the International Agency for Research on Cancer, which defines this compound as being carcinogenic to humans. In addition the USEPA term it a class A carcinogen. Numerous case reports and series have suggested a relationship between exposure to benzene and ill health. Three independent cohort studies have demonstrated an increased incidence of acute nonlymphocytic leukaemia in workers exposed to benzene (Arp *et al.*, 1983; Decoufle *et al.*, 1983, Bond *et al.*,1986). In a Chinese retrospective cohort study, encompassing 28 460 workers exposed to benzene in 233 factories, 30 cases of leukaemia (23 acute, seven chronic) were found, as compared to four cases in a reference cohort of 28 257 workers in 83 machine production, textile and cloth factories (Yin *et al.*, 1987).

Chronic exposure to low concentrations of benzene also causes blood disorders and damage to bone marrow, inducing aplastic anemia. Reproductive effects have also been reported for women exposed by inhalation to high levels, and adverse effects on the developing fetus have been observed in animal tests. (www.epa.gov/ttnatw01/hlthef/benzene.html).

Acute health effects in humans include dizziness, headaches, irritation of skin, eyes and throat and unconsciousness. However the concentrations frequently encountered in the ambient atmosphere are unlikely to be a the requisite levels to cause such short term effects.

Table 2.4 below describes the health effects due to inhalation of benzene (Rushton and Cameron, 1999).

Effect	Description	Length of exposure	Concentration (ppm)
Death		5-10 min	20000
Central Nervous System	Vertigo, drowsiness, headache	Hours	250-500
Haematological	Aplastic anemia, Pancytopenia	Years	100
Mutagenic	Chromosome aberrations	Years	20-100
Carcinogenic	Leukaemia	Years	20-50

Table 2.4 Health effects due to inhalation of benzene (Rushton and Cameron, 1999)

1,3 butadiene

1,3 butadiene is a probable carcinogen for humans, as defined by the IARC Group 2A, and is classified as Group B2, probable human carcinogen, by the USEPA.

Irritation or effects on the central nervous system may be associated with acute exposure to high concentrations of butadiene. However, the potential carcinogenic effect of long term exposure is the cause for most concern in regard to this compound.

1,3-butadiene has induced a wide variety of tumours in rats and mice, with mice being considerably more sensitive than rats. There are widely divergent points of view as to which animal species – the rat or the mouse – is most appropriate for use in human risk assessments for butadiene (Bond *et al.*, 1995; Melnick *et al.*, 1995).

Epidemiological studies, while relatively few in number, suggest that there is equivocal evidence for an association between exposure to butadiene and lymphohaematopoietic cancer (WHO, 1995). A large epidemiological study of synthetic rubber industry workers demonstrated a consistent association between 1,3-butadiene exposure and occurrence of leukemia (Delzell *et al.*, 1996; Macaluso *et al.*, 1996). Several epidemiological studies of workers in styrene-butadiene rubber factories have shown an increased incidence of

respiratory, bladder, stomach, and lymphato-hematopoietic cancers. However, these studies are not sufficient to determine a causal association between 1,3-butadiene exposure and cancer due to possible exposure to other chemicals and other confounding factors (USEPA 1999a, CalEPA 1997).

The studies carried out to date do not produce a conclusive picture, and it is clear that there is a high degree of uncertainty in any conclusions drawn from these studies. The Expert Panel on Air Quality Standards (EPAQS) conducted an assessment of the health impact of 1,3-butadiene and recommended an air quality standard of 1 ppb expressed as an annual running mean (Dollard *et al.*, 2001) in the UK.

Acute (short-term) exposure to 1,3-butadiene by inhalation in humans results in irritation of the eyes, nasal passages, throat, and lungs (www.epa.gov/ttnatw01/hlthef/).

In addition to the two compounds discussed above, several HC compounds, which in addition to benzene make up the BTEX are also of significant interest. Toluene, ethylbenzene and the xylene monomers complete this group.

Toluene

The USEPA has classified toluene as a Group D, not classifiable as to human carcinogenicity. However the WHO guidelines on exposure recommend an air quality limit of 2 ppbv averaged over 24 hours (WHO, 1995). The central nervous system (CNS) is the primary target organ for toluene toxicity in both humans and animals for acute (short-term) and chronic (long-term) exposures. CNS dysfunction and narcosis have been frequently observed in humans acutely exposed to toluene by inhalation; symptoms include fatigue, sleepiness, headaches, and nausea. CNS depression has been reported to occur in chronic abusers exposed to high levels of toluene. Chronic inhalation exposure of humans to toluene also causes irritation of the upper respiratory tract and eyes, sore throat, dizziness, and headache. Human studies have reported developmental effects, such as CNS dysfunction, attention deficits, and minor craniofacial and limb anomalies, in the children of pregnant women exposed to toluene or mixed solvents by inhalation. Reproductive effects, including an association between exposure

to toluene and an increased incidence of spontaneous abortions, have also been noted. However, these studies are not conclusive due to many confounding variables.

The xylene monomers

Acute (short-term) inhalation exposure to mixed xylenes in humans results in irritation of the eyes, nose, and throat, gastrointestinal effects, eye irritation, and neurological effects. Chronic (long-term) inhalation exposure of humans to mixed xylenes results primarily in central nervous system (CNS) effects, such as headache, dizziness, fatigue, tremors, and incoordination; respiratory, cardiovascular, and kidney effects have also been reported. EPA has classified mixed xylenes as a Group D, not classifiable as to human carcinogenicity. (www.epa.gov/ttnatw01/hlthef/).

Ethyl benzene

Chronic (long-term) exposure to ethylbenzene by inhalation in humans has shown conflicting results regarding its effects on the blood. Animal studies have reported effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene (www.epa.gov/ttnatw01/hlthef/). Limited information is available on the carcinogenic effects of ethylbenzene in humans. In a study by the National Toxicology Program (NTP), exposure to ethylbenzene by inhalation resulted in an increased incidence of kidney and testicular tumors in rats, and lung and liver tumors in mice. EPA has classified ethylbenzene as a Group D, not classifiable as to human carcinogenicity. The IARC classifies ethylbenzene as a possible human carcinogen, in Group 2B.

The compounds detailed above are generally termed toxic hydrocarbons. Others may be classified as asphyxiants (e.g propene, ethane) while others can act as halucinogens at high concentrations (e.g n-pentane).

Although everyone is at risk from the health effects of air pollution, certain sub-populations are more susceptible of which age and health are important factors. The elderly and people suffering from cardio-respiratory problems such as asthma appear to be the most susceptible groups (Niven and Longhurst, 1995).

Many studies have already linked environmental or occupational exposure to air pollutants with adverse health effects in adults (Nakai *et al.*, 1995). However, children differ from adults as regards exposure, physiological factors, and pharmacokinetics (Needham and Sexton, 2000). Moreover, children are considered as potentially more vulnerable than adults, because their health is more susceptible to hazardous pollutants (Guzelian *et al.*, 1992; Asprea *et al.*, 2000). Consequently, within the last decade or so, there has been a growing concern over the relationship between children's environmental exposure and the health effects (Rogan *et al.*, 1995). For example, (Pearson *et al.*, 2000) reported that exposure to air pollutants emitted from automobiles is closely associated with childhood leukemia and other childhood cancers. Wang *et al.* (1999), observed a statistically significant association between outdoor air pollution and asthma in adolescents, after controlling for potential confounding variables and White *et al.* (1994), found that among black children from low-income families in Atlanta, asthma may be exacerbated following periods of high ozone pollution.

Effects on plants

Unlike other air pollutants, ethylene is a plant hormone and endogenous ethylene controls a variety of plant phenomena including growth, flowering and senescence (Tonneijck *et al.*, 2003). Tonneijck used data from a multi-year (1977–1983) biomonitoring programme with marigold and petunia around polyethylene manufacturing plants and analysed plant responses to atmospheric ethylene to determine the area at risk for the phytotoxic effects of this pollutant. In both species, flower formation and growth were severely reduced close to the emission sources and plant performance improved with increasing distance. The general effect of atmospheric ethylene is a reduction in vegetative growth, flower and fruit development and an acceleration of normal ageing of plant tissues (Manning and Feder, 1980).

Plant response to ethylene is highly species-specific (Heck and Pires, 1962 and Woltering, 1987) and sensitive plant species, which respond with rather specific and visible symptoms, can be used as indicators in monitoring networks to demonstrate the adverse effects of atmospheric ethylene.

Effects on the atmosphere

Virtually all HC compounds of anthropogenic origin, are emitted into the atmospheric boundary layer, the shallow region of the troposphere next to the earth's surface. The more reactive compounds are oxidised in the boundary layer, however, the less reactive compounds survive and are transported above the boundary layer and into the free troposphere, during particular meteorological events (i.e convection). If any of these compounds have the ability to absorb solar or terrestrial infrared radiation, then they may contribute to the greenhouse gas effect. Such compounds would be classified as radiatively active gases and their relative effectiveness compared with CO_2 can be expressed through their global warming potentials (Derwent, 1995).

2.4.2 Tropospheric Ozone formation and effects

The presence of relatively low levels of ozone in the troposphere is extremely important, as photolysis at wavelengths >290nm occurs in the troposphere to form the excited oxygen, O (^1D) atom, which are then deactivated to ground state oxygen O (^3P) or react with water vapour to form OH radicals. OH radicals are the key reactive species in the atmosphere, reacting with the vast majority of organic compounds, acting as a "garbage disposal" system or low temperature combustion system (Atkinson, 1995).

However, elevated concentrations of ozone at ground-level are known to cause negative impacts on human health, ecosystems and materials. Average ozone concentrations in the troposphere have been rising during this century as a result of increased input of the precursors of ozone, nitrogen oxides (NO_x) and volatile organic compounds (VOCs), into the atmosphere (Syri *et al.*, 2001). In recent years there has been an increased concern about European population and vegetation being exposed to harmful ozone concentrations. The World Health Organization has established threshold values for the protection of human health and vegetation, respectively (WHO, 1995). With these levels, of all the compounds present in troposphere, ozone has the smallest margin between natural background levels and those considered harmful to human health and ecosystems (Syri *et al.*, 2001).

Ozone (O_3) is formed in the atmosphere by a series of complex chemical reactions. The basic photolytic production and loss processes for O_3 can be summarised by the equations 3.4 to 3.6 (Kiely, 1997):

$NO_2 + h\nu \rightarrow NO + O$ (where $h\nu$ = energy photon) (3.4)

$O + O_2 \rightarrow O_3$ (3.5)

$O_3 + NO \rightarrow NO_2 + O_2$ (3.6)

HC compounds make the above cycle unbalanced, otherwise the amount of ozone produced and destroyed would be in balance.

HC compounds play a crucial role in ground level photochemical oxidant formation since they control the rate of oxidant production in those areas where NO_X levels are sufficient to maintain ozone production (Derwent, 1995.). In the late 1970s, Fishman and Crutzen, showed that ozone could be formed from oxidation of methane and carbon monoxide in the troposphere in processes involving the OH radical (Harrison, 2001):

$CH_4 + OH^{\bullet} \rightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CO + OH^{\bullet} \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

(where M is an unreactive third molecule such as N2)

In the presence of NO :

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

Thus via the reactions of the peroxy radicals HO_2 and RO_2 (R= alkyl group), NO is converted into NO2. Then:

$NO_2 + h\nu \rightarrow NO + O(^3P)$ $\lambda<435nm$

$O(^3P) + O_2 + M \rightarrow O_3 + M$

However, in general, in the continental boundary layer, the oxidation of methane or CO is not expected to be the most important factor controlling the photochemical production or loss of ozone. The ample concentrations of non-methane hydrocarbons, with their higher photochemical reactivities, can dominate ozone production. However, the presence of NO is expected to determine whether the oxidation leads to ozone production or loss. The process can be approximately represented by a simplified scheme (Hewitt *et al.*, 1993):

NMHC	+	$OH^{\bullet}$	+	O_2	→	RO_2				
RO_2	+	NO	+	O_2	→	NO_2	+	HO_2	+	CARB
	HO_2		+	NO	→	NO_2	+	OH		
2 (NO_2	+	*hv*	+	O_2	→	NO	+	O_3)		
net : NMHC	+	$4O_2$	+	*hv*	→	$2O_3$	+	CARB		(3.7)

Where R stands for a hydrocarbon radical and CARB denotes a carbonyl compound.

The net reaction in equation 3.7 shows that two ozone molecules are produced for every hydrocarbon oxidised. In addition the carbonyl compound may undergo additional photochemical reactions and as a result more radicals will be produced further increasing the production of ozone. However, in the absence of NO, the oxidation of NMHCs can lead to ozone destruction (Hewitt *et al.*, 1993).

Ozone is a powerful oxidant and toxic air pollutant. As a gaseous pollutant, its primary target tissue is the lung and breathing slightly elevated concentrations of ozone results in a range of respiratory symptoms. It causes direct cellular damage by damaging the anti-oxidant mechanisms in cells lining the airway walls (Harrison, 2001). The symptoms include decreased lung function and increased airway hyper-reactivity in 10-20% of the healthy population. Moreover, those with conditions such as asthma and chronic obstructive pulmonary disease (COPD) generally experience an exacerbation of their symptoms. Together, these observations suggest that certain individuals are particularly susceptible to this oxidant gas (Mudway and Kelly, 2000).

In addition to the adverse health effects caused by elevated ambient concentrations, ozone can be highly damaging to plants. At relatively high concentrations (>100ppb) ozone causes a characteristic brown or white flecking in foliage (Harisson, 2001). At lower concentrations, when no visible damage can be observed, ozone may reduce the growth rate and physiological activity of plants (Boubel *et al.*, 1994).

2.5 FATES OF HYDROCARBONS

As discussed in section 2.6.4, atmospheric dispersion reduces the concentrations of hydrocarbon emissions, the ultimate fate of these hydrocarbons however depends upon other atmospheric processes, primarily chemical in nature. The troposphere can be thought of as chemical "processor" resulting in the partial or complete degradation of almost all organic compounds emitted (Atkinson, 1995). In addition to chemical removal processes, the physical processes of removal, wet and dry deposition also play a significant role (Atkinson, 1995; Derwent, 1995).

Chemical removal processes

Gas phase organic compounds in the troposphere are degraded by photolysis and /or reactions with OH radicals, NO_3 radicals or O_3. The resulting oxidised organics are transformed into generally more polar products which have less carbon atoms than the parent compound (Atkinson, 1995). These degradation reactions continue until the original organic has been degraded to CO_2 and H_2O, or the products are removed by physical processes.

The Oxidation by the OH radical plays a central role in tropospheric chemistry (Levy, 1971) by cleansing the troposphere through chemical reactions with most trace gases. It is generally agreed that the reaction between hydrocarbons and the OH radical is the most important daytime tropospheric removal process.

The primary source of OH radical is the photolysis of O_3 to produce an excited state of atomic oxygen, $O(^1D)$, which then reacts with water vapour to give oxygen and OH radicals (Potter *et al.*, 2000).At 298K and atmospheric pressure with 50% relative humidity, 0.2 OH radicals are produced per $O(^1D)$atom formed (Atkinson, 1995). As the formation process involves the photolysis of O_3, the formation of OH radicals occurs only during daylight. Based on

spectroscopic measurements at ground level, peak daytime OH radical concentrations were found to be of the order of 10^6-10^7 molecules cm^{-3} (Atkinson, 1995; Potter, 2000). Alkanes generally have lifetimes of about 2-30 days as a result of oxidation by OH radicals, methane and ethane are the exception with lifetimes of 10 years and 3 months respectively. Alkenes generally have the shortest lifetimes of the major classes of organics found in the troposphere, with a range of about 0.4-4 days. Aromatics show lifetimes in the range of 0.4-5 days, with benzene showing uncharacteristically long lifetime of 25 days (Derwent, 1995).

The reaction of NO_2 with O_3 leads to the formation of the NO_3 radical and O_2. The NO_3 radical photolyses rapidly, with a photolysis time of approximately 5seconds. Hence, NO_3 radical concentrations are at their highest at night (Atkinson, 1995). During this period NO_3 radicals may react with reactive alkenes and dialkenes to form nitrato-carbonyl compounds by addition reactions. For a large number of organic compounds, however, NO_3 radicals are not reactive enough to contribute significantly to atmospheric removal (Derwent, 1995).

For a chemical to undergo photolysis in the troposphere, it must absorb radiation in the wavelength range of 290-800nm. Furthermore, having absorbed radiation, the chemical must undergo chemical transformation in the form of dissociation or isomerization (Atkinson, 1995). This removal process is only important for a limited range of organic compounds, namely the aldehydes and ketones. It is however an important source of free radical species (Levy, 1971).

In addition to the species outlined above, chlorine and fluorine radicals share a wide spectrum of reactivity similar to the OH radical. These compounds however lack significant atmospheric sources to be significant removal mechanisms (Derwent, 1995).

Physical removal processes

Deposition onto water surfaces, plants, vegetation and soil surfaces is generally termed dry deposition. Dry deposition only tends to act efficiently on those organic compounds present in the atmosphere close to the surface where biological uptake occurs. The general impression is that this form of removal is not significant.

The removal of trace gases by precipitation, referred to as wet deposition, results from the incorporation of material into falling precipitation (wash out) and by incorporation into cloud droplets (rain out). These removal processes are only significant for those compounds which are readily soluble in water and as the vast majority of low molecular weight organics are insoluble in water, this removal process is not deemed to be significant (Derwent, 1995).Dry and wet deposition rather than oxidation by OH radicals are the major removal mechanisms for semi-volatile organic compounds.

Overall

The overall lifetime, $\tau_{overall}$, of an organic compound is given by the equation (Atkinson, 1995):

$$1/\tau_{overall} = 1/\tau_{wet\ dep.} + 1/\tau_{dry\ dep.} + 1/\tau_{phot} + 1/\tau_{OH} + 1/\tau_{NO3} + 1/\tau_{O3} + 1/\tau_{Cl}$$

where, $\tau_{overall}$ = overall atmospheric lifetime of the compound

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

$\tau_{dry\ dep.}$ = lifetime due to dry depostion

τ_{phot} = lifetime due to photolysis

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

τ_{NO3} = lifetime due to reaction with NO_3 radical

τ_{Cl} = lifetime due to reaction with Cl radical

Examples of several atmospheric lifetimes are given in Table 2.5. For the bulk of organics emitted anthropogenically in the northern mid latitudes, atmospheric lifetimes are generally one hundred days or less. For those with lifetimes of 5 days or less, they are likely to be found to any significant extent within the boundary layer and within 1000kms of major source regions (Derwent, 1995).

	lifetime due to reaction with:		
Compound	OH radical	NO_3 radical	O_3
propane	13 days	-	> 4500years
ethene	1.7 days	225 days	10 days
propene	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

Table 2.5 Atmospheric lifetimes of sample hydrocarbons (Atkinson, 1995)

2.6 METEOROLOGY AND AIR POLLUTION

The atmosphere serves as the medium through which air pollutants are transported and dispersed. In recent years considerable resources have been devoted to the measurement of ambient HC concentrations. These measurements treated in isolation are of little use in determining the origin of the pollutants in question, on the dispersal process in the atmosphere and on the impact of new sources or the benefits of control. Therefore, there is frequently the need for detailed knowledge of the characteristics and quantities of HC pollutants emitted to the atmosphere and on the atmospheric processes, which govern their subsequent dispersal and fate.

2.6.1 Atmospheric stability

When solar radiation heats the earth's surface, lower layers of the atmosphere increase in temperature and driven by buoyancy forces, convection begins. The motion of air parcels from the surface are unstable, as an air parcel in rising finds itself warmer than its surroundings and will continue to rise. As a result large eddies of convective circulations are set up in the boundary layer. At night when the surface of the earth cools due to a lack of solar radiation, temperature increases with height and turbulence tends to be suppressed. Generally, when the atmosphere resists vertical motions, it is called *stable,* when the atmosphere enhances vertical motions it is called unstable, or in a state of instability (Boubel *et al.*, 1994)

It is convenient to classify the possible states of the atmosphere into what are usually termed stability categories. These are classified according to the amount of incoming solar radiation, wind speed and cloud cover (Harrison, 2001) A semi-quantitative guide is given in Table 2.6,

and typical temperature profiles can be seen in Figure 2.6 for unstable, neutral and stable cases. The adiabatic lapse profile in Figure 2.6a is the vertical temperature profile for the atmosphere in a stage of adiabatic equilibrium, where a parcel of air can rise and expand or descend and contract, without the gain or loss of heat. The temperature of the parcel of air is always the same as that of the surrounding air, and the conditions correspond to neutral stability.

	Insolation			Night	
Surface wind speed (m/s)	Strong	Moderate	Slight	Thickly overcast	>3/8 cloud
<2	A	A-B	B	-	G
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Strong insolation corresponds to sunny midday in midsummer. Slight insolation is similar conditions in Winter.

Table 2.6 Pasquill stability categories (Harrison, 2001)

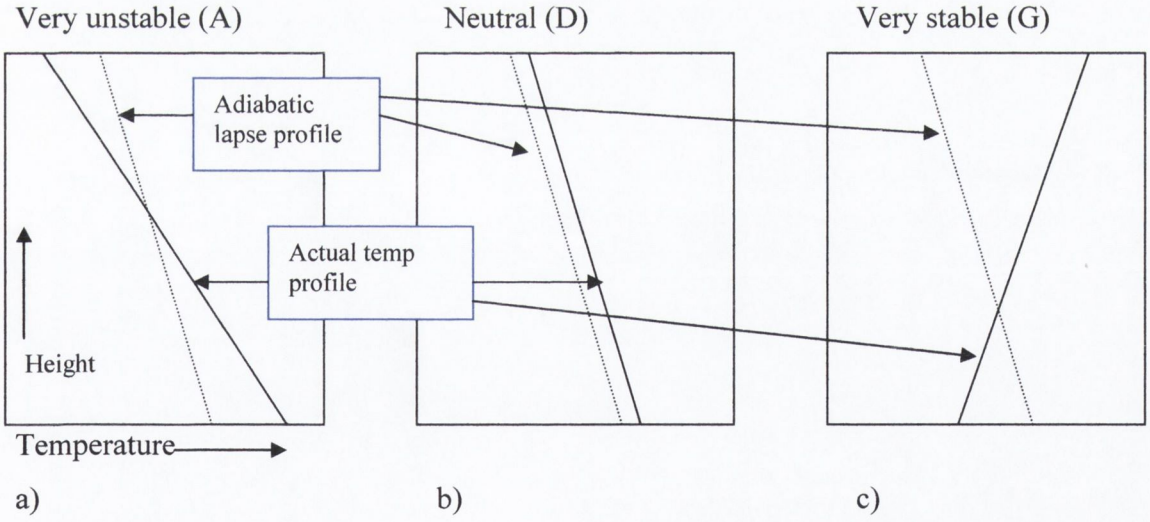


Figure 2.6 Typical atmospheric temperature profiles and corresponding stabilities

2.6.2 Mixing height

Although there is no unique definition of mixing height (Salcido *et al.*, 2003), it can be thought of as the height above the ground, which is well mixed due to either mechanical or convective turbulence.

In Figure 2.6c, the stable atmosphere shown depicts a ground based temperature inversion (i.e, the temperature increases with height unlike the normal decrease). An inversion is usually seen when a region of stable air caps a region of unstable layer below. Pollutants emitted below this height can be mixed up to this vertical mixing height but not through the inversion. In the case of emissions above this height, the pollutant will be prevented from reaching the ground by the mixing height. The mixing height can therefore be thought of as the height of the boundary between two stability regimes.

The variation of mixing heights throughout the day due to solar heating and atmospheric cooling can have a profound effect on ground level pollutant concentrations. Maximum mixing heights and corresponding maximum periods of atmospheric dilution are generally observed during periods of increased solar activity with associated convective eddies, while shallow mixing heights and periods of limited atmospheric dilution are associated with stable, inactive solar nightime periods.

2.6.3 Urban-Rural circulations

Urban areas have roughness and thermal characteristics different to rural areas. Due to the amounts of concrete and steel in urban areas, they have higher specific heat capacity than rural areas and therefore heat up quicker during the day and release this heat at night, keeping them generally warmer than the surrounding rural areas. Under stable conditions, with associated low wind speeds, this warmer air rises and colder air is drawn in, from all surrounding directions. This "doughnut shaped" circulation pattern is known as the urban heat island, and the flow strength is dependant on the temperature difference between the urban centre and its surroundings. Under less stable conditions where wind speed allows flow to occur in one general direction, the resultant flow is termed an urban plume.

2.6.4 Transport and dispersion of pollutants

wind direction

The initial direction of transport of pollutants from their source, is in the main determined by wind direction at the source. If the wind is blowing directly toward a receptor, a shift in direction of as little as 5° causes concentrations at the receptor to drop about 10% under unstable conditions, about 50% under neutral and 90% under stable conditions (Boubel *et al.*, 1994). The direction of plume transport is of paramount importance in impact assessment and in source apportionment when dealing with more than 1 source.

wind speed

Wind speed generally increases with height. A number of expressions describe the variation of wind speed in the boundary layer. A power law has frequently been used in air pollution work (Boubel *et al.*, 1994):

$$U(z) = u(z_a)\,(z/z_a)^p$$

Where u(z) is the wind speed at height z, $u(z_a)$ is the wind speed at the anemometer height z_a, and p an exponent varying from about 0.1 to 0.4. The exponent varies with stability, surface roughness and boundary layer depth.

Wind speed is an indirect indicator of atmospheric stability and the atmosphere's dilution capability. The effect of this is to continuously dilute air pollution at the point of emission, the greater the wind speed, the greater the effective dilution. Whether the source is elevated or at the surface, the dilution takes place in the direction of the plume transport. Wind speed also effects the travel time of pollutants from source to receptor, halving of the wind speed will double the required travel time.

Turbulence

Atmospheric flow is not a continuous, smooth flow, but more a highly irregular motion of wind associated with turbulent eddies. The manifestation of turbulent eddies is gustiness and is displayed in the fluctuations seen on a continuous record of wind or temperature. Turbulent dispersion is the most important mixing process in the atmosphere, and results in the mixing of

polluted air with relatively unpolluted air, causing a serial dilution effect where polluted air at successively lower and lower concentrations is forced to occupy larger volumes of air.

2.6.5 Meteorological conditions during pollution episodes

Historically, meteorological conditions have been central to episodes of high levels of tropospheric pollution and subsequent human exposure. In December 1930, in Meuse, Belgium, an intense fog occupied this heavily industrialised region. Several hundred people had respiratory attacks and 63 people died over the four day episode. When the fog dissipated, the respiratory difficulties people were suffering ceased. In Donora, Pennsylvania, in October 1948, a severe pollution episode caused the deaths of twenty people,17 of them within 14 hours. In 1952, London suffered a major air pollution episode over a four day period in December. From the commencement of the fog, many people experienced respiratory difficulties and the number of deaths increased with increasing levels of SO2 and smoke (PM< 20μM) (Boubel *et al.*, 1994).These are extreme pollution episodes by modern standards and there can be little doubt that poor air quality standards played a significant role in these episodes. The similarities between all three episodes however lie in the meteorological conditions observed during these periods.

All three areas were influenced by high pressure with almost non existent surface air motion. Surface inversions caused the condensation of fog, which, once formed, persisted throughout the day. In each case the fog layer was shallow, extending to approximately 100 m. The persistence of the fog past three days and the subsequent lack of air transport out of the region, allied to the considerable emissions of pollutants, seem to separate these episodes from more common meteorological occurrences (Boubel *et al.*, 1994).

On a more recent level, (Stedman, 2004),showed that during an August 2003 heat wave in the UK, an excess of 2045 deaths in England and Wales for period from 4 to 13 August 2003 above the 1998–2002 average were observed. It was estimated using previously established dose–response functions, that there were between 423 and 769 excess deaths in England and Wales during the first two weeks of August 2003 associated with the elevated ambient ozone and PM_{10} concentrations. This represented 21–38% of the total excess deaths.

Klemm *et al.* (1998), showed how under favourable meteorological conditions, sea breezes could penetrate the entire Athens basin, resulting in an upward flow at the foothills of Parnitha and Pendeli mountains, and filling the lower troposphere with high levels of air pollution at altitudes of up to 2000 m and more. From these layers of high photochemical activity (O_3 levels up to 200 ppb), air pollution may have been incorporated into long-range transport.

On a more "every day" basis, the influence meteorological conditions have on HC concentrations in two European cities was investigated by Vignati *et al.*, (1996). The first city, Milan was located in Italy, the second, Copenhagen in Denmark. It was found that the frequency of low wind speed conditions were considerably higher in Milan than in Copenhagen. These lower wind speeds were more associated with ground level inversions, and as a result, the pollution levels observed in Milan were much higher than in Copenhagen.

2.7 HYDROCARBON SAMPLING AND ANALYSIS TECHNIQUES

Sampling

The primary methods for sampling hydrocarbons involve or whole air (grab) sampling and adsorbant sampling. Whole air sampling involves collecting a representative average sample of the atmosphere in the sampling location over a desired sampling time. Stainless steel or aluminium canisters, or bags lined with Teflon or Tedlar are commonly used for this form of sampling.

The most common sampling procedures for this form of sampling are carried out in accordance with EPA methods TO-14 (USEPA,1999b) and TO-15 (USEPA,1999c), which outline the sampling procedures when sampling into stainless steel or aluminium canisters.

Adsorbant sampling involves passing the sample through a stainless steel or glass tube filled with the desired adsorbant substance which absorbs the HC compounds of interest. Sorbant sampling can be either pumped (active), where a pump is used to draw the air sample through the tube, or diffuse (passive), where the sample is allowed to permeate through the tube naturally.

Analysis

The primary method of separation of HC compounds for analysis is through gas chromatography. Chromatographic methods in general are separation techniques applied to a mixture of compounds in an attempt to separate and isolate the compound of interest. Gas chromatography, specifically gas-liquid chromatography, involves a sample being vapourised and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. The column separates the mixture of compounds according to their individual affinity for the stationary phase. Upon elution from the column the compounds are passed through a detector for quantitation and quantification.

Detection of hydrocarbons is typically carried out by flame ionisation detection (FID) or mass spectroscopy (MS), the latter allowing a more positive identification of the individual compounds (Harrison, 2001). The process of GC/FID is discussed in greater detail in Chapter 3.

Recent years have seen the development of automated systems for GC measurements of hydrocarbons on a cyclic basis of about one hour from sampling to analysis. Such equipment has been incorporated into such national hydrocarbon networks as the UK Hydrocarbon Network (Dollard *et al.*, 1995; Derwent *et al.*, 1994) and the US Photochemical Assessment Monitoring Network (Demerjian, 2000). This form of analysis is discussed in great detail in Chapter 3.

In addition to the techniques outlined above; as magnetic minerals are common amongst anthropogenically derived particulate matter, magnetic properties of soils (Leocoanet *et al.*, 2001;Schu *et al.*, 2001), filters (Muxworthy *et al.*, 2001; Xie *et al.*, 2001) and leaves (Georgeaud, 1999; Matzka and Maher, 1999) have been used for identifying the spread of pollution derived from vehicular or industrial emissions. Mareno *et al.* (2003), showed that a magnetic survey of tree leaves, which is relatively rapid and inexpensive, may be used in addition to the classical air quality monitoring systems to identify and delineate high-polluted areas in urban environments. Padola *et al.*, (2004) proved the concept of the detection and

identification of two different VOCs with a non-selective biochip-based algal biosensor. Environmental biosensors represent a significant breakthrough for the monitoring of pollutants in contaminated matrices since they have the unique ability to measure the interaction of specific compounds with biological systems through highly sensitive biorecognition processes (Keane, 2002).

2.8 CONTROL OF EMISSIONS

The two main areas that deal with the control of pollutant emissions and hence have a direct bearing on ambient air quality are regulatory and engineering control of emissions.

2.8.1 Regulatory control

Air quality standards prescribe pollutant levels that cannot legally be exceeded during a specific time period in a specific geographic area. Air quality standards are based on air quality criteria, which are cause-effect relationships, observed experimentally, epidemiologically, or in the field, of exposure to various ambient levels of specific pollutants (Boubel *et al.*, 1994). Some of the more important EU directives relating to air quality are outlined below:

Directives relating to general air quality

Directive 96/62/EC (CEC, 1996), establishes the basic principles of a common strategy to define and set objectives for ambient air quality in order to avoid, prevent or reduce harmful effects on human health and the environment. The only hydrocarbon of interest, for which there is an air quality standard is benzene, covered in daughter directive 2000/69/EC (CEC, 2000). It specifies an annual average concentration of no greater than 1.45ppb as an annual average to be achieved by 2010. The hydrocarbon of note, for which there is no EU limit value is 1,3 butadiene, however at least one member state has imposed a limit. In 1994, the UK Expert Panel on Air Quality Standards (EPAQS) published a report on 1,3-butadiene, considering not only current concentrations, but studies of human and animal exposure to elevated levels of 1,3-butadiene (1, 3 butadiene, 1994). The study accepted that 1,3-butadiene is a genotoxic carcinogen, and consequently no safe level can be defined. However, the panel agreed on a recommended concentration that would ensure the risks are exceedingly small and unlikely to be detectable by any practicable method. The panel recommended that an Air

Quality Standard for 1,3-butadiene in UK of 1 ppb measured as a running annual average be introduced (Dollard *et al.*, 2001).

Additional noteworthy directives include 99/30/EC (CEC, 1999b) which covers air quality limits for NO_X, SO_2, particulate matter and lead. This directive along with 2000/69/EC, covering the limit values of benzene and CO has recently been transcribed into Irish law under Air Quality Standards Regulations 2002. Appendix C outlines these limit values. A third daughter directive, 2002/3/EC (CEC, 2002), relating to limit values of ground level ozone was published in February 2002 and is due to be transposed into Irish law imminently.

Directives relating to mobile sources

Aware of the fact that air quality in urban areas is significantly affected by emissions from mobile sources, various Directives have been implemented to limit the emissions from such sources.

A variety of amendments to Directive 70/220/EEC (CEC, 1970) establish limit values for emissions from petrol and diesel engine passenger cars and light commercial vehicles. The most stringent values, laid down by Directive 98/69/EC (CEC, 1998b), apply from 2000 for spark ignition and 2005 for compression ignition engines. The Directives apply to tailpipe emissions, evaporative emissions, emissions of crankcase gases and the durability of anti-pollution devices for all motor vehicles equipped with spark-ignition engines and to the tailpipe emissions from and durability of the anti-pollution devices of vehicles equipped with compression-ignition engines.

As mentioned previously, Directive 98/70/EC (CEC, 1998a) was drafted to reduce pollution from car emissions by introducing new environmental specifications applicable to fuels which included a reduction in benzene content to 1% v/v. In addition, the Directive included a ban on the marketing of leaded petrol and the obligation to make sulphur-free fuels available within the Union.

Directives relating to point sources

Various Directives have been drafted to control emissions from point sources. Included in these is Directive 94/63/EC (CEC, 1994), which aims to reduce losses due to evaporation of

the petrol at all stages of the fuel storage and distribution chain. Directive 99/13/EC (CEC, 1999a) aims to prevent or reduce the direct and indirect effects of emissions of volatile organic compounds (VOCs) in the environment and on human health, by setting emission limits for such compounds and laying down operating conditions for industrial installations using organic solvents.

2.8.2 Engineering control of emissions

During the last two decades there has been a considerable effort, particularly in the United States to develop alternatives to the use of petrol and conventional diesel fuel for transportation. The primary motives for this effort have been two-fold: energy security and improvement in air quality, most notably ozone. The anticipated improvement in air quality is associated with a decrease in the atmospheric reactivity, and sometimes a decrease in the mass emission rate of the organic gas emissions from vehicles using alternative fuels when compared to conventional transportation fuels. The most common alternative transportation fuels in the US are methanol, ethanol, compressed natural gas (CNG), liquefied petroleum gas (LPG), reformulated gasoline, and electricity (Sawyer *et al.*, 2000).

In Europe, the main alternatives are natural gas (liquefied or compressed), liquid petroleum gas and electric vehicles. In general there has been little support for the use of alcohol based fuels There are several technical problems with the use of alcohol as a fuel, firstly its miscibility with water, second, emissions of some ozone pre-cursors can increase and third it burns with an invisible flame making it potentially dangerous in accidents.

The main advantage of using gaseous fuels is their significantly lower particulate matter emissions when compared to diesel engines. Duel fuel vehicles running on petrol and compressed natural gas can have higher HC emissions when the vehicle is running on petrol compared to a conventional petrol vehicle. Dedicated compressed natural gas (CNG) vehicles offer greater benefits, with all regulated emissions lower or similar to a petrol vehicle. CNG vehicles also have lower CO, NO_x and particulate matter than diesel vehicles. However, total HC emissions tend to be higher than petrol vehicles due to the level of methane (greenhouse gas) in the emissions (Harrison, 2001).

In addition to reducing vehicle emissions through the use of better quality and alternate fuels, advances in vehicle technology have also played a role, necessary due to the regulatory requirements imposed on manufacturers to continuously reduce emissions from new vehicles.

In the early stages of such emission control, the emphasis was on improving fuel injection systems and combustion chamber designs. The focus was on minimising the deposit of fuels on the chamber walls, which leads to HC emissions. However, to comply with emission limits, "after treatment systems" have been implemented which remove pollutants in the exhaust rather than controlling their formation in the engine. Over 85% of all new cars produced world wide are equipped with after treatment systems (Searles, 2000). Such after treatment systems developed include the three way catalytic converter, diesel oxidation catalysts and particulate traps.

Diesel oxidation catalysts can lower particulate matter emissions by 50% by destroying the organic fraction and also lower significantly the HC and CO emissions. Particulate traps include ceramic wall –flow filters or traps which remove well over 90% by weight of the total particulate matter contained in diesel exhaust. Another area of development is the HC adsorber, which incorporates adsorbing materials into or ahead of the three way catalytic converters in petrol cars. HC emissions are collected when the exhaust temperature is too low for optimum catalyst conversion. The HCs are then desorbed when the catalyst has lit-off.
By far the greatest reduction in vehicle emissions is as a result of the introduction of the three way catalyst into petrol fuelled vehicles.

Exhaust catalysts were first required on European gasoline cars with the introduction of Euro-1 emission limits in the early nineties (CONCAWE, 2003).

The basic reactions for CO and HC in the exhaust are oxidation, with the desired product being CO_2, while the NO_x reaction is a reduction with the desired product being N_2 and H_2O. A catalyst promotes these reactions at lower temperatures than a thermal process giving the following desired reactions for HC, CO and NO_X (Harrison, 2001):

Oxidation reactions

$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_20$$

Reduction reactions

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

$$HC + NO \rightarrow CO_2 + H_20 + N_2$$

All the above reactions required some heat or temperature on the catalyst surface for the reaction to occur. When the automobile first starts, both the engine and catalyst are cold. After startup, the heat of combustion is transferred from the engine and the exhaust piping begins to heat up. Finally, a temperature is reached within the catalyst that initiates the catalytic reactions. This light-off temperature, and the concurrent reaction rate, is kinetically controlled (i.e. depends on the chemistry of the catalyst since the transport reactions are fast).

Typically, the CO reaction begins first followed by the HC and NO_x reaction. When all three reactions are occurring, the term three-way catalyst or TWC is used. In order to accomplish even lower emissions, a number of approaches have been taken, primarily to reduce the amount of cold start emissions, as 60-80% of HC emissions take place at this stage of catalyst operation (Heck and Farrauto, 2001). These include close-coupled catalysts, electrically heated catalyzed metal monoliths, hydrocarbon traps, chemically heated catalysts and pre-heat burners.

In addition a more fundamental understanding of the function of various components of the three way catalytic converter, is now allowing more precisely defined washcoats with less expensive metals and enhanced performance for 160000 km (Farauto *et al.*, 1999).

2.9 COMPARISONS OF WORLD WIDE STUDIES

2.9.1 Europe

Ireland

Ireland's small population and generally good standard of air quality mean that a small number of measurement stations are sufficient across the four zones defined for the purposes of EU Directives and Air Quality Standards Regulations. The zones were determined from an analysis of historical air quality data and other factors including population (McGettigan, 2001). The four air quality zones designated for Ireland are as follows;

- Zone A Dublin City and environs
- Zone B Cork City and environs
- Zone C 16 urban areas with population greater than 15,000
- Zone D remainder of the country

Local Authority continuous air monitoring is largely confined to Dublin (Zone A) and Cork (Zone B), although additional continuous monitors have been established by the EPA at a number of rural sites providing data in areas with lower population densities. Local Authority monitoring is still largely concentrated on SO_2 and black smoke, though the number of such sites in operation is continuing to decline (EPA, 2002).

Mobile monitoring units carry out air quality monitoring primarily in Zones C and D where no continuous monitoring was previously conducted. The units are equipped with instrumentation for the monitoring of all the pollutants covered by the Air Quality Standards Regulations 2002.

Few hydrocarbon studies have been carried out in Ireland, with the majority of previous monitoring tending to focus on SO_2 and more recently NO_X and O_3.

Of the hydrocarbon compounds of interest benzene monitoring has been carried out by the EPA in order to comply with EU directive 2000/69/EU (CEC, 2000) and subsequently the Air

Quality Standards Regulations 2002. In 2001 the EPA monitored benzene at 5 different locations. The results are shown in Table 2.7.

The annual mean concentration at the Wood Quay site is close to the limit value of 1.5ppbv, while the annual mean at Anglesea Street was over the upper assessment threshold of 1.05ppbv. The average concentrations obtained at Crumlin were above the lower assessment threshold of 0.6ppbv. The data for the other sites suggest that the average benzene levels are well within the 2010 limit.

benzene (ppbv)	Zone A		Zone B	Zone C	Zone D
	Wood quay, Dublin	Crumlin, Dublin	Anglesea street, Cork	Three zone C sites	Mullingar
Average (ppbv)	1.47	0.63	1.14	0.2	0.12
Median (ppbv)	1.08	0.42	0.15	0.12	0.09
Max (ppbv)	27.3	8.4	4.5	9.9	2.4
% data capture	88	91	54	15	9

Table 2.7 Benzene concentrations in Ireland in 2001 (EPA, 2001)

Similar monitoring was carried out in 2002 by the EPA, the result of which can be seen summarised in Table 2.8. Benzene levels measured at all five stations in 2002 were low apart from Winetavern Street, where the annual mean level measured exceeds the Upper Assessment Threshold of 1.05ppbv. Concentrations from other locations were less than the Lower Assessment Threshold of 0.6ppbv indicating that benzene levels are well within the 2010 limit for these areas. All concentrations were seen to decrease from those values obtained for similar sites in 2001.

benzene (ppbv)	Zone A		Zone B	Zone C	
	Wood quay, Dublin	Crumlin, Dublin	Old station road, Cork	Drogheda	Dundalk
Average (ppbv)	1.14	0.39	0.30	0.39	0.12
Median (ppbv)	0.66	0.12	0.12	0.27	0.09
Max (ppbv)	31.8	7.77	9.00	6.27	1.65
% data capture	68	76	79	21	65

Table 2.8 Benzene concentrations in Ireland in 2002 (EPA, 2002)

The majority of research into ambient levels of HC's in Ireland has been carried out at a North Atlantic background site, at Mace head in the West of Ireland. Examples of such studies are outlined below.

Diurnal hourly concentrations of reactive alkenes were reported by Lewis *et al.*(1998). Species seen to exhibit distinct cycles included isoprene, ethene, propene, 1-butene, iso-butene and a substituted C_6 alkene. During periods when airflow resulted from unpolluted oceanic regions, a clear daily cycle in concentrations was observed, peaking at around solar noon for all species. The species short atmospheric lifetimes indicated that the source of emission was from local coastal waters within close proximity of the sampling site. At solar noon, concentrations of reactive alkenes from oceanic sources were responsible for up to 88% of non-methane hydrocarbon reaction with the hydroxyl radical at this coastal marine site.

Sartin *et al.* (2002), estimated Emission fluxes for a range of C_8–C_{15} volatile organic compounds (VOCs) from the seaweed *Fucus spiralis* (spiral wrack) and an adjacent sand surface during low tide on the coastline of Mace Head, Ireland. . A range of *n*-alkanes and oxygenates were routinely identified. Comparison with previous flux estimates from coastal seawater indicates that the two source types (*Fucus spiralis* and bare sand) were significant but not dominant sources of these VOCs.

In addition a technique was described by Ryall *et al.* (2001), for identifying probable source locations for a range of greenhouse and ozone-depleting trace gases from the long-term measurements made at Mace Head. The results indicated that whilst there are limitations, useful information about source distribution could be extracted from continuous measurements at a remote site. It was concluded that much improved estimates could be derived if observations were available from a number of sites.

In Dublin, hourly roadside hydrocarbon concentrations were measured over a six-week period at a heavily trafficked junction in Dublin city centre by Broderick and Marnane (2002). Samples of unleaded petrol fuels used in Irish vehicles were also collected and their hydrocarbon compositions determined. The measured ambient hydrocarbon concentrations were presented, as were the properties of each of the analysed fuels. Comparison of the

ambient hydrocarbon concentrations and the fuel hydrocarbon composition revealed a strong correlation for most hydrocarbons, except those compounds that were wholly combustion derived (i.e. acetylene, not present in the fuel).

United Kingdom

A fully automatic network with 11 urban background and one rural site (UK Hydrocarbon Monitoring Network) has been set up and operated successfully in the UK to measure, continuously, hourly concentrations of C_2–C_8 hydrocarbons; the measurements collected form one of the largest data sets of urban hydrocarbon air quality data available anywhere in Europe. Hourly archived data are provided for each site and can be accessed through the associated website (www.airquality.co.uk).

Results from the monitoring network and other HC monitoring sites are presented in the Reports of the Photochemical Oxidant Review Group (PORG) "ozone in the United Kingdom", which includes information on ozone precursors (PORG, 1993 and 1997) Information on UK HC concentrations for 2001 can be found in the publication by the AEAT, (Durnitrian, 2002a) for the DETR. The Quality of Urban Air Review Group (QUARG) also publish reviews of urban air quality data (QUARG, 1993).

The 15th annual report from the UK National Atmospheric Emissions Inventory (NAEI), has recently been published (Dore *et al*, 2003), it includes a comprehensive review of HC emission trends form 1970-2001.

Hourly data from the UK hydrocarbon monitoring network was analysed by Derwent *et al.* (2000), on a site-by-site and hydrocarbon-by-hydrocarbon basis by constructing scatter plots against benzene. From these scatter plots a number of important sources of hydrocarbon emissions were identified including: motor vehicle exhaust and evaporative emissions, natural gas leakage, petrol station forecourt evaporative emissions and industrial sources. Overall, urban background hydrocarbon air quality was found to be heavily influenced by motor vehicles.

The on-road hydrocarbon emissions of vehicles at four sites in the UK were monitored using remote sensing equipment by Revitt *et al.* (1999). Analysis of the results showed that there is both a large majority of low emitting vehicles which contribute little to fleet hydrocarbon emissions and a small minority of high emitting vehicles which contribute significant proportions to fleet hydrocarbon emissions at all sites.

Leung and Harrison (1999), investigated the concentrations of mono-aromatic hydrocarbons both inside and outside passenger vehicles and came to the conclusion that pollution inside the car is derived from pollutants outside entering with ventilation air.

Clarke and Ko (1996), estimated the speciation of VOC emissions in Leeds, using fingerprints for different types of source. The results for the city as a whole indicated that the greatest contributors were motor vehicles, followed by industrial and domestic use of solvents. The result of spatial disaggregation indicated substantial differences in the relative significance of vehicular emissions from one place to another. In the city centre, the contributions of motor vehicles were found to be lower than outside the city centre due to the large emissions from a number of point sources in the inner city area.

France

In France work has been carried out by Bourbon *et al.* (2002 and 2003), into the identification of urban hydrocarbon sources, including their spatial and temporal variations. Results were based on 4-years of continuous and hourly measurements of nearly 40 C_2–C_9 ambient NMHC carried out at two urban sites of the medium-sized city of Lille, northern France. Four main categories of sources were consistently identified: (1) motor vehicle exhaust, which dominated the NMHC distribution, particularly in winter (2) wintertime stationary combustion and activities related to general fossil fuel consumption (3) summertime evaporative emissions from fuel and solvents (4) summertime biogenic emissions for isoprene and their dependence on temperature.

In addition, hydrocarbon speciation of vehicle emissions was carried out by Touty and Bomsang (2000), in the Thiais tunnel, close to Paris. The major compounds observed, and expressed in terms of % w/w of total hydrocarbons, were ethene, (21.4%), acetylene and

propyne, accounting for 10% each. Other measured HCs were emitted in very low amounts of about 1% or less. Expressed in terms of a mixing ratio percentage, alkenes, alkanes and alkynes accounted for 46, 35% and 19%, respectively of the total identified HCs.

Holland

Measurements of C_2–C_5 hydrocarbons on an hourly basis at two sites in Holland, the first in Delft from 1982 to 1984 and the second at Moerdijk over the period 1981 to 1991 were presented by Roemer *et al.* (1999). Under conditions of high wind speed the concentrations measured at Moerdijk in the marine sector were found to be close to the Atlantic background concentrations in winter and somewhat above this in summer. The continental background concentrations were higher than the marine background concentrations by a factor of almost two. The observations showed that at Moerdijk C_2–C_4 concentrations measured, have decreased considerably since the early 1980s, corresponding with changes in emissions in that area. Averaged over all wind directions the trend of all species was downward, but for acetylene the trend was significant at a 95% confidence interval. The acetylene concentrations showed an annual downward trend of 3% during the 1980s.

Denmark

A method to determine emissions from the actual car fleet under realistic driving conditions was developed by Palmgren *et al.* (1999). The method was based on air quality measurements, traffic counts and inverse application of street air quality models. Measurements of benzene, toluene and xylenes were carried out in central Copenhagen between 1994-1997. Hourly mean concentrations of benzene were observed to reach values of up to 20 ppb. Based on inverse model calculation of dispersion of pollutants in street canyons, an average emission factor of benzene for the fleet of petrol fuelled vehicles was estimated to be 0.38 g/km in 1994 and 0.11 in 1997. It was concluded that this decrease was caused by the reduction of benzene content in Danish petrol since summer 1995 and increasing percentage of cars equipped with three-way catalysts.

Hourly measurements of 23 hydrocarbons ranging from C_5 to C_8 were measured in a busy central Copenhagen street during 5 working days in December 1997 by Christensen *et al.* (1999). The compounds were concentrated on absorbent tubes by active sampling and

subsequently analyzed by thermal desorption and gas chromatography. Average benzene concentrations were found to be 3.4 ppbv, alkanes, 0.2–2.4 ppbv and the alkenes 0.03–0.4 ppbv.

Switzerland

A detrending technique was developed by Keubler *et al.* (2001), for short-term and yearly variations in order to identify long-term trends in primary and secondary pollutants. It was shown that primary pollutants at urban and sub-urban stations have shown a downward trend over the last decade which correlated well with the reductions in estimated Swiss emissions.

Volatile organic compounds were measured with a motor-glider during six days of July and August, 1996, in Switzerland's Mesolcina valley by Prevot *et al.* (2000). Morning and afternoon profiles from the motor-glider reached up to 4000 m above sea level (m asl). The results showed that due to vertical transport of air, VOC concentrations can increase strongly during daytime at high altitudes (~2000–4000 m asl) over the Alps.

Time-resolved chemical ionization mass spectrometry (CIMS) was used to investigate the variations of the mixing ratios of benzene, toluene and the C_2-benzenes (xylenes and ethyl benzene) in automotive exhaust during transient engine operation by Heeb *et al.* (1999). A significant increase of the benzene/toluene ratios from 0.35 to 1.31 (median) was found upon introduction of a catalytic converter system. At this site, the atmospheric concentrations of benzene and alkyl benzenes were detected at hourly intervals since 1993. A steady decrease of the yearly mean from 3.54 to 2.00 ppb for toluene and from 2.87 to 1.33 ppb for the sum of C_2-benzenes was found from 1994 to 1998, respectively, when the proportion of three-way catalyst passenger cars increased from 60 to 82%. Nevertheless, the mean benzene concentration was only affected to a small degree (from 1.10 to 0.97 ppb) within the same period of time. Reduced catalyst conversion efficiency for benzene with respect to alkylated benzenes was used to explain most of the observed increase of the benzene/toluene and benzene/C_2-benzenes mixing rations.

Portugal

C_2–C_6 hydrocarbons, including isoprene, were measured in a forested area of Portugal from June 20 to July 12, 1994 as part of the FIELDVOC'94 project (Bonsang *et al.*, 2001). The day-to-day variability of the measured NMHC was clearly linked to the air mass origin. The longest-lived ethane did not show any significant diurnal variation. The short-lived alkenes showed a well-defined diurnal variation with maximum mixing ratios during night-time and minimum during daytime resulting from both dynamical and photochemical sinks. Isoprene presented a very different trend with minima of 0.1 ppbv at night and maxima up to 12 ppbv occurring between 16:00 and 18:00 (UT).

Greece

Benzene, toluene, sulphur dioxide, ozone and nitrogen dioxide were measured by Kourtidis (2002), in a four-lane street canyon in Thessaloniki, Greece, during the period January–July 1997 by means of a commercial differential optical absorption spectrometer (OPSIS DOAS). Primary pollutant levels were found to be 2.5–4.4 times higher during the cold part of the year than during the warm part of the year, the winter/summer ratio increasing with the reaction rate constant with OH for each of the measured species. Pollution levels were influenced considerably by wind speed, while for the street canyon under study wind direction did not influence pollutant levels considerably. While primary pollution was found to decrease with increasing wind speed, ozone increased. Benzene mean levels during the study period were around 6 ppb and hence much higher than the EU annual limit value of 1.44 ppb at STP. Toluene mean levels were around 14 ppb and hence also several times above the WHO recommendation of 2 ppb for a 24 hour period.

Non-methane hydrocarbon concentrations (NMHC) were determined in samples collected in electropolished canisters aboard a Falcon aircraft in Athens and Thessaloniki by Moschonas *et al.* (2000). Some canisters were also collected on the ground in Athens. Chemical analysis by cryoconcentration facilitated the speciation of NMHC. The aircraft samples allowed the determination of the background concentrations in the periphery of each city. The aromatic hydrocarbon fraction was found to dominate the measured species.

Acetylene, C_3–C_{10} paraffins, olefins, aromatic hydrocarbons and the biogenic isoprene, were determined in six sampling periods from May to October in 1996–1997 by Moschones *et al.*

(2001). Acetylene and C_3–C_5 hydrocarbons exhibited seasonal variation with higher concentrations in the late October sampling period. The hydrocarbons, except benzene, exhibited maximum concentrations in the summer. The main destruction route of all hydrocarbons was determined to be due to their photochemical reactions. The photochemical reactivity, calculated in terms of propylene equivalent concentration, was in the summer dominated by isoprene which accounted for 69% of the total, aromatics with 16%, olefins with 11% and paraffins with 4%. In the May and October periods, the aromatics contributed the most (~37%) to the photochemical reactivity. Air mass back trajectories indicated higher concentrations when air masses arrived from northwestern and northeastern, compared to southern, directions.

2.9.2 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. Compounds measured at the PAMS sites include 56 individual hydrocarbons, NO_X, ozone and meteorological data. Demerjian (2000), has recently reviewed the state of national air quality monitoring networks in North America and assessed the effectiveness and adequacy of these networks in addressing the critical needs of the various user communities they were designed to serve.

Hourly volatile organic hydrocarbon concentrations measured at a Photochemical Assessment Monitoring Station, located in the Baltimore, MD area, during the summer months from 1996 to 1999 were investigated by Choi *et al.* (2004). Petrol-related sources such as vehicle exhaust, petrol vapor, and liquid petrol contributed more than half of the total NMHC concentration. Natural gas, surface coatings, and biogenic source categories accounted for 13%, 12% and 11% of the total NMHC, respectively, when all hourly measurements were considered.

Non methane hydrocarbon (NMHC) measurements were made at remote upwind locations in Southern California in order to establish the boundary conditions for input into air quality simulation modeling for the 1997 Southern California Ozone Study (Zielinska, 2003). Results showed that the mixing ratios and composition of NMHCs are impacted at these sites by local emissions as well as transported aged emissions.

Ambient air quality measurements of 54 VOCs including hydrocarbons, halogenated hydrocarbons and carbonyls were conducted in or near 13 urban locations in the United States during September 1996 to August 1997 by Mohamed *et al.* (2002). Air samples were collected and analyzed in accordance with US Environmental Protection Agency-approved methods. The target compounds most commonly found were benzene, toluene, xylene and ethylbenzene. These aromatic compounds were highly correlated and proportionally related in a manner suggesting that the primary contributors were mobile sources in all the urban locations studied. Concentrations of total hydrocarbons ranged between 1.39 and 11.93 parts per billion, by volume (ppbv).

Ambient air HC samples were collected at surface air quality monitoring sites by Seila *et al.* (2001), near sources of interest, and aloft on the US (El Paso) and Mexican (Ciudad Juárez) side of the border during a six-week period of the 1996 Paso del Norte Ozone Study. Samples were collected at five sites, three on the US side and two on the Mexican side, during nine intensive operation days when high ozone levels were forecast for the area.. Most samples were collected in electro-polished stainless steel canisters for determination of C_2 to C_{10} hydrocarbons by GC–FID. Spatial and temporal characteristics of HC species concentrations and compositions were examined. Overall, total non-methane hydrocarbon values ranged from 0.1 to 3.4 ppmC with the highest concentrations being recorded in the morning and evening at five vehicle-dominated sites, three in Cd. Juárez and two in El Paso. Toluene in El Paso samples and propane, which is used as a cooking and transportation fuel in Cd. Juárez, were the most abundant hydrocarbons.

The magnitudes, distributions, controlling processes and uncertainties associated with North American natural emissions of oxidant precursors were reviewed by Guenther *et al.* (2000). Vegetation was predicted to contribute about 98% of the total annual natural NMVOC emission. The uncertainty associated with natural emissions was estimated to range from less than 50% for midday summer isoprene emission for some locations to about a factor of 10 for other compounds and landscapes.

2.9.3 Other countries of interest

Hong Kong

Ambient VOCs samples were collected at three locations, (PolyU campus (PU), Kwun Tong (KT), Hok Tsui (HT)) in Hong Kong during the periods of November 2000–February 2001 and June 2001–August 2001 by Ho *et al.* (2004). Toluene was found to be the most abundant VOC detected in Hong Kong. At the PU station, which is close to a main road, the concentrations of most VOCs were higher in summer than in winter. However, at the background location HT, the concentrations of all VOCs were higher in winter than in summer. The xylene/ethylbenzene (X/E) ratio was used to assess the relative age of the air parcels in this study, where values of 1.5 to 3.2 were obtained. The concentrations in the atmosphere in Hong Kong were mainly affected by direct emissions from vehicles, evaporation of fuels, photochemical reactions and few industrial emissions. The X/E ratio measured in a nearby tunnel was higher than that in the ambient air. Vehicular exhaust was the dominant source at PU and KT stations, and less evaporation of fuel or additive occurred at low temperature in winter. Diurnal variations of mean BTEX concentrations at the roadside monitoring station (PU) showed two peaks associated with traffic density.

The characteristics and concentrations of volatile organic compounds (VOCs) in the roadside microenvironments of metropolitan Hong Kong were investigated by Chan *et al.* (2002). The VOC concentrations, especially toluene and benzene were found to be very high when compared with those in most developed cities. The average and maximum concentration of toluene was 19.5 and 84ppbv, respectively. The respective values for benzene were 7.8 and 39 ppbv. There were strong variations in the spatial fluctuation and characteristic of VOC concentrations. The average benzene/toluene ratio in Hong Kong was 0.5 suggesting that vehicular emission was the dominant VOC source in most areas of Hong Kong. The common usage of organic solvents in the building and construction industries, and in the small industries in the industrial and commercial districts were believed to be important sources of VOC in Hong Kong.

Non-methane hydrocarbons (NMHCs) were also measured from January to December 2001 at two sampling sites: Tsuen Wan (TW) and Central & Western (CW) Toxic Air Pollutants Monitoring Stations in Hong Kong by Guo *et al.* (2004). It was found that vehicle emissions

and LPG or natural gas leakage were the main sources of C_3–C_5 alkanes and C_3–C_5 alkenes, while aromatics were predominantly released from paints. Comparison of source contributions to ambient NMHCs at the two sites indicated that the contribution of LPG or natural gas at CW site was almost twice that at TW site.

In an additional study, the real world on-road petrol vehicle emissions of carbon monoxide (CO), hydrocarbons (HC) and nitric oxide (NO) were investigated at nine sites in Hong Kong by Chan *et al.* (2004). A regression analysis approach based on the measured petrol vehicle emission data was also used to estimate the on-road petrol vehicle emission factors of CO, HC and NO with respect to the effects of instantaneous vehicle speed and acceleration/deceleration profiles for local urban driving patterns. The results showed that the petrol vehicle model years, engine sizes and driving patterns have a strong correlation on their emission factors. A comparison of average petrol vehicle emission factors in different engine sizes and European vehicle emission standards was also presented.

China

Urban roadside levels of benzene, toluene, ethylbenzene and xylenes (BTEX) were investigated in three typical cities (Guangzhou, Macau and Nanhai) in the Pearl River Delta Region of south China by Wang *et al.* (2002). Air samples were collected at typical ground level microenvironments by multi-bed adsorbent tubes. The BTEX concentrations were determined by thermal desorption–gas chromatography–mass selective detector (TD–GC–MSD) technique. The mean concentrations of benzene, toluene, ethylbenzene and xylenes were, respectively, 15.5, 23.2, 5.34 and 24.4 ppbv in Guangzhou, 10.9, 22.6, 5.5, 21.7 ppbv in Macau, and 6.2, 10.3, 0.7 and 3.2 ppbv in Nanhai. The relative concentration distribution pattern and mutual correlation analysis indicated that in Macau BTEX were predominantly traffic-related while in Guangzhou benzene had sources other than vehicle emission. In Nanhai, both benzene and toluene had different sources other than vehicle emission. The samples collected from Guangzhou showed that BTEX had significant higher concentrations in November than those in July.

South Korea

Chemical analysis of volatile organic compounds VOCs for five emission sources in Seoul was conducted by Na *et al.* (2002). The source categories included motor vehicle exhaust, gasoline evaporation, paint solvents, natural gas and liquefied petroleum gas (LPG). Measured and estimated gasoline vapour compositions were found to be in good agreement.

Mexico

Measurements of ambient volatile organic compounds (VOCs) were reported from several field campaigns of simultaneous measurements in the Mexico City Metropolitan Area (MCMA) by Colina *et al.* (2004). Conducted between 1992 and 2001, these measurements represented the longest and most complete record of VOC measurements available for Mexico City. Ambient air VOC samples were collected at surface air quality monitoring sites in electro-polished stainless-steel canisters, and analyzed by Gas Chromatography with Flame Ionization Detection for the C_2 to C_{12} hydrocarbons. The possible decrease in emissions observed suggests that VOC emission control measures have been effective at reducing emissions.

Pakistan

Mixing ratios of carbon monoxide (CO), methane (CH_4), non-methane hydrocarbons, halocarbons and alkyl nitrates (a total of 72 species) were determined for 78 whole air samples collected during the winter of 1998–1999 in Karachi, Pakistan by Barletta *et al.* (2002). This was the first time that volatile organic compound levels in Karachi had been extensively characterized. Methane (6.3 ppmv) and ethane (93 ppbv) levels in Karachi were found to be much higher than in other cities that have been studied. High levels of benzene (0.3–19 ppbv) also appear to be of concern in the Karachi urban area. Emissions from vehicular exhaust were found to be the main source for many of the hydrocarbons reported.

Taiwan

Concentration profiles of C_2–C_6 non-methane hydrocarbons (NMHCs) were obtained in metropolitan Taipei, Taiwan by Wang *et al.* (1999), based on 50 air samples collected simultaneously during an evening traffic rush hour. Although motor vehicle exhaust contributed most of the measured hydrocarbons in the city, levels of propane and butane were

significant, and did not correlate well with typical NMHCs emitted from vehicle exhaust, suggesting that the leakage from liquefied petroleum gas (LPG) was the primary source. The reactivity of ethane, propane, iso-and *n*-butanes released from NG and LPG was estimated to be about 5–6% of the total reactivity summed from C_2–C_6 NMHCs, compared to their mass fraction of about 27%.

Japan

The measurement for 1 year from March 1998–February 1999 was achieved for 28 non-methane hydrocarbons (NMHC) at a remote site, Happo, Japan by Sharma *et al.* (2000a). The mixing ratio of NMHC showed well-defined seasonal cycles with winter maximum and summer minimum for ethane, propane, C_4–C_5 alkanes, *n*-hexane and acetylene consistent with the seasonal variation of OH radical. Ethene and propene did not show clear seasonal cycles. Trajectory analyses showed that NMHC in the Pacific rim region at this remote site was affected by anthropogenic emissions from the Asian continent.

Nepal

The total of 28 different C_2–C_6 non-methane hydrocarbons including isoprene emitted from natural and anthropogenic sources in urban and rural sites of Kathmandu, capital of Nepal, were characterized for the first time in Nepal, in November 1998 by Sharma *et al.* (2000b). Thirty-eight whole air samples were analyzed by using GC/FID. Ethene, acetylene and C_4–C_5 alkanes were identified as the source signature in Kathmandu urban ambient air. Hydrocarbon emissions from vehicular exhaust and gasoline evaporation sources were confirmed to outweigh natural gas and biogenic sources. Photochemical ageing analysis showed that the mixing ratio variation of urban air transported towards the rural was due to OH radical initiated oxidation and the observed alkanes in the rural site were mostly from transported urban air.

The Arctic

C_2–C_7 non-methane hydrocarbons were measured in clean maritime boundary layer air at latitudes between 53°N and 81°N by Hopkins *et al.* (2002). Measurements were made using a high sensitivity automated gas chromatography system. The data was collected during the summer of 1999, a period of continuous Arctic sunlight. Hydrocarbons of anthropogenic

origin were observed to decrease in concentration with increasing latitude, due to a combination of dispersion and extensive atmospheric chemical processing. At high latitudes, low boundary layer conditions were common and species of exclusively anthropogenic origin reached highly stable although non-zero values (e.g. acetylene 27.8±2.4 pptV). A number of hydrocarbons believed to be of oceanic origin showed wide variability in these regions of atmospheric boundary layer stability (average ethene =37.2±20.9 pptV), highlighting inhomogeneity in the ocean to atmosphere flux rates. Removal mechanisms for atmospheric hydrocarbons were generally dominated by OH chemistry.

From the selection of studies outlined above, it is readily apparent the emphasis being placed world-wide on investigating the concentrations of various hydrocarbons in the troposphere. A broad comparison between studies is difficult due to differences in sampling campaigns, especially in relation to meteorological and topographical conditions and campaign length. As a result, monitoring campaigns are necessary on a city by city basis. It is hoped that the study carried out and outlined in this thesis can add to the current state of knowledge in regard to ambient hydrocarbon levels, particularly in the greater Dublin area where limited studies have been carried out.

3. ONLINE HYDROCARBON MONITORING SYSTEM

This chapter describes the online measurement method and associated equipment employed throughout this research. The content and layout of the chapter is largely based on Marnane (2000), who obtained first view of the monitoring system during and after expert installation of the system by Perkin Elmer. Relevant additional information is also supplied, in the main obtained from the PAMS hydrocarbon monitoring programme in the US, supplemented by the authors experience with the equipment.

3.1 INTRODUCTION

The hydrocarbon monitoring system used during this study is the Perkin Elmer "Ozone Precursor System". Similar systems are used for the National Hydrocarbon Monitoring Network in the UK (NPTBC, 2000), and the PAMS Hydrocarbon monitoring program in US (USEPA, 1998c). It is a robust system comprising of a number of individual components, which are described along with the system operation in the following sections.

3.2 SYSTEM OVERVIEW

The Perkin-Elmer Ozone Precursor System is an adaptation of the standard Automated Thermal Desorber Model ATD 400 to include a special means for introduction of ambient sample air. This is achieved via a modified internal standard valve mounted at the rear of the ATD 400, which incorporates a dehumidifying system. The ATD 400 desorber is connected to the gas chromatograph via a heated transfer line. Carrier and combustion gases and dry zero air supplies are derived from both cylinders and generators. Separation of the target analytes is achieved through the use of a dual-column system with column switching facilitated by a Deans switch. The system includes two flame ionization detectors (FIDs) for signal detection. Voltage signals from the detectors are collected by a dual-channel buffered digital-to-analog interface, which supplies data to a personal computer running the Turbochrom data handling software.

3.3 SYSTEM COMPONENTS

The monitoring system is composed of several instruments, each of which required expert installation and continued competent maintenance. Each component must be in good working order to ensure the reliability of results, this is ensured by the application of good quality control procedures on a routine basis. The system is housed in a mobile laboratory which also has an in-built meteorological station. The principal components of the on-line HC monitoring system are the air sampler, ATD 400, Autosystem GC, 900series interface and the Turbochrom analytical software.

3.3.1 The air sampler

The air sampler is attached to the rear 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 ATD400. Dry air, from a zero air generator, is circulated through the Nafion drier to dry the ambient sample prior to analysis. It is necessary to dry the air stream in order to prevent blockage by ice on the cold trap (which remains at -30°C during sample collection), PLOT column deterioration, baseline shifts due to elution of the water profile and FID flame extinction.

The Nafion membrane consists of a hygroscopic copolymer of tetrafluoroethylene and a perfluorosulfonic acid that is coaxially mounted within a larger Teflon or stainless steel tube. The humid sample stream is passed through the membrane tube, allowing water to pass through the walls by a process called "perevaporation" into a dry zero air purge stream that is counter-currently flowing through the annular space between the membrane and the outer tube. The result is that water is drawn out of the sample stream as shown below in Figure 3.1. Figures 3.2 and 3.3 show front and rear views of the air sampler.

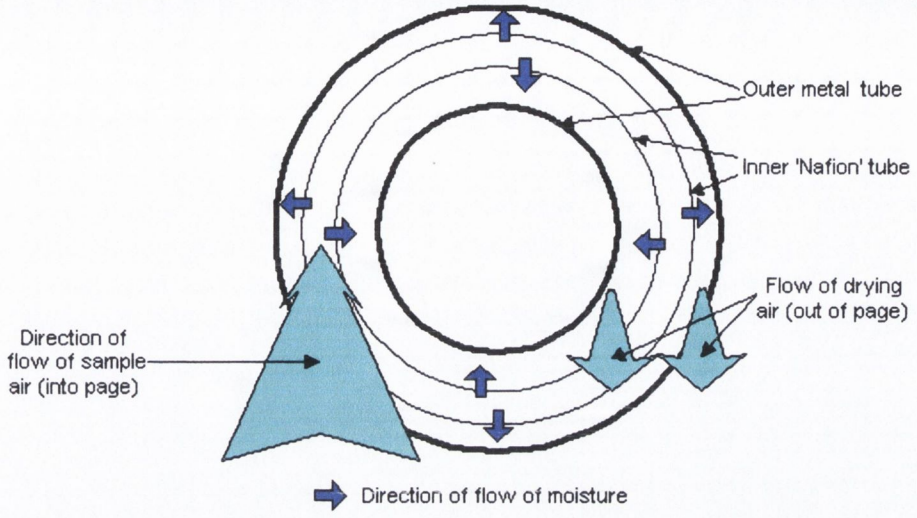


Figure 3.1 Air flows in Nafion drier (NPTBC, 2000)

The dryer will pass almost all normal hydrocarbons with the exception of iso-butylene which is almost entirely removed from the chromatogram (USEPA, 2000). Experience has shown that the drying device is robust under normal use, however replacement is recommended every year.

A mass flow controller is used to control the flow of the sample through the system. It is an integrated part of the air sampler but can be adjusted via the readout box, by the operator. The mass flow controller measures the flow of air by the pressure drop across a venturi. Any change in flow causes a corresponding change in the measured pressure drop, which is detected by a pressure transducer, and a compensating circuit causes the flow to increase or decrease to restore equilibrium. The sampling rate is normally set between 10 and 15ml/min. For all analysis carried out during this research project the flow was maintained at 10ml/min.

The air sampling pump is an external device, whose inlet port is connected to the pump port of the air sampling unit using nylon tubing. The pump is used to draw the sample or calibration gas through the cold trap in the ATD400.

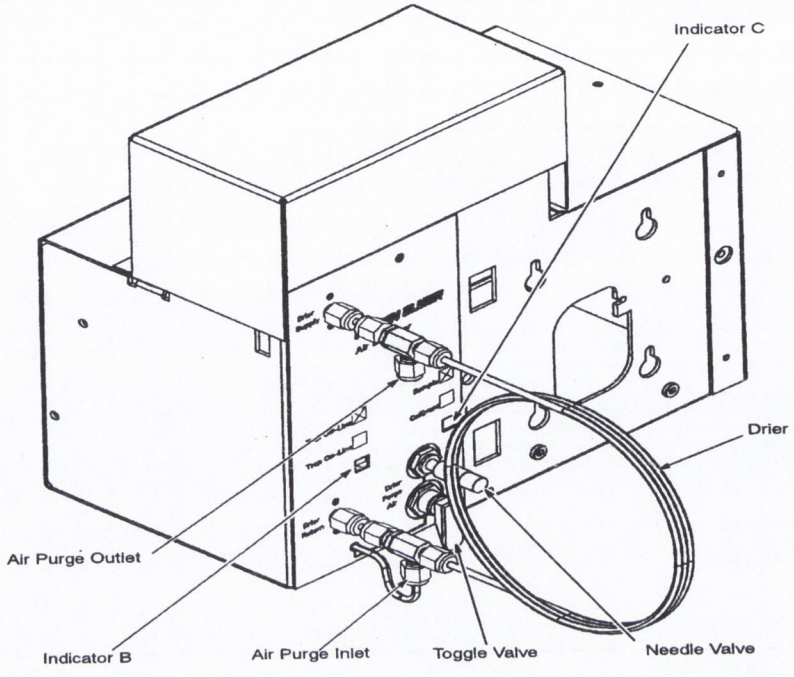


Figure 3.2 Front view of the air sampler before attaching to ATD400

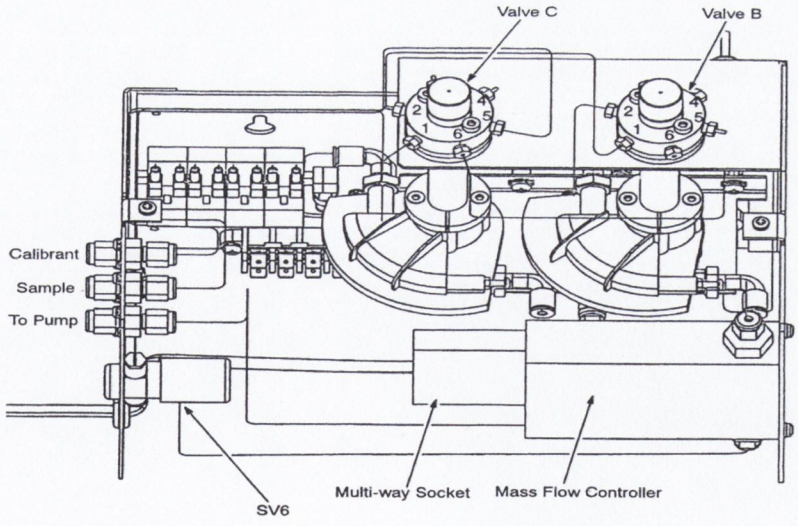


Figure 3.3 Rear view of the air sampler with cover removed

3.3.2 ATD 400 Thermal Desorption Unit

Thermal desorption is a type of dynamic headspace analysis which allows for the collection of volatiles from materials heated in the range of 45 to 400°C. The collected volatiles are then transferred to the GC for separation and analysis. The capability to handle large sample volumes and the absence of solvents permits very low detection limits and little interference in the analysis of samples.

It is a technique which can be used to extract volatile compounds from a non-volatile matrix by heating the sample in a stream of inert gas. In the ATD400, the compounds are desorbed from an adsorbant filled cold trap. The cold trap is packed with two sorbent materials, one is a form of graphite, the other a carbon molecular sieve, designed to trap hydrocarbons in the C_2-C_{10} range. Once the hydrocarbons have been desorbed from the cold trap, they are transferred via a heated transfer line to the gas chromatograph.

A picture of the ATD400 can be seen in Figure 3.4. The instrument can be controlled from either the GC or directly from an attached keyboard. The latter option was used in this research project.

Figure 3.4 ATD400

The ATD400 is fitted with a carousel (shown on the top of the ATD in Figure 3.4), which can be used if samples collected in sorbent tubes are to be analysed. However in the online method, air is delivered directly onto the cold trap of the ATD, negating the need for a separate sampling phase before analysis is carried out. This is achieved using a blank glass tube inserted in the carousel to complete the sample path circuit. The carousel is fixed in position during online sampling, and at no stage in the sampling stage rotates.

An oven is installed in the ATD to heat the sample during thermal desorption. The oven can be set to between 50 and 400°C. For the method employed during online operation, the upper limit was set at 325°C.

The ATD400 heated valve is a 6 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 employed. The heated valve allows a constant temperature to be maintained during the desorption process when the trapped components are being transferred through the heated transfer line to the GC.

The cold trap concentrates the hydrocarbons in the sampled gas before they are injected into the columns in the GC. The trap consists of a straight quartz tube approximately 165mm long by 3mm internal diameter and is cooled electrically to between –30 and 30°C. The tube is contained within a metal jacket which is made to be cooled in a manner like a thermocouple in reverse. A thermocouple measures temperatures by observing the change in voltage with a change in temperature when two particular metals of requisite composition are in contact. This process can be reversed by altering the applied voltages, thereby controlling the temperature of the metal itself. In the ATD400, this process is enhanced by stacking three of these stages one top of one another allowing a temperature of -30°C to be attained. This is shown illustrated in Figure 3.5.

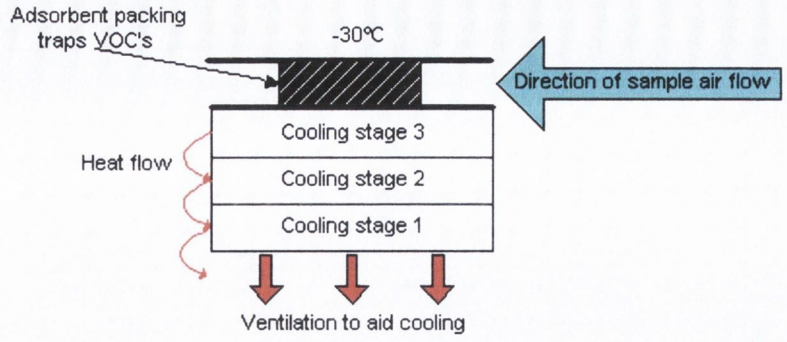


Figure 3.5 Schematic of cold trap in ATD400 (NPTBC, 2000)

With the aid of the adsorbants in the tube, hydrocarbons with boiling points as low as -90°C can be trapped. The sampling method used for the online system run as standard holds the cold trap at -30°C during sampling while the desorb temperature is 325°C. A full list of method specifications is given in Appendix A.

A heated transfer line connects the ATD400 to the GC 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.

3.3.3 Autosystem GC

The autosystem GC is a dual channel, temperature programmable gas chromatograph. The GC is connected to the ATD400 via the heated transfer line through which the sample stream is passed after desorption. Two separate detectors analysing eluent from two separate columns can be installed on the GC. The types of detectors which can be installed include Flame Ionisation Detectors (FID), Electron Capture Detectors (ECD), Thermal Conductivity Detectors (TCD), Photoionisation Detectors (PID) and Flame photometric Detectors (FPD). The Flame Ionisation Detector (FID), responds in proportion to carbon content of the sample, and hence most organic compounds can be detected. For the type of monitoring carried out during this study, the FID is the most widely used detector as it is non-selective. The FID is known to be reliable, robust, highly sensitive for HC detection and relatively rugged in comparison to other detectors. It is known to have a wide linear response from sub-ppb to ppm concentrations (USEPA, 1999d), ideal for ambient HC sampling in varied environments. For these reasons two FIDs were fitted to the GC to be used in the online system.

The GC also contains an oven in which the analytical columns are housed. The oven temperature is programmed from the keyboard on the GC. Two analytical columns were installed for use with the online-system.

3.3.4 Analytical Columns.

In order to obtain optimum separation of lighter (C_2-C_4) as well as heavier compounds (C_6-C_{10}), a dual column, dual detector configuration is utilized. In this case two columns can be judiciously selected to provide optimal separation of hydrocarbons without sub-ambient column oven temperatures. Because both columns are contained within a single GC oven, columns must be selected that will provide the desired separation with a single GC oven temperature program. The columns installed are the same as those used in the PAMS monitoring network and the UK hydrocarbon monitoring network programmes, namely a 50m PLOT (porous layer open tubular) column and a 50m BP-1 (bonded phase) column. Each column is connected to one of the FID detectors, allowing better resolution between peaks and a wider range of compounds detectable, than the single column / detector configuration.

3.3.5 900 series interface

The interface contains dual channel, analog-to-digital circuitry, memory and an IEEE interface to the PC. The PC sends a sequence, which is a list of analyses that are to be performed. The interface then proceeds to process the incoming analog data (FID response) every time it receives a start signal from the GC, and associates that data with a line in the sequence. These data are then sent on request up to the PC in packets or bursts of data points (or time slices), which the PC stores under the heading of the Run File Name. This is called raw data, and Turbochrom gives this data the filename extension of .RAW. The PC need not be active in order for the A/D interface to do its job. Once the sequence is downloaded the interface will acquire data. If the PC is not available the Interface will accumulate data in its on-board memory buffer. When the PC is available it will request the data from the interface by continuous polling. Runs stored in the buffer will be uploaded as a backlog. If the PC does not request the data the interface buffered memory will eventually fill (about 4 to 6 hours of data) and the interface will stop acquiring data. (The whole system will then stop, since the GC will then not become "Ready"). Two connectors, located on the left hand side are the detector

connections, one for channel A and the other for channel B, allowing data from the two detectors to be processed. The relays are located on the bottom left of the interface and are used to control external devices such as the air sampler valves B and C discussed earlier.

3.3.6 Turbochrom Analytical Software

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

The software has two purposes, firstly 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. Once the sequence has been written it is downloaded to the 900 series interface which controls the operation of the ATD and GC once analysis begins.

The second purpose is associated with data analysis. The Turbochrom software scans a series of data points (time slices), which represent the chromatogram. Each data point represents an analog voltage acquired at a nominal time into the run. Data are normally acquired at 3 points per second: more is unnecessary for this analysis and less is unsatisfactory. From this data, Turbochrom determines the baseline signature and identifies peaks according to the criteria in the Turbochrom Method. With this peak information, Turbochrom is able to match peaks with a list of pre-defined target components and parameters, and calculate the amounts of each based on a previous calibration run (a process known as the external standard method of analysis).

3.3.7 Gas supplies

Four gas supplies are required for the online monitoring system. These gases are;

a) *Zero air*

Zero air is used as a combustion gas in the FIDs, to operate pneumatic processes within the ATD400, to purge the peltier cooling system and to remove moisture from the air sample in

the Nafion drier. The system uses 1200 ml/min of air, hence a 5 foot cylinder will be consumed in approximately 6 days. As a result, the zero air supply in most field-deployed systems is generated by means of an electrical compressor and zero-air generator, consisting of a catalytic converter and drying unit. The unit that has been selected to meet the criteria of this application is a modified TOC (total organic carbon) zero air generator from Whatman (previously Balston). It is imperative that the air supply used meets the stringent humidity criterion otherwise the system will be adversely affected. The zero air generator used is able to supply up to 1500 ml/min. of dry (dew point < -100°F) air to the system consistently, over a relatively long period of time.

b) *Helium*

Helium is used as the carrier gas. It is inert to all compounds under investigation. As it flows through the system at a relatively low flow rate of 5ml/min, a cylinder size PT10 will last approximately 3 months. The Helium must be premium grade with <2.0ppm O_2 and <5.0 ppm H_2O. Hydrogen can not be used as the carrier gas for this system as it reacts with acetylene, removing it from the air sampled.

c) *Hydrogen*

Hydrogen is used as the fuel for the FIDs, along with zero air. Approximately 80ml/min is used, so a large cylinder will last approximately 6 weeks. The Hydrogen must be 99.999% pure and not contain more than 0.5ppm total hydrocarbons.

d) *Calibration gas*

The calibration gas is the most expensive gas used in the operation of the on-line system. The calibration gas used during this project was identical to that used in the UK Hydrocarbon Monitoring Network, supplied by the National Physical Laboratory (UK). The components contained in the mix are listed in table 2.1. The compounds are divided according to the analytical column on which they separated. Although 30 compounds are present in the mix, not all of these were analysed in the present study, due to time contraints. The standard obtained from the NPL is certified traceable, ensuring the accuracy of the stated concentrations in the gas mix.

PLOT column	Conc (ppbv)	BP1 column	Conc (ppbv)
ethane*	5.82	cyclohexane	3.38
ethene*	3.04	n-hexane	2.24
acetylene (ethyne)*	6.44	benzene*	3.83
propane*	2.59	n-heptane	1.73
propene*	2.91	toluene*	2.96
propyne	1.80	ethylbenzene*	1.21
n-butane*	1.35	o-xylene*	0.99
iso-butane*	0.86	m+p xylene*	1.50
iso-butene	2.87	1,2,4-tri methylbenzene	0.76
1-butene*	2.85	1,3,5-tri methylbenzene	0.89
trans-2-butene*	0.97		
cis-2-butene*	1.91		
1,3 butadiene*	3.87		
n-pentane*	0.79		
i-pentane*	0.99		
trans-2-pentene*	3.32		
cis-2-pentene*	1.71		
isoprene	2.08		
2-methylpentane	1.27		
3-methylpentane	1.97		

* = compounds analysed during this research project

Table 3.1 Concentrations in parts per billion volume for each hydrocarbon in the calibration mix

3.4 THE MOBILE MONITORING UNIT

The online system is housed within a mobile trailer unit. There are two main sections, one containing monitoring equipment, the second containing the gas cylinders used in the running of the online system. For safety reasons the second compartment is self enclosed with a separate access. A photograph of the main compartment is shown in Figures 3.7 and a schematic plan of the interior of the mobile unit is shown in Figure 3.6.

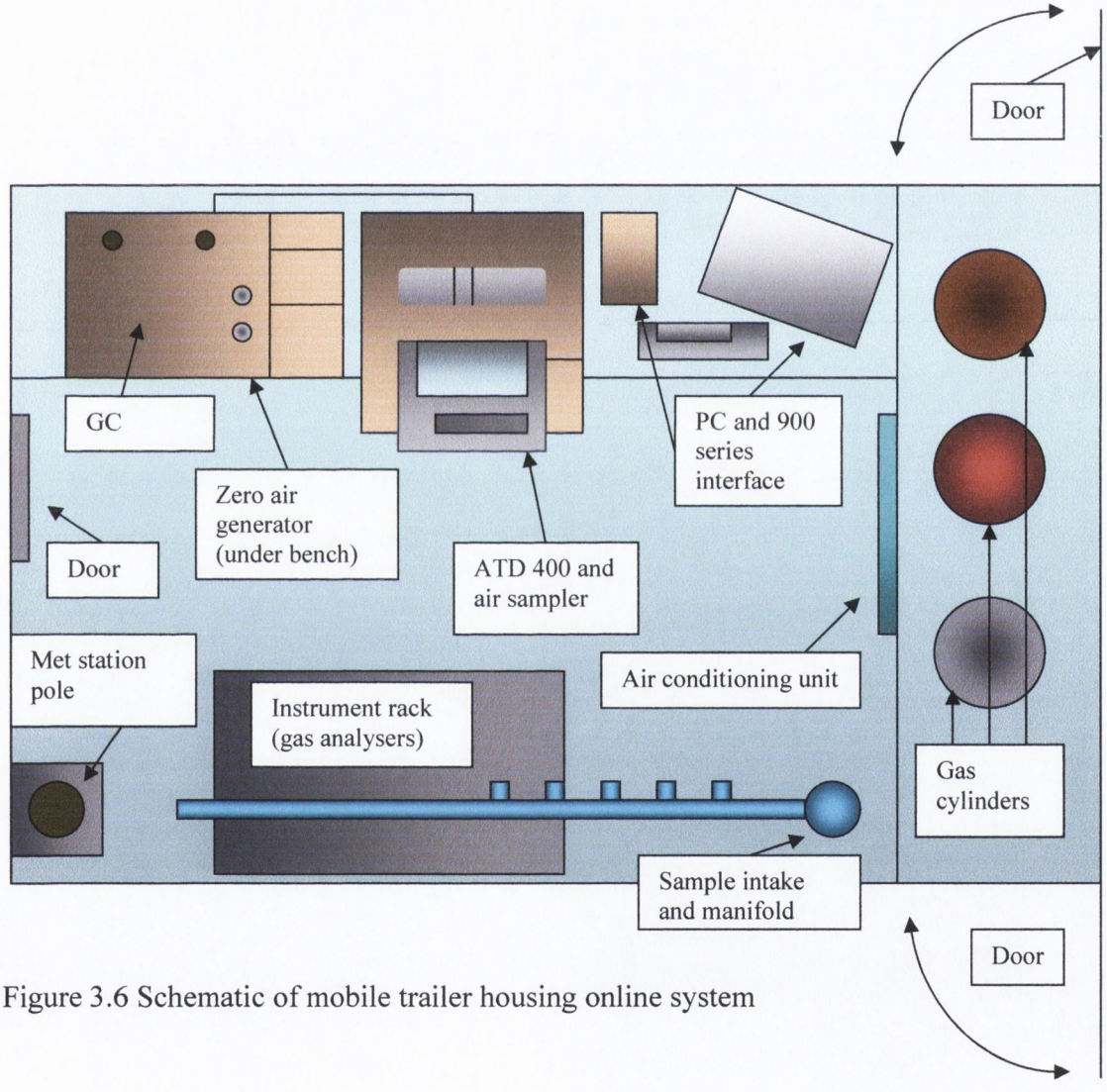


Figure 3.6 Schematic of mobile trailer housing online system

The Autosystem GC, the ATD400, the 900 series interface and the PC are all located on the same bench in the main section. The zero air generator is situated directly beneath the Autosystem GC underneath the bench.

Additional monitoring equipment for other pollutants is situated on an instrument rack opposite the online system. The weather station telescopic pole and the hydrocarbon intake manifold are also on this side. The weather station monitors wind speed and direction, temperature and humidity. The detectors and sensors are located on top of a telescopic pole which is raised to a height of approximately 10 metres.

The sample intake and manifold assembly is used to provide a representative air sample for collection and subsequent analysis. The sample manifold is constructed of glass, approximately 1.5 inches O.D. The manifold has ports used for sample distribution. The number of ports located on the manifold is greater than the total number of monitoring systems to which samples will be delivered. To reduce the potential for bias, the port nearest to the inlet of the manifold is reserved for HC sampling.

Teflon bushings are used to connect sample lines to the manifold. For HC sampling, the sample lines are constructed of 1/8 inch O.D. nylon tubing. The 1/8 inch tubing is flexible and will accommodate the flow rates associated with HC sample collection.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the inlet while manifold, while the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is pulled through the sample inlet and manifold to prevent back diffusion of room air into the manifold and to ensure that the sample air is representative of outside ambient air. Sample air flow through the sample inlet and manifold is at least two times greater than the total air flow being removed for collection and analysis by all systems on the manifold.

The manifold is assembled in a horizontal configuration (Appendix E, Figure E.1), as a result the sample ports point upward so that material that may be present in the manifold will not be transferred into the sample lines.

The trailer is also fitted with an air conditioning system which is necessary to regulate the temperature within the trailer. The ATD400 and GC oven cooling processes require the warm air to be expelled into the main compartment, resulting in a rise in temperature with continued online system use.

Excessive temperatures in the trailer will result in the GC automatically shutting down as a safety precaution, resulting in a discontinuation of online sampling. The air conditioning unit regulates the temperature at a modest 17°C, ideal for continued use of the online system. The power requirements of the system are very high and an internal fuse board is fitted to regulate power supply.

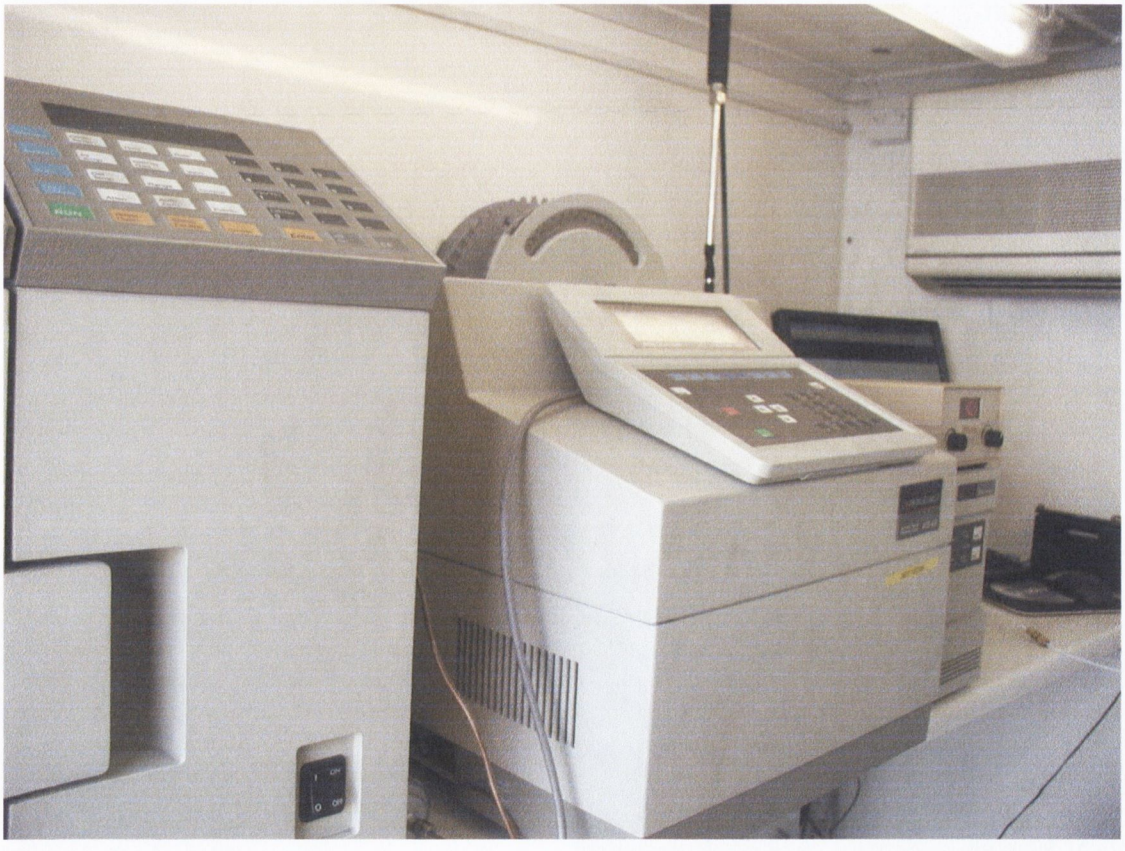


Figure 3.7 P-E ozone precursor system, in main compartment

3.5 PHYSICAL CONNECTION OF COMPONENTS.

The central system around which all connections are made is the ATD 400, as this is the system which controls the starting and ending of a sampling sequence. The ATD 400, through information sent from the 900 series interface, controls the time of operation of the GC.

The ATD400 is connected to the GC via a 25-pin cable connector. This connector allows synchronisation of the GC analysis start time when desorption begins on the ATD 400. As stated earlier, the sample is passed from the ATD 400 to the GC via the heated transfer line. This line is connected from the outlet splitter on the ATD 400 to the analytical columns on the GC.

The helium carrier gas and the zero air are both connected to ATD and GC. These supplies are passed through filters prior to entering the instruments in an attempt to guarantee their purity. Contaminants in either gas will adversely affect the quality of results obtained.

Non soldered copper tubing (to limit potential leaks) is used to carry the gases from the cylinders and generator to the instruments. Swagelok compression fittings are used to connect joints. The air sampler and integrated mass flow controller were connected to the ATD prior to delivery.

The sample manifold (Figure E.1) discussed in the preceding section is attached to the sample port of the air sampler via 1/8 inch nylon tubing. The calibration gas cylinder, which is connected to the calibration port on the air sampler via 1/8 inch stainless steel tubing, requires a specially adapted regulator (Figure 3.8).

This regulator is not fitted with a gauge as loss of trace HC compounds could occur with such a device. Figure 3.8 shows how the delivery pressure is regulated with the HC regulator and read on pressure gauge, but the gas passed to the gauge is not passed on to the air sampler due to the inclusion of a t-piece. The required pressure is approximately 2-3 psi.

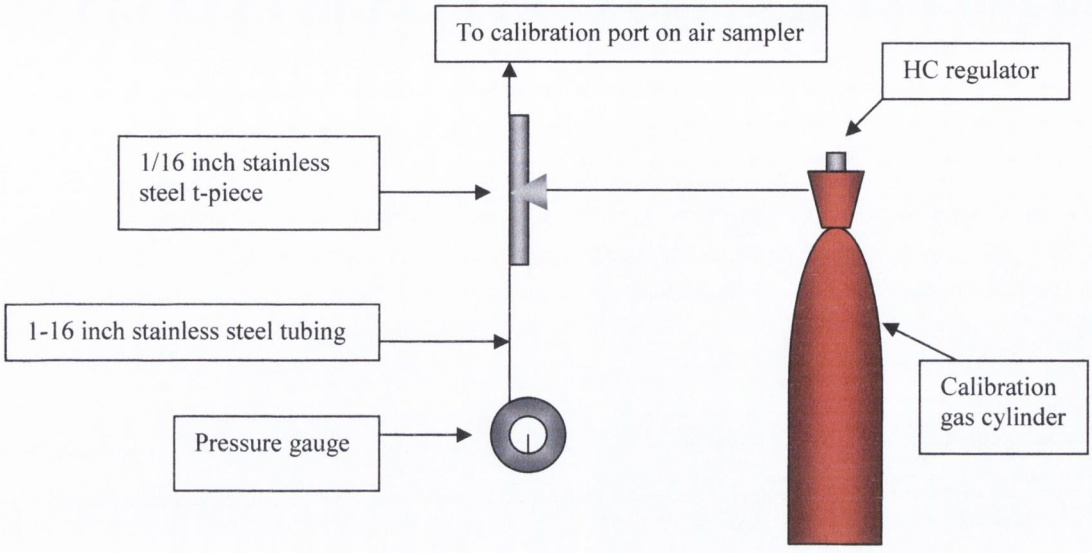


Figure 3.8 Calibration gas supply and pressure measurement system

The ATD is connected to the 900 series interface at the relay 6 and 7 connections. These relays control valve C in the air sampler and dictate whether ambient air or calibration gas is drawn through the system. This is discussed further in the next section.

The 900series interface is connected to the PC via a connection on the "Ziatech" IEEE card installed in one of the expansion slots on the PC. An IEEE 488 cable connects the two instruments.

The Nafion drier is connected between the dryer return and the dryer supply on the front of the air sampler (Figure 3.2) The zero air flow through the dryer should be approximately 250 ml-min, which is adjusted using a needle valve.

3.6 SAMPLE FLOW THROUGH THE SYSTEM

The complete online sampling and analysis procedure takes approximately 95 minutes. However, after the initial sample "run", hourly data is available as the ATD can collect a new

sample while the GC is analysing the previous one. Several stages can be outlined from initial sampling to analysis. These stages are illustrated in Figure 3.9 and discussed in detail below.

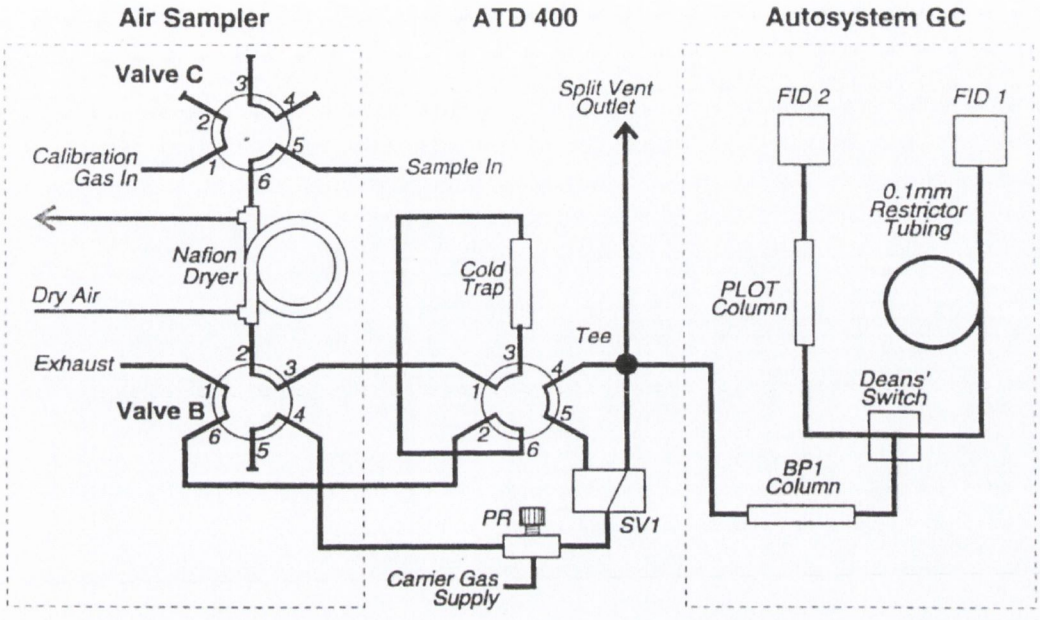


Figure 3.9 Schematic of sample flow through the entire system

3.6.1 Ambient or calibration gas sampling

The sample / calibrant valve (valve C) in the air sampler is controlled by the 900series interface. The position of this valve, which determines whether ambient or calibration gas is drawn through the system is determined by relays 6 and 7 on the 900 series interface. Relay 6 is associated with the calibration gas and when this relay is "on", calibration gas is drawn through the system.

Figure 3.9 shows a simplified schematic diagram of the flow through the entire system. The diagram shows that as valve C is rotated, the input gas switches from calibrant to sample gas (relay 7 on the 900 series interface "on"). These relays are controlled by the "sequence" written in the Turbochrom software. Once the valve switches to either the calibrant or ambient sampling positions, the sampling and analysis stages for both forms of gases are the same.

3.6.2 Sample intake and concentration

Figure 3.15 illustrates the flow through the system for this stage of the procedure. With valve C in the sample intake position (relay 6 "on"), ambient air is drawn through the system. The sample is drawn through the sample inlet and manifold and into the nafion drier where excess moisture is removed from the sample.

The sample then passes through the empty glass tube in the carousel of the ATD and into the cold trap (-30°C) where volatiles are trapped on the adsorbant material. After passing through the cold trap (minus the HCs of interest which will have adhered to the adsorbant in the cold trap), the remaining sample passes through a filter before being released via the exhaust port of the pump attached to the ATD which draws the sample through the system.

The time over which sampling occurs is known as "sample injection time". In the standard method, this lasts for exactly 40 minutes, which at a flow rate of 10ml/min equates to 400cm^3 of sample volume passing through the system. During this sample injection stage, the helium carrier gas only passes through the analytical columns in the GC, with the excess flowing through the outlet split vent.

3.6.3 Desorption

During the desorption stage, outlined in Figure 3.16, valve B in the ATD is rotated and sample is no longer drawn through the cold trap. Air is removed from the cold trap by passing helium (inert) through the cold trap, leaving only the volatiles trapped on the adsorbant. This stage is known as the desorb time and is set at 1 minute in the standard method being employed.

3.6.4 Trap heating and sample transfer

Following desorb time, valve A in the ATD400 is rotated to achieve the flow path illustrated in Figure 3.17. Solenoid valves 2 and 1 (SV2 and SV1) are switched, reversing the carrier gas flow through the cold trap (i.e in the opposite direction to that of the sample when drawn through the trap). Concurrently the trap is quickly heated to a temperature of 325°C at a rate of 45°C / second, to remove all volatiles from the cold trap as quickly as possible. The reversed carrier gas flow allied to the rapid heating creates a narrow vapour band which is sent via the heated transfer line to the analytical columns in the GC.

3.6.5 Passage through the analytical columns

After the sample has passed through the heated transfer line, it is sent to through the BP-1 capillary column and then via the Deans switch, either directly to the FID1 or into the PLOT column and from there to the FID2. A schematic flow diagram is shown in Figure 3.10.

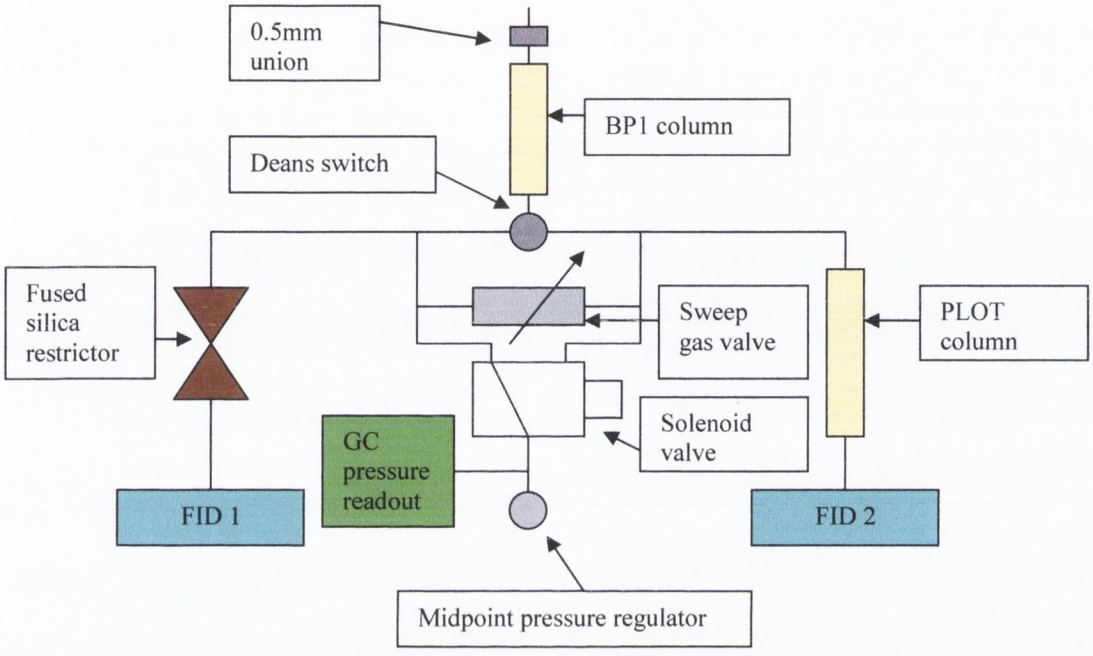


Figure 3.10 Schematic of column connections to GC

The entire sample is first passed through the BP-1 column, which consists of a non-polar dimethyl polysiloxane stationary phase. In most cases, compounds will elute from this column primarily in order of increasing boiling point. As a result, compounds with lower boiling points are not well resolved and are instead passed on to a separate PLOT column for separation via a Dean's switch.

The Deans switch, is a fluidic valve located at the exit of the BP-1 column. It is not a complicated device in principle, but it can be difficult to assemble and re-assemble without the proper knowledge. It uses a switching pressure supplied by the carrier gas and a second pressure regulator to send the eluent from the BP-1 column to the FID directly or to the PLOT column.

This second regulator pressure is termed the "mid-point" pressure supply. At a certain time during the analysis, known as the "heart cut time", the Dean's switch is activated and the higher boiling point compounds which are well resolved on the BP-1 column are sent directly to FID 1 for detection. The lower boiling point compounds are sent to the PLOT column for complete separation and then to FID 2 for detection. PLOT chromatography is accomplished through the gas/solid interactions between the solutes and the solid adsorbent coated on the column tubing wall.

The "heart cut time" is set by manually observing the time at which Hexane and Hexene elute from the columns. The "heart cut time" should be set between these two times. Incorrect setting of the "heart cut time" will result in some of the heavier, higher boiling point HC compounds being transferred to the PLOT column. These compounds can be very hard to remove from this column resulting in poor resolution and possible "ghost peaks".

Due to the large difference in boiling points for the compounds being analyzed, a gradient temperature profile must be applied in the GC oven, to ensure optimum separation. The temperature is programmed to gradually increase from 45°C to 200°C over the 48 minute analysis time. The higher temperature of 200°C should never be exceeded as irreversible damage can be done to the PLOT column above this higher temperature (see appendix B for temperature profile specifications). This gradient program ensures satisfactory resolution and speedy analysis of samples.

3.6.6 Flame Ionisation Detection

Following the sample's passage through either the BP-1 or PLOT columns, the eluent from each is directed to either FID1 or FID2. The FID detector employs hydrogen as a combustion gas which is mixed with the column eluent and burnt at a small jet situated inside a cylindrical electrode. A potential of a few hundred volts is applied between the jet and the electrode and when a carbon containing solute is burnt in the jet, the electron/ion pairs that are formed are collected at the jet and cylindrical electrode. The resulting current is amplified and fed to the 900 series A/D converter and then to the PC acquisition system with incorporated Turbochrom software for concentration quantification. A diagram of the basic FID is shown in Figure 3.11. During the process of oxidation, oxidized or partially oxidized fragments of the solute are

formed in the flame which are thought to generate electrons by thermionic emission (Scott, 1997).

The background current (ions and electrons from the hydrogen flame alone) is very small (1-2 x 10^{-12} amperes) and consequently, the noise level is also commensurably small (about 10^{-14} amperes). Although the column eluent is mixed with the hydrogen prior to entering the detector, because the measurement is mass sensitive rather than concentration sensitive, the diluting effect has no impact on sensitivity.

The FID detects virtually all carbon containing solutes and its response is proportional to the carbon content of the solute (Willet, 1997), with the exception of a small number of small molecular compounds such as carbon disulfide and carbon monoxide. In fact, due to its diverse and comprehensive response, it is considered a universal detector (Scott, 1997).

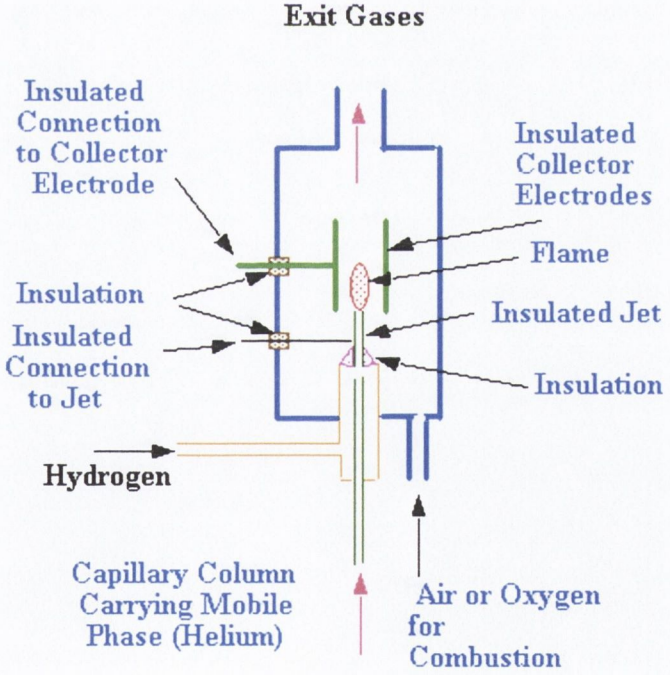


Figure 3.11 Inner workings of a flame ionisation detector (Scott, 1997)

3.6.7 Data processing using Turbochrom software

Turbochrom is a hardware and software system developed by Perkin Elmer to perfrom the following tasks:

- Control supported chromatographs through serial communications.
- Acquire analog or digital chromatography data from chromatographs.
- Analyze the raw data and report results.
- Control the acquisition and analysis of data from large batches of samples.
- Work interactively with instruments to change instrument of interface setting before, during or after a run.
- Store the raw data and calculated results.
- Create methods that define acquisition and analysis parameters.
- Optimise analysis parameters graphically and use the improved parameters to reprocess raw data.
- Compare chromatograms; subtract, add, and calculate the ratio of chromatograms; and manipulate calibration curves.
- Communicate with other software applications.

Turbochrom software processes the digital signal received from the 900 series interface, and chromatograms are prepared as soon as the GC has completed the sample analysis (48 minutes analysis time). These chromatograms are prepared in accordance with specifications outlined in the pre-programmed software method. As a result, operator involvement is not required once a sequence has been downloaded to the series 900 interface.

The "real-time" FID response for both columns can be observed with the aid of the *real time plot* icon from the Turbochrom menu on the PC. This enables the operator to observe how the FIDs are responding and if the system is behaving as expected. The processed results from each run are located in separate .RST result files, whose name and hard drive locations are defined in the Turbochrom sequence. A summary results file can also be created, the specifications of which are operator defined. Sample chromatograms for both columns are shown in Figures 3.12 and 3.13.The slightly noisier plot seen in Figure 3.13 for Channel B is characteristic of this column.

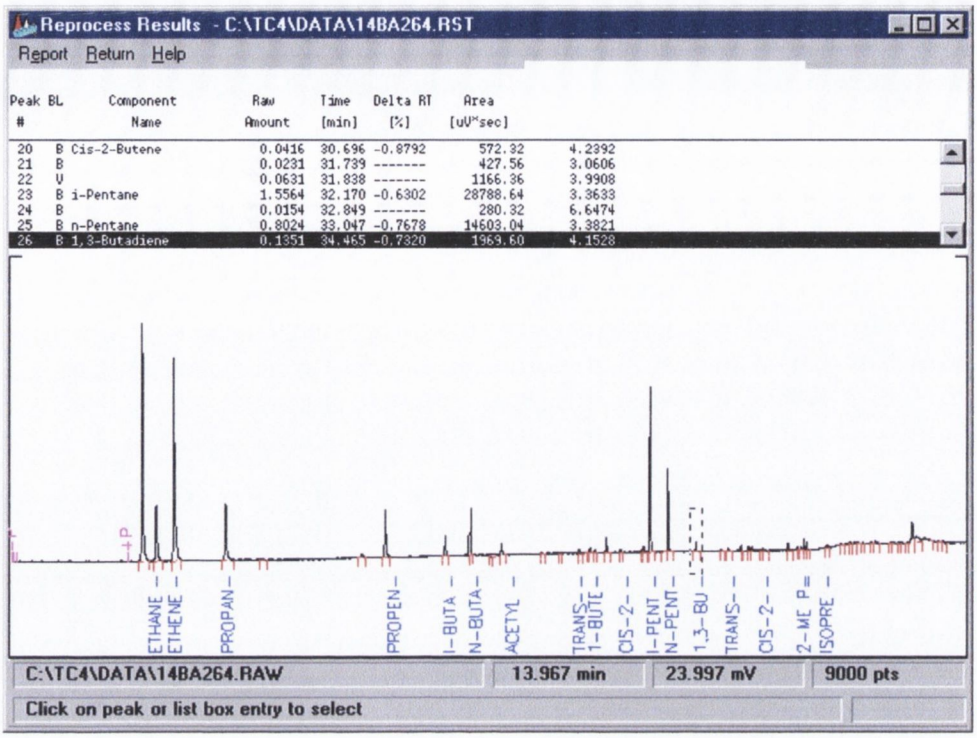


Figure 3.12 Sample Chromatogram for Channel A

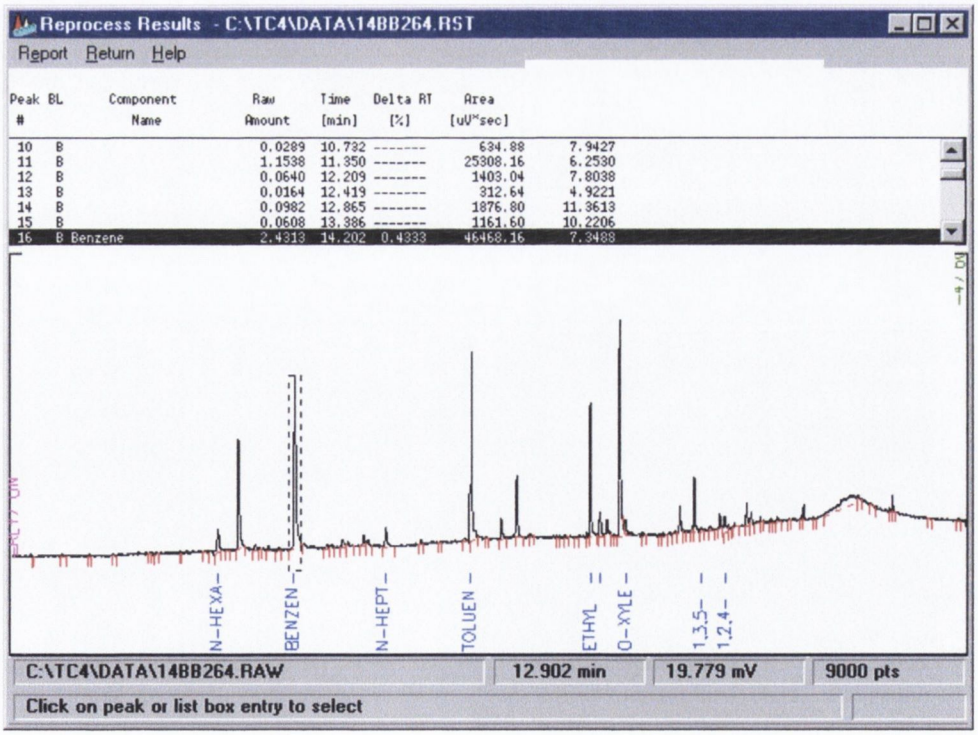


Figure 3.13 Sample Chromatogram for Channel B

3.7 ANALYTICAL METHODS

For the operation of the Perkin-Elmer online system as standard, only dedicated methods for the ATD400, GC and Turbochrom software are required. Each of these methods controls a number of parameters, which will affect the outcome of the sampling and analysis. The GC instrument method, for example controls the temperature gradient profile and the detector temperature. The ATD method controls such parameters as desorb time and temperature, sampling time and cold trap temperature. The Turbochrom software controls operations such as, how the data is analysed, reported, or whether a calibration or ambient sample is taken. The individual instrument methods are specific to that instrument, but act in unison due to communication between the three components. Individual method specifications can be seen in Appendix A.

3.8 WRITING A SEQUENCE

A sampling sequence is written using the Turbochrom software. Each row in a sequence relates to an individual sampling and analysis procedure, the addition of all rows makes up a run. The most important columns of the sequence define separate controlling "methods" for the sampling and analysis of each row.

These four columns relate to Instrument, Processing, Calibration and Report methods. The Instrument method defines the analytical methods to be used by the ATD and GC. It controls such parameters as whether calibrant or ambient air is passed through the air sampler on the ATD and the analysis time on the GC.

The Processing method controls how data received from the GC via the 900 series interface is to be analysed. It controls such parameters as how many times to scan for information per second or the lower peak area limit, values lower than which the system does not report.

The Calibration method relates to the calibration procedure. Parameters such as the concentration of species in the calibrant mix are entered into this method. These responses obtained from certified known concentrations of relevant species are later used to quantify the concentrations of relevant species in ambient samples by a direct comparison of peak areas for the relevant compounds.

The Report method dictates the format of the final result report and controls such parameters as what units concentrations are to be reported in. An example sequence can be seen below in Figure 3.14. The first 6 columns are in the main cosmetic, with the majority of the most relevant information contained in columns 7 to 11. The 11th column relating to "data", controls the naming of each row's file and its hard drive storage location on the PC.

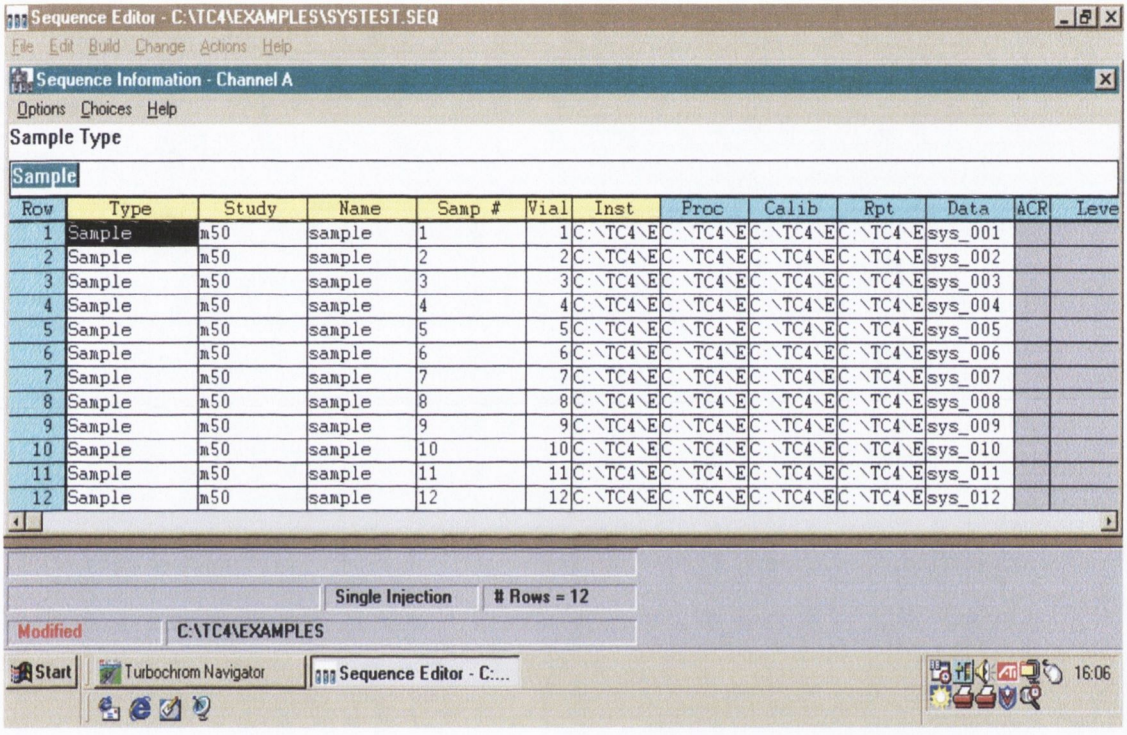


Figure 3.14 Screen-shot of Turbochrom sequence

3.9 QUALITY CONTROL

It is necessary to carry out certain control procedures in order to assure the validity of the data and subsequent results acquired.

3.9.1 Initial procedures before acquiring data

Periods of "operational down time" for the online-system will occur, whether due to a pre-planned break in the research being undertaken, or due to equipment malfunction. After such periods of online-system inactivity, it is not possible to simply switch on the system and acquire valid data. Prior to any quantitation or quantification of data, the system must first be

conditioned. To remove any stubborn contaminants which may be residing on the stationary phases of the analytical columns, the GC oven should be heated to 190°C for 24-48 hours, with the helium carrier gas passing through the columns (as normal). This procedure has the added benefit of rejuvenating the PLOT column, especially if this column is relatively old. Following this, the columns are conditioned with a multi-cycle temperature programme starting at 50°C and increasing by 5°C/minute up to the maximum PLOT column temperature (200°C). If an analysis is carried out on the eluent from this procedure, it will be noted that the initially large peaks obtained will decrease with time (after several days). When satisfactory chromatography has been obtained after the conditioning procedure, the systems response must be calibrated.

3.9.2 Calibration

Calibration was carried out using a 30 component HC calibration mixture, at the trace concentrations, anticipated to be encountered during ambient sampling. This certified, traceable, calibration gas mix was obtained from the National Physical Laboratory (NPL).

Traceability is the 'property of the result of a measurement or the value of a standard whereby it can be related with a stated uncertainty, to stated references, usually national or international standards (i.e. through an unbroken chain of comparisons)' (ISO / IEC, 1992).

A one-point calibration was carried out for each compound in the mix approximately every 14 – 20 days. The calibration mix was passed through the system for 10 consecutive analyses. The first 3 analyses carried out were not used to calibrate the system but were intended to flush any contaminants in the calibration line through the system. The remaining 7 analyses was used to calibrate the system.

The average retention times for each compound were obtained from these 7 replicate analyses and the average peak area response for each compound was used to calibrate the detector response. Response factors for each compound were calculated (average peak area / concentration) which are used to calculate the concentrations of the relevant HC compounds in ambient samples (effectively, by simple cross multiplication). Response factors will differ for

each compound, as the detector response and hence peak area (for FIDs) is proportional to carbon number.

The above procedure also gives an indication as to how effectively the complete online system is operating. The average peak area response obtained for each compound should not be significantly different (±10%) to the average peak area response obtained for the last calibration procedure carried out. If a significant reduction is seen in average peak area response (for the same flow rate), there is a problem with the system, possibly associated with leaks in the calibrant line or a decrease in adsobant efficiency of the cold trap.

The calibration chromatographs should also be visually examined for any obvious signs of column degradation such as excessive peak tailing. Excessive noise noticed in these examinations is probably an indication of either column degradation or inefficient working of the FID (one for each column).

To avoid problems such as those outlined above, and to ensure accurate and reliable results, continued maintenance should be carried out on the system. Appendix B contains details of maintenance procedures employed in this research and are included as a guide for future users.

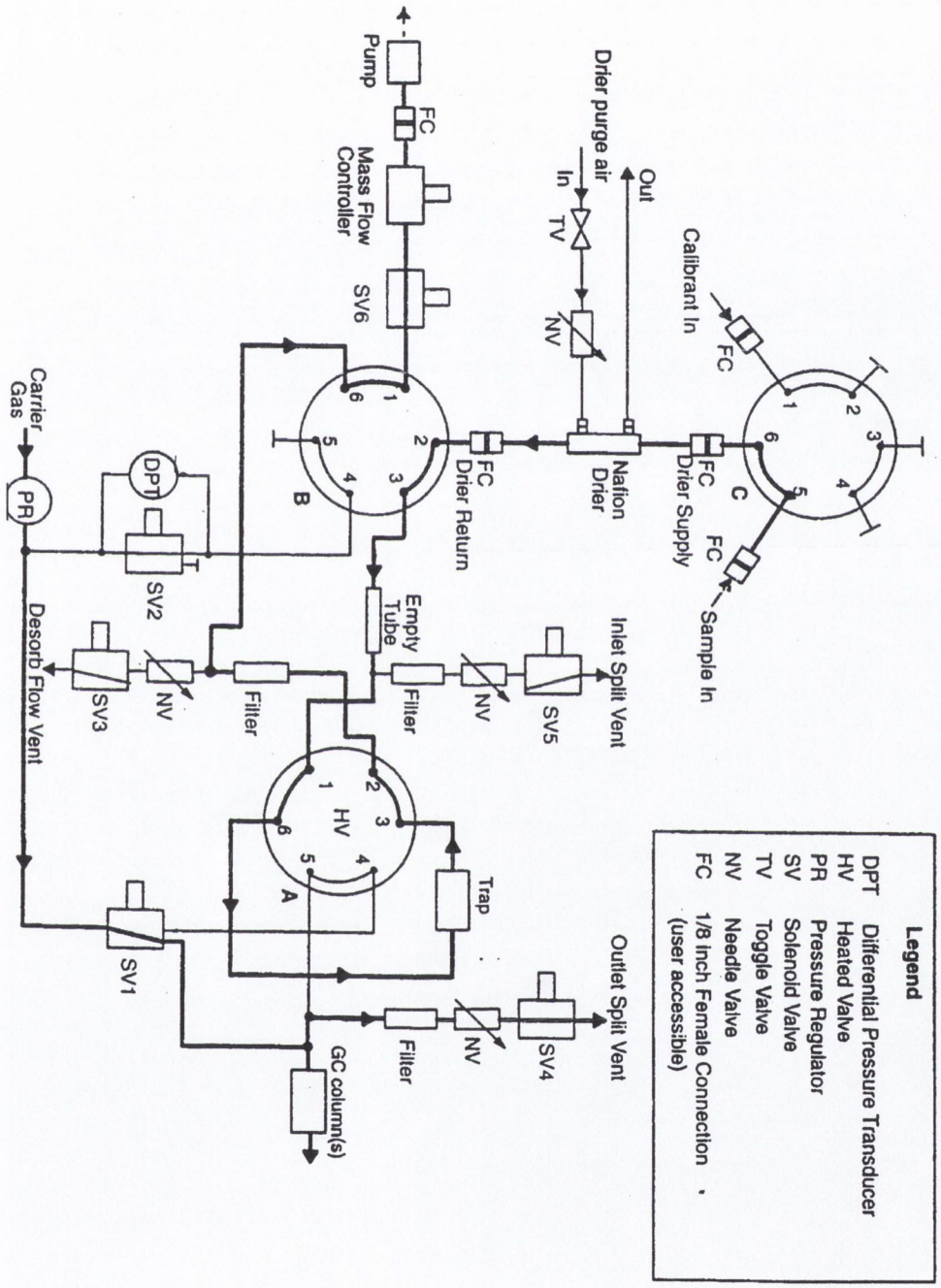


Figure 3.15 Sample intake and concentration

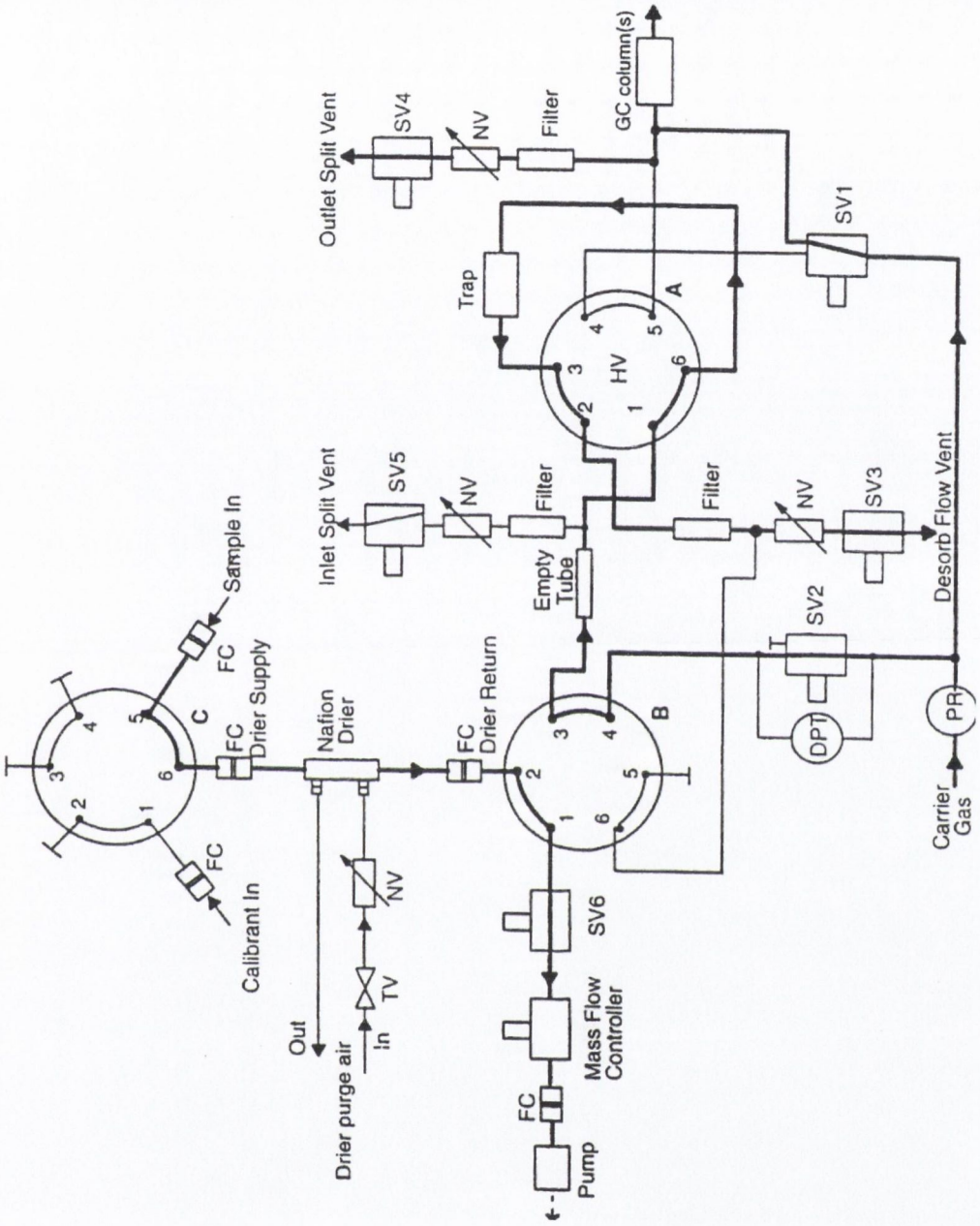


Figure 3.16 Sample desorption stage

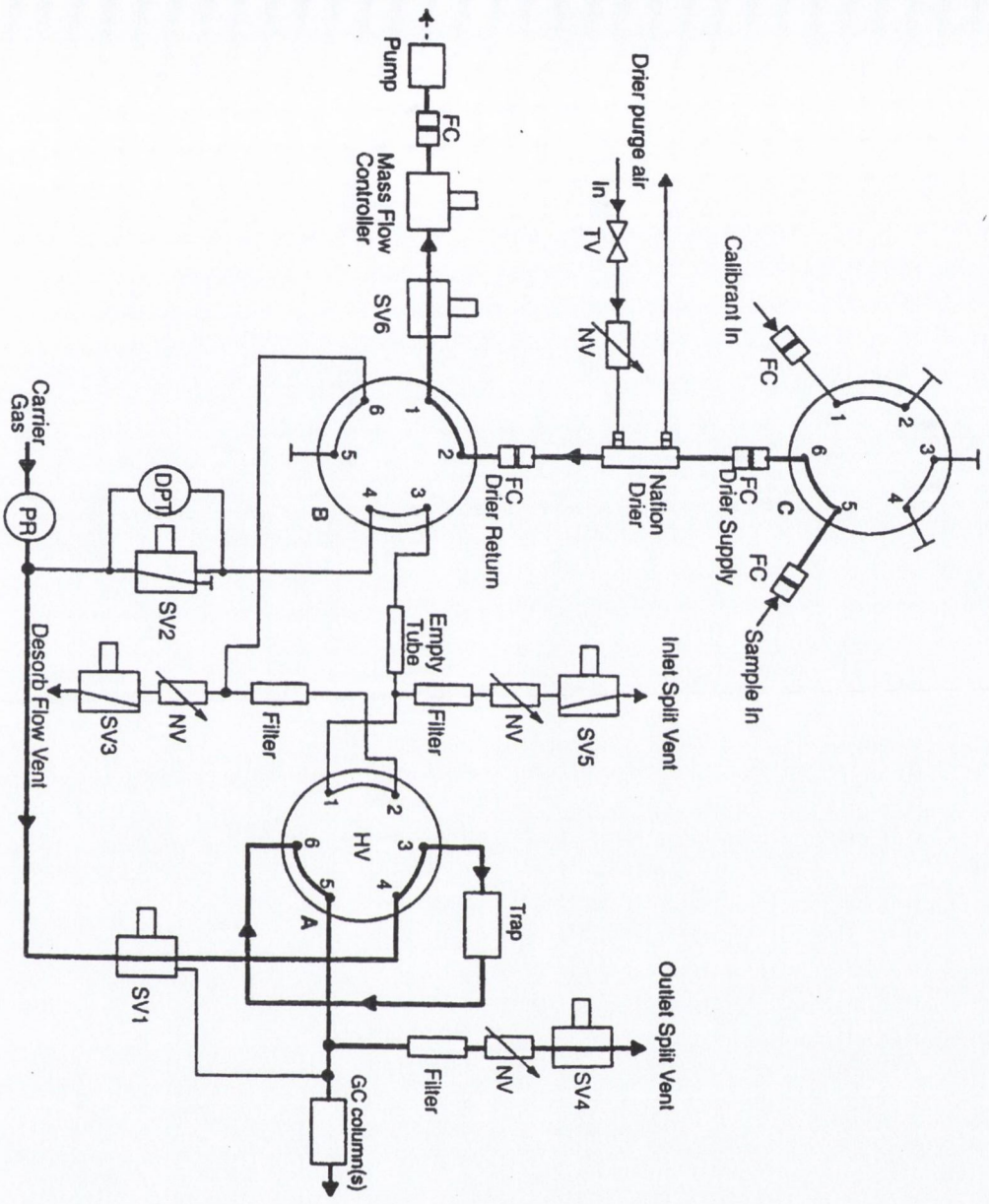


Figure 3.17 Trap heating and sample transfer stage

4. MOBILE SAMPLING METHOD

This chapter describes, the development of a versatile sampling method, for use in conjunction with the hydrocarbon measurement techniques outlined in Chapter 3. This new sampling method was applied in a number of measurement campaigns, as described in later chapters.

4.1 METHOD DEVELOPMENT

The Perkin-Elmer ozone precursor system, run as standard, is an excellent system for sampling and analysing air quality at one particular location over a relatively long period of time. It is generally situated in a single location for a specific sampling requirement, i.e, to obtain general background levels at a background site, or roadside monitoring in the vicinity of a heavily trafficked motorway. Due to logistical problems associated with power supply and security, once a suitable location has been found for the intended sampling purpose, the online-system is generally not moved for a relatively long period of time. Although the temporal resolution of sampling is not a serious problem with the online system, as hourly measurements can be obtained, investigation of the spatial variation of concentrations is not possible. As a result, if for example, a monitoring study was being carried out in the vicinity of a suburban motorway, only concentrations on one side of the road can be determined using the online-system. Hence, no background concentrations are available, making it difficult to establish the source effect from the motorway.

To remedy this lack of spatial resolution and the limited temporal resolution, it was decided to develop an alternate mobile sampling method whose samples could be analysed by the existing P-E precursor system. The aim was to develop a sampling method that could provide the ability to sample in a wide variety of sampling environments, from background ambient sampling to indoor sampling.

The potential use of sorbent tubes as sample tools was first investigated. However, the online system run as standard would have to be significantly adapted to facilitate the analysis of these. In addition, several different tubes may have to be employed to sample the desired range of hydrocarbon compounds, thus making the procedure very labour intensive. Also, sorbents with sufficient retention of C_2 compounds at room temperature, namely ethane, ethene, and acetylene, are not yet available (Wang *et al.*, 2003). Ethene and acetylene are

known markers for road traffic emissions (Borbon *et al.*, 2002) and their omission from the sampling method would vastly reduce the usefulness of the method.

A second option for sampling concerned the use of stainless steel or aluminium canisters as sampling vessels. This approach is outlined in detail in EPA methods TO-14A (USEPA, 1999b) and TO-15 (USEPA, 1999c), where sampled canisters are attached to pre-concentration systems and analysed using GC. The main restriction in applying this procedure is the cost of the canisters, which are relatively expensive. As several canisters would be required to carry out any meaningful spatial studies over a relatively short period of time, the purchase cost of these proved prohibitive for the current research project. Instead, the approach outlined in EPA methods TO-14 and TO-15 was amended, using an alternate form of sampling vessel, namely Tedlar bags.

Tedlar® polyvinyl fluoride (PVF) is a polymer developed by DuPont in 1961. Initially developed for residential use, its use has expanded into many markets, including aircraft interiors, motorway sound barriers, air supported structures and wall coverings. The Tedlar bags used for gas sampling are produced by heat sealing non-adherable "S" surface film, type TST20SG4, to itself. Unlike other sample bag materials, Tedlar film resists gas permeation, both into and out of the bag. This is essential for sample integrity, for all applications. Due to Tedlar's fluorocarbon nature, it is both tough and flexible. As Tedlar contains no plasticizers the film retains its tensile strength and toughness allowing for reuse and a long service life for many applications. Tedlar is rated for continuous use from -98 to 225 F. This wide range of operation facilitates use in very cold or very hot environments including stacks, vents, and flues. Tedlar film is also inert to a wide range of chemicals. Since it will not react with or alter the composition of collected chemicals, sample integrity is not affected. Tedlar bags are widely used in various sampling applications as diverse as ground water sampling to gas grab and stack sampling. They are usually used in conjunction with a pump, to fill the bag with the required sample. For air sampling, the usual approach is to connect a bag of requisite size to the exhaust of the sampling pump and to collect the sample gas after it passes through the pump. However, this approach is unacceptable for the type of quantitative analysis required in this project, as potential contamination may arise due to compounds adhering to the interior of the pump. Instead, a sampling technique where the gas is sampled directly into the Tedlar

vessel is required. Such an approach is possible with the use of an SKC Vac-U-Chamber™. The Vac-U-Chamber consists of a rigid case and connecting fittings, which allows the direct filling of a gas sample vessel using negative pressure. Utilizing the change in pressure drop inside the chamber when connected to a vacuum source (pump), gas will be pulled into the sample bag directly, eliminating the possibility of sample contamination from components inside the pump. The sampling set up is illustrated in Figures 4.1 and 4.2.

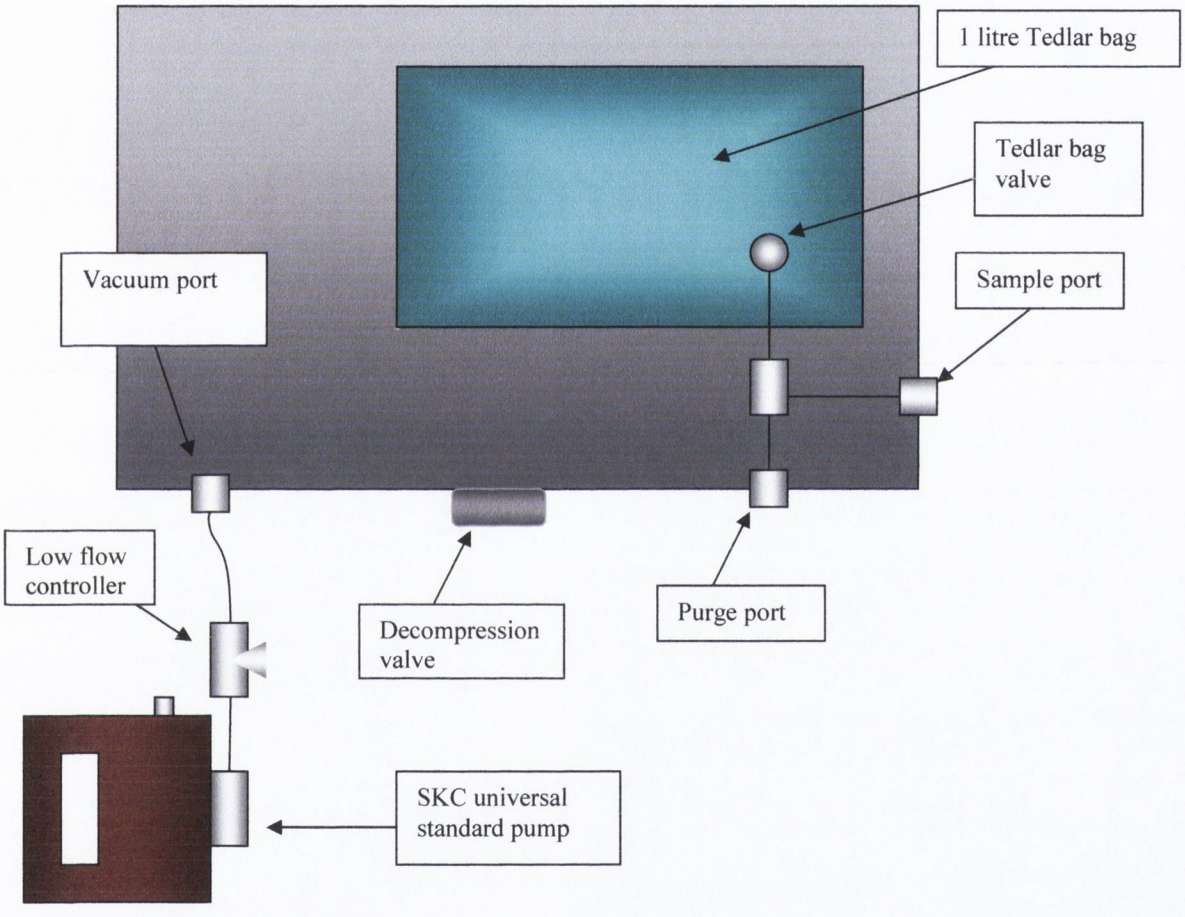


Figure 4.1 Mobile sampling setup with Vac-U-Chamber

Three ports are located on the outside of the chamber. The pump is attached to the vacuum port which is used to inflate the Tedlar vessel. The purge port is used to clean the Tedlar vessel. The sample is drawn into the Tedlar bag through the sample port. All interior tubing which is in contact with the sample is composed of inert, non-stick teflon. Industry standard

SKC 1 litre Tedlar bags were used in the Vac-U-Chamber. These sample bags utilise a lightweight, patented single fitting of inert polypropylene that combines the hose/valve and the septum holder into one compact fitting (Appendix D, Figure D.1). The pump used was an SKC universal standard pump, type 224-44EX. The pump with an additional low flow controller allowed sample flow rates of between 5 and 5000 cm^3/min, more than adequate for most sampling applications. Most importantly the pump was a certified constant flow pump, which ensured homogenous sampling over the desired sampling time. Specifications can be seen in Appendix C, Table C.1. A pump diagram can be seen in Appendix C, Figure C.1. The low flow controller (Appendix D, Figure D.3) which was necessary to ensure constant flow at low flow rates (5-500cm^3/min), was attached via ¼ inch tygon tubing between the pump and the vacuum port.

Figure 4.2 Mobile sampling setup

4.1.1 Mobile sampling procedure

To obtain an air sample the following steps are carried out in sequence.

- The 1 litre tedlar vessel was connected to the 3/16 inch internal tubing of the Vac-U-Chamber.

- The pump and low flow controller are attached to the vacuum port via "quick disconnect" tygon tubing supplied with the Vac–U-Chamber. The vacuum port is only operational when the "quick disconnect" connection is inserted in to the port.

- The tedlar sample bag is opened by turning the valve one turn (max) anti-clockwise. The Vac-U-Chamber was closed securely using both latches.

- The decompression valve located below the handle is closed and the pump turned on. A "trial" sample is used to set the flow to the required rate, i.e, sufficient flow so as to approximately ¾ fill the Tedlar bag in the required sampling time. The flow is adjusted using the screw located on the side of the low flow adapter (Appendix D, Figure D.3).

- Once the required flow rate is established, the pump is turned off and the decompression valve opened.

- The Vac-U-Chamber is then opened and the valve on the Tedlar bag closed.

- This bag is then replaced with a clean sample bag for quantitative analysis. The above procedure is repeated, sampling at the established flow rate for the required time.

- The Tedlar vessel is removed upon sample completion and is ready for analysis using the P-E ozone precursor system.

4.1.2 Mobile sample analysis

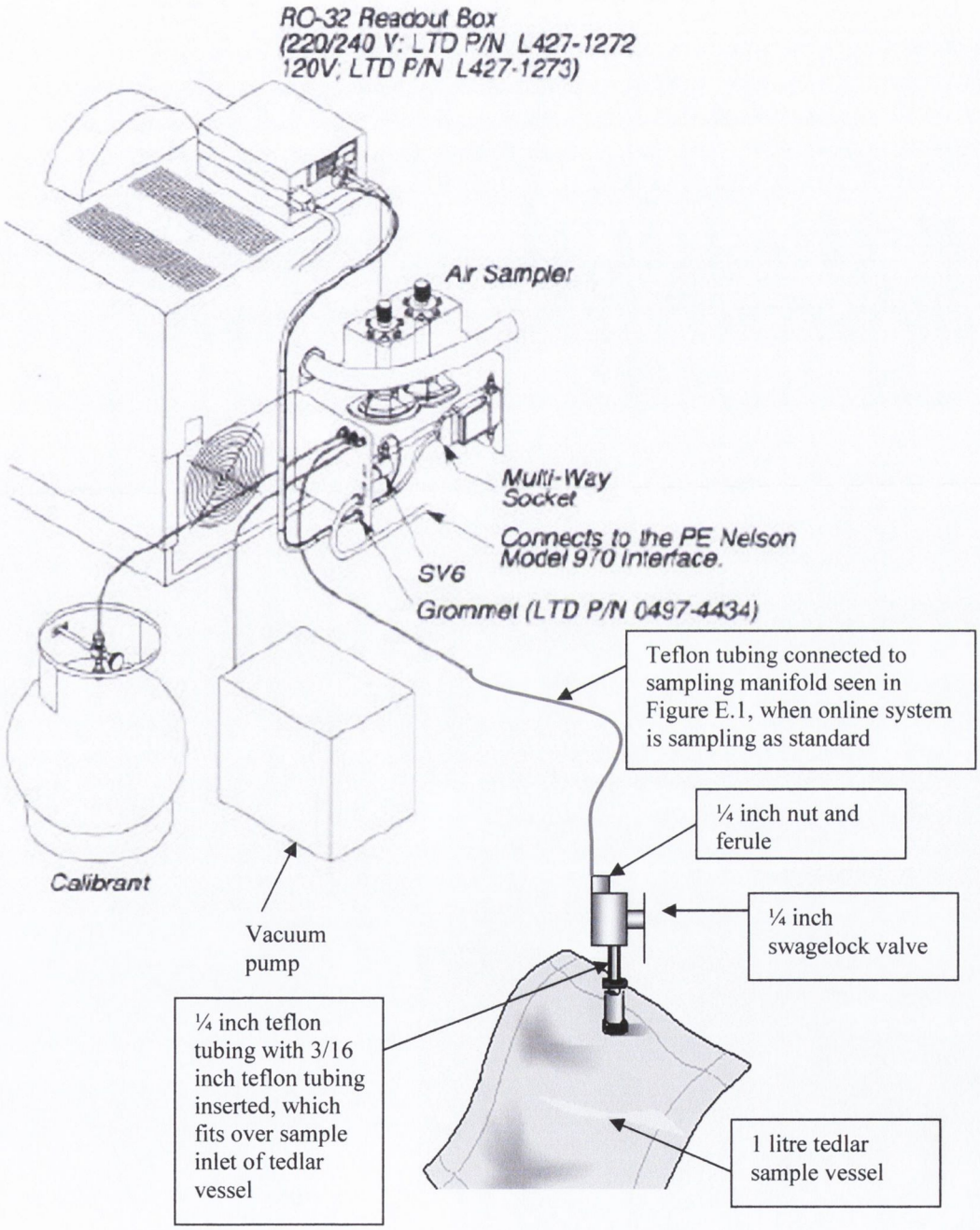
- Sample analysis utilised the P–E ozone precursor system's ability to pre-concentrate samples with a relatively low sample volume (<1 litre). The connection of the Tedlar vessels to the P-E system is shown in Figure 4.3.

- The connections used to attach the bags to the P-E system were checked daily to ensure that no leaks were present. This was done by attaching an evacuated, empty Tedlar bag to the system as shown in Figure 3.3, and ensuring that the flow meter on the system read and remained at 0ml/min.

- The P-E ozone pre-cursor system was run as normal (Chapter 3 describes the online system operation), but instead of ambient air being sampled through the sample manifold as in Appendix E, Figure E.1, air was sampled from the attached Tedlar vessel.

- After attaching the Tedlar vessel to the P-E system, the valve on the vessel is opened for 3-4 minutes prior to the system drawing air through the cold trap. This is done to ensure a homogenous sample through the sample lines prior to sampling.

Figure 4.3 Connections to P-E system for Tedlar vessel sampling



4.1.3 Cleaning procedure required for quantitative analysis

Prior to any sampling method validation or subsequent mobile sampling applications, it was essential to ensure that the Tedlar vessels could be cleaned consistently to an acceptably low level of contamination. The degree to which the vessels could be cleaned would dictate the accuracy, precision and method detection limits of the mobile sampling method.

Air was sampled using the mobile method outlined in section 4.1.1 above, in the vicinity of very slow moving traffic to ensure that high concentrations of hydrocarbons were sampled in the Tedlar vessel. Four Tedlar vessels taken at random were filled at this location. The samples were left to equilibrate for several hours before an investigation into cleaning requirements was carried out.

After several hours the sample vessels were emptied by attaching the sample valves of the Tedlar bags to the inlet on the sampling pump and drawing the sample out of the vessel. The bags were then flushed through with high purity zero air by attaching the vessels to a zero air cylinder and filling the bags approximately half full. Zero air was flushed through each bag on a different number of occasions for each vessel, ranging from 5 to 20 times.

After each bag was cleaned the requisite number of times, a blank sample was taken, by filling the bag with zero-air. This was analysed using the P-E system, as in section 4.1.2. The subsequent chromatograms were visually examined for peaks relating to bag contamination. This allowed the required number of times a Tedlar vessel must be flushed with zero air to obtain a desired low level of contamination to be established.

The results are shown in Table 4.1. It can be seen that no practical level of cleaning could completely remove the mono-substituted aromatics (toluene,o-xylene, m+p xylene and ethylbenzene) from the Tedlar vessels. This is probably due to these compounds "sticking" to the walls of the Tedlar due their substituent nature, making their removal very difficult, and the extent to which it can be achieved very unpredictable. As the level of contamination varies, even with increasing flushes, it is not possible to apply a correction factor for contamination of these compounds in the vessels.

Therefore, as only qualitative assessments can be carried out they are not included in the validation study. Due to the limited additional information which could be gathered from sampling the cis and trans isomers of pentene and butene, over and above that given from ethene, propene and 1,3 butadiene, these compounds were not included in the validation study. For all other hydrocarbons investigated, after visual inspection of the chromatograms, no evidence for the presence of any of the compounds in the blank analysis could be detected after at least 10 flushes of zero air.

To ensure reproducible cleaning using zero air flushes, it was decided to flush 15 times after each bag use. To validate this cleaning procedure further, 10 ambient samples were taken using the mobile sampling method, the bags were evacuated and each vessel then flushed 15 times using zero air. Zero air blanks were then taken and the chromatograms visually inspected for peaks. On no occasion were peaks relating to the compounds of interest present, thus verifying the effectiveness of this cleaning procedure. Example blank chromatograph's for both channel A and B are shown in Figures 4.4 and 4.5.

	Conc after flushing 5 times (ppbv)	Conc after flushing 10 times (ppbv)	Conc after flushing 15 times (ppbv)	Conc after flushing 20 times (ppbv)
ethane	ND	ND	ND	ND
propane	0.1	ND	ND	ND
n-butane	0.1	ND	ND	ND
i-butane	0.1	ND	ND	ND
n-pentane	ND	ND	ND	ND
i-pentane	0.1	ND	ND	ND
ethene	0.1	ND	ND	ND
propene	0.2	ND	ND	ND
1-butene	0.1	ND	ND	ND
1,3 butadiene	0.1	ND	ND	ND
acetylene	0.2	ND	ND	ND
benzene	0.1	ND	ND	ND
toluene	0.8	1.0	0.2	0.9
o-xylene	0.4	0.2	0.2	0.3
m+p xylene	0.3	0.4	0.2	0.3
ethylbenzene	0.2	0.2	0.1	0.1

ND = not detected

Table 4.1 Compounds investigated for bag contamination and number of flushes required to clean tedlar vessels

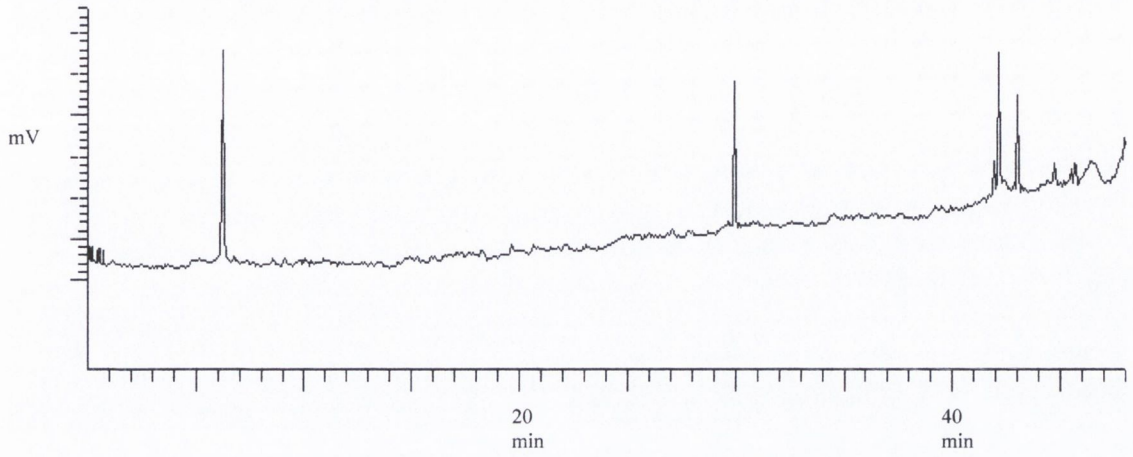


Figure 4.4 Blank chromatogram (Channel A) after 10 flushes

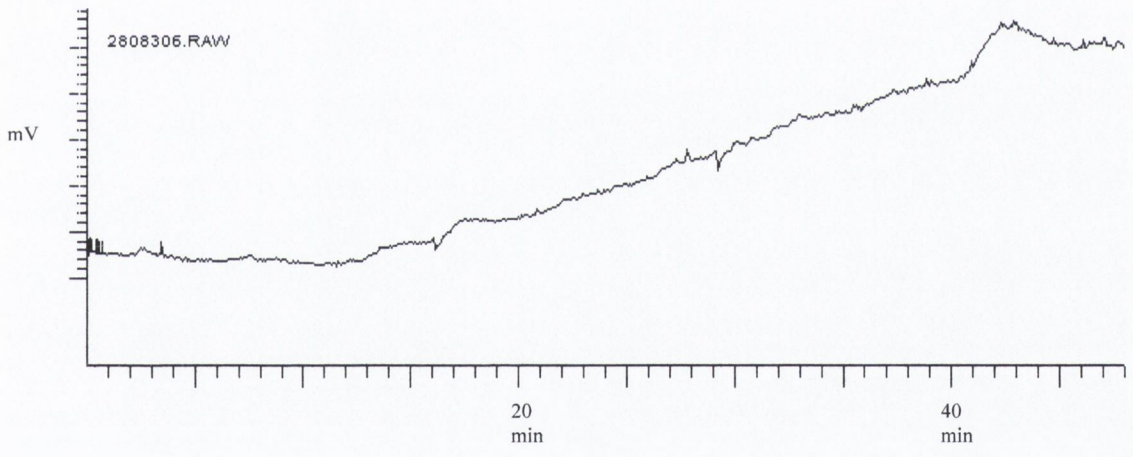


Figure 4.5 Blank Chromatogram (Channel B) after 10 flushes

The peaks observed in Figure 4.4 do not effect the quantification or quantitation of the compounds of interest eluting from this column. In Figure 4.5, no peaks are observed in the vicinity of benzene, which elutes at approximately 11 minutes. The baseline rise observed in Figure 4.5 is due to the pre-programmed temperature gradient in the GC method to ensure adequate separation of compounds.

4.2 VALIDATION OF MOBILE SAMPLING METHOD

4.2.1 Objectives

The aim of this study, was to demonstrate that the mobile sampling procedure outlined in section 4.1.1 and 4.1.2 above, would provide accurate and precise results for those hydrocarbon compounds which showed no evidence of Tedlar bag contamination after the cleaning procedure outlined in section 4.1.3 had been applied. Sampling method performance was to be ascertained over a wide concentration range, thus facilitating the application of the mobile sampling method to wide and varied sampling environments.

4.2.2 Introduction

Method validation is the process to confirm that the analytical procedure employed for a specific test is suitable for its intended purpose. ISO defines validation as *"confirmation by examination and provision of objective evidence that the particular requirements for a specified intended use are fulfilled*" (ISO 8402, 1994).

An implication of this definition is that a method must generate results that have demonstrable "fitness for purpose". For an analytical method to be fit for its intended purpose it must be sufficiently reliable for any decision based upon it to be taken with confidence. To demonstrate this it is necessary to evaluate the method's performance capabilities in terms of key method parameters.

These parameters for method validation have been defined in different working groups of national and international committees and are described in literature (Eurachem, 1998; FDA, 2000; FDA, 1994; ICH, 1995). Unfortunately some of the definitions differ between different organizations.

An attempt at harmonization was made for pharmaceutical applications through the International Conference on Harmonization (ICH, 1995) where representatives from the industry and regulatory agencies from USA, Europe and Japan defined parameters, requirements and, to some extent, also methodologies for analytical method validation.

The parameters used in our validation study as defined by the ICH and by other organizations and authors are summarized below.

- Specificity
- Linearity
- Limits of detection
- Accuracy
- Precision
- Robustness
- Range

It is usually left to the analyst's discretion to decide which performance criteria are to be met in relation to method validation parameters (Eurachem, 1998). These are normally dictated by the intended application of the method of interest. The application of our intended method shall take place in a research environment where a wide variety of sampling projects are anticipated.

Technically, as this method is a modification of a standard method (the P-E ozone pre-cursor system for online HC measurements) the only parameters which are necessary to ascertain are limits of detection, accuracy and precision (Wood, 99). However, as complete a validation as practical has been carried out. Performance criteria for each parameter shall be discussed in the following sections.

In regard to estimating validation parameters, often a particular set of experiments will yield information on several areas of performance. Consequently, the data obtained to investigate the method performance in one area can, with planning be applied to several areas (i.e, calibration data can be used to determine method detection limits).

4.2.3 Specificity / Selectivity

It is necessary to establish that the signal produced at the measurement stage, or other measured property, which has been attributed to the analyte, is only due to the analyte and not

the presence of something chemically or physically similar, or simply arising as a coincidence. This is confirmation of identity (Eurachem, 1998).

Selectivity can be defined as '*The ability of a method to determine accurately and specifically the analyte of interest in the presence of other components in a sample matrix under the stated conditions of the test.*' (NATA, 1998).

Specificity is described as '*The ability of a method to measure only what it is intended to measure.*' (AOAC – PVMC, 1993).

The two terms are often used interchangeably. However, Huber (1998), refers to a detailed discussion on the topic by Vessman, where different definitions were employed by different organisations, i.e IUPAC, WELAC and ICH. Huber outlines that the term *specific* generally refers to a method that produces a response for a single analyte only while the term *selective* refers to a method which provides responses for a number of chemical entities that may or may not be distinguished from each other.

Specificity is generally thought of as being 100% selective but again agreement is not universal (Eurachem, 1998). In practical terms, there are very few specific methods and the identification of hydrocarbons with GC / FID is most certainly not amongst them, hence the term selective is deemed the more apt description for this study.

Whether or not other compounds interfere with the measurement of the analyte will depend on the effectiveness of the isolation stage and the selectivity of the measurement stage. As these stages are not changed with the addition of the Tedlar sampling vessel to the Perkin-Elmer precursor system run as standard, a comparison of the selectivity of the online system and that of the bag sampling method should provide sufficient information.

To do this, the relative retention times of the online-system run as standard and the system run with a sampled Tedlar vessel attached, were compared for 10 ambient sample and calibration analyses. This data used was taken from sections 4.2.4 and 4.2.5 dealing with method linearity and accuracy.

Slight differences were observed between the ambient sample and calibration retention times due to a difference in relative humidity between both sets of samples. Accordingly, relative retention times were used to compensate for the proportional shift in elution rates that occurred. That is, the retention times of all compounds eluting from a particular column are ascertained relative to one or more other compounds eluting from that column.

Put simply, the relative retention time is the retention time of the HC of interest divided by the retention time of a set HC in the calibration mix. The values obtained can be less than or greater than unity, depending on whether the HC's of interest elute before or after the set HC to which they are being compared.

Although in section 4.1.3 we saw that toluene could not be accurately quantified due to the difficulty in removing trace amounts from the Tedlar bags, this compound is still very useful for providing a reference retention time for column BP1 (USEPA, 1999d). This is due to its prevalence in environmental samples, relatively good peak resolution and its lack of co-elution with other compounds.

For the PLOT column n-butane is used for similar reasons. Compounds on the PLOT column are more affected by changes in humidity, as a result a reference compound is far more necessary (USEPA, 1999d).

Table 4.2 presents the relative retention times obtained (for both calibration and ambient sample analysis) for the online system run as standard and the mobile bag sampling method. For the calibration samples, the bags were filled with the same NIST traceable standard mix used to calibrate the online system run as standard.

For the ambient samples, the online system was run as standard and the mobile sampling method was used to concurrently sample ambient concentrations at the same location (i.e, beside the air sampling inlet on the roof of the trailer housing the pre-cursor system), for the same time period. The specifics of the sampling procedures are discussed in more detail in sections 4.2.4 and 4.2.6.

	Average relative retention times for calibration samples (n=10)		Average relative retention times for ambient samples (n=10)		Relative retention times for average ambient and calibration samples (n=20)		Rsd % for ambient and calibration samples (n = 20)	
	online	mobile	online	mobile	online	mobile	online	mobile
ethane	0.34	0.34	0.34	0.34	0.34	0.34	2%	2%
propane	0.46	0.46	0.46	0.45	0.46	0.46	1%	2%
n-butane	1.00	1.00	1.00	1.00	1.00	1.00	-	-
iso-butane	0.93	0.93	0.92	0.93	0.93	0.93	1%	1%
n-pentane	1.49	1.49	1.49	1.49	1.49	1.49	1%	1%
iso-pentane	1.44	1.44	1.44	1.44	1.44	1.44	1%	1%
ethene	0.37	0.37	0.37	0.37	0.37	0.37	2%	2%
propene	0.81	0.81	0.82	0.81	0.82	0.81	1%	1%
1-butene	1.36	1.36	1.36	1.36	1.36	1.36	1%	1%
1,3 butadiene	1.60	1.60	1.60	1.60	1.60	1.60	1%	1%
benzene	0.58	0.58	0.57	0.58	0.58	0.58	1%	1%
acetylene	1.14	1.13	1.13	1.14	1.14	1.14	1%	1%

Table 4.2 Comparison of relative retention times for the online system operated as standard and the mobile sampling method, using ambient and calibration samples

In Table 4.2, the differences in the relative retention times for both methods are small for all compounds, showing that the addition of Tedlar bag sampling vessels to the standard online method does not significantly affect selectivity. Ideally selectivity should be verified by the application of a separate analytical technique, a confirmatory mass spectrometer scan for example, however, economic constraints make this approach impractical.

4.2.4 Linearity and calibration curve

Linearity can be defined as the "*ability of the method to obtain test results proportional to the concentration of analyte*".

Note: *The Linear Range is by inference the range of analyte concentrations over which the method gives test results proportional to the concentration of the analyte.* ' (AOAC – PVMC, 1993)

Linearity should be determined using dilutions of the compounds of interest over a defined concentration range. It is envisaged that the mobile sampling method will be applied to a wide

variety of sampling situations and environments, hence linearity should be verified over as wide a concentration range as practical.

Due to cost constraints, the upper concentration limit was determined by the concentrations in the NIST traceable standard (Table 3.1). As linearity at higher concentrations is not anticipated to be a problem (USEPA, 1998c), the emphasis was placed on determining linearity over a concentration range from very low concentrations up to the limit of estimation. If system linearity could be established at very low concentrations, potential applications of the sampling method could encompass background ambient air sampling.

For estimating linearity and the necessary calibration procedure, four separate investigations were carried out and compared. These included:

(i) a four point calibration procedure, utilising Tedlar sampling vessels and varying the weight of each hydrocarbon deposited on the cold trap.
(ii) a two point calibration procedure, using Tedlar sampling vessels to manually dilute the NIST certified calibration gas mix.
(iii) a one point calibration, utilising the online system operated as standard.
(iv) a one point calibration, using Tedlar sampling vessels.

In addition, an investigation was carried out into the number of compounds required in the calibration mix to fully calibrate the system.

Four point calibration

As direct dilution of the NIST traceable standard mix was not routinely practical, an alternate approach was employed. Tedlar sample vessels were filled with calibrant gas using the normal sampling procedure outlined in section 4.1.1. The sample inlet on the mobile sampler was connected directly to the calibrant gas cylinder with the aid of 0.5m teflon tubing (3/16 inch).

The flow on the calibrant gas was set to a very low flow (0.5-1.5psi), and the calibrant gas was sampled into the Tedlar vessel over a 5-10 minute period. The resulting sampled calibrant gas

was attached to the P-E system and analysed as per section 4.1.2. As no effective dilution had been carried out on this sample, it yielded the upper limit on our linearity estimate.

The sampling procedure was then repeated, with the sampled Tedlar bag being attached and the P-E system run as standard. This time, however, the valve on the tedlar bag was closed after 20 minutes, effectively diluting the upper limit sample by a factor of two. As the sample flow is always kept constant by the mass flow controller on the P-E system, the weight of each compound being deposited on the cold trap is halved using this technique. This effectively allows us to estimate the system response to approximately half the original stimulus and allows us to estimate linearity over the desired concentration range.

As the desired range was not simply from 0.5 to 1.0 times the NIST standard concentrations, the above procedure was repeated for 10 minutes and 5 minutes "open valve time". This effectively gave system responses for serial dilutions of approximately 0.5, 0.25 and 0.125 of the original upper limit (represented by the NIST standard run with a valve open time of 40 minutes). Standards at each concentration level should be analysed a minimum of three times (Green, 1996), but in this case six analyses were performed at each level.

To calculate the exact dilution factor for each concentration level, the time taken for the flow through the system to drop to 0 ml / min after the valve on the Tedlar bag was closed was required. The decrease in flow after the Tedlar bag valves were closed, versus time is illustrated in Figure 4.6.

This average flow reduction was estimated by observing the change in flow rate with time after the valve was closed for all dilutions carried out above. The rate of change in flow rate was observed to be consistent for all dilutions carried out. Consequently, this excess sampled volume could be accounted for when estimating diluted concentrations.

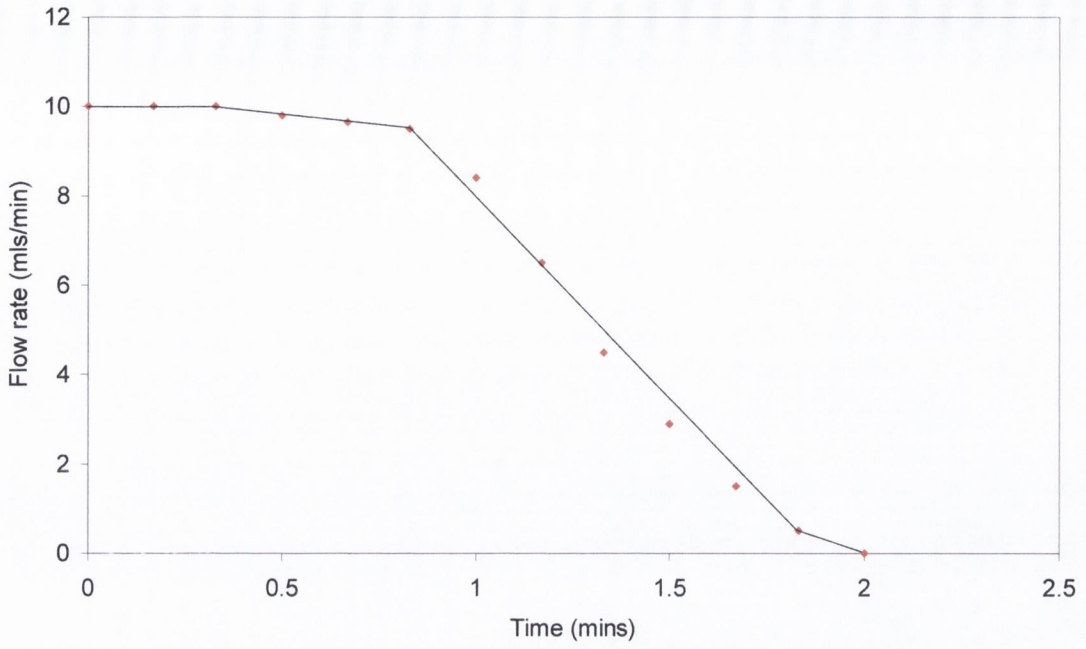


Figure 4.6 Average decrease in flow with time after tedlar bag valve has been closed

Figure 4.6 shows the trend is not linear, with no change in flow observed for 20 seconds followed by a slight decrease for 30 seconds and concluding with a period of sharp flow decrease for 70 seconds, after which time the flow stops. The trend observed was approximately linearised by dividing the graph into similar sections of flow rate decrease. The sum of the areas under each section was than calculated.

This value is proportional to the additional volume of gas sampled after the Tedlar bag valve is closed. At a flow of 10ml/min (the flow at which the samples were run), this extra volume corresponds to 80 seconds equivalent additional time sampled. This value is then added to all "valve open times" to obtain the concentrations for each dilution level. Table 4.3 presents the average peak area responses for each concentration level, for all compounds of interest.

	Level 1 (n=6) 5 minutes valve open time (+ 1.3 minutes additional)		Level 2 (n=6) 10 minutes valve open time (+ 1.3 minutes additional)		Level 3 (n=6) 20 minutes valve open time (+ 1.3 minutes additional)		Level 4 (n=6) 40 minutes valve open time (0 minutes additional)	
	Conc (ppbv)	Response (peak area)	Conc (ppbv)	Response (peak area)	Conc (ppbv)	Response (peak area)	Conc (ppbv)	Response (peak area)
ethane	0.92	3934.50	1.64	7004.20	3.10	13695.20	5.82	25122.00
propane	0.41	2535.00	0.73	4459.50	1.38	8797.17	2.59	16240.00
n-butane	0.21	2102.83	0.38	3464.80	0.72	7486.60	1.35	14068.00
i-butane	0.14	1162.17	0.24	2061.17	0.46	4227.67	0.86	7949.00
n-pent	0.12	1381.33	0.22	2312.33	0.42	4614.00	0.79	8586.00
i-pent	0.16	1783.67	0.28	3029.60	0.53	6114.50	0.99	12376.00
ethene	0.48	1919.33	0.86	3426.00	1.62	6626.67	3.04	11875.00
propene	0.46	2879.00	0.82	5091.33	1.55	9646.33	2.91	18129.00
1-butene	0.45	4789.33	0.81	7736.50	1.52	14006.00	2.85	21097.00
1,3 but	0.61	4511.17	1.09	8096.00	2.06	15778.17	3.87	29620.00
benzene	0.60	3999.17	1.08	6719.33	2.04	13686.17	3.83	25890.00
acet	1.01	3026.83	1.82	5463.60	3.43	10374.83	6.44	19780.00

Table 4.3 Average peak area response for each concentration level, for HC compounds of interest

The linearity of data is reflected in the correlation co-efficient of the linear regression line in a response versus concentration plot. A correlation coefficient of >0.999 can be considered as evidence of an acceptable fit of the data to the regression line (Green, 1996), and the y-intercept should not be significantly different from 0 (Huber, 1998). An example calibration plot demonstrating the linearity of propene is shown in Figure 4.7.

An R^2 value of 0.9999 (rounded to 1) is shown with a y-intercept close to 0. Table 4.4 summarises the results obtained for all compounds considered, using these linearity criteria. Calibration plots for all compounds are shown in Appendix F, Figures F.1 to F.12. The only compound which shows an R^2 value <0.999 is 1-butene, whose corresponding y-intercept is also significantly greater than 0.

Compounds which exhibit a y-intercept significantly different from 0 can only be investigated if it can be shown that the intercept value does not affect the accuracy of results (Huber,1998). This is unlikely to be the case with this method as it is intended to be employed in environments with low concentrations, e.g, background sampling.

	Regression equations			
	4 point calibration[1] (R^2 value)	2 point calibration[2]	1 point calibration[3] (online)	1 point calibration[4] (tedlar vessels)
ethane	Y = 4333X + 3.8 (0.999)	Y = 4306X + 60	Y = 4285X	Y = 4294X
propane	Y = 6301X – 48.8 (0.999)	Y = 6275X - 19	Y = 6410X	Y = 6339X
n-butane	Y = 10679X – 328 (0.999)	Y = 10485X – 87	Y = 9757X	Y = 10230X
i-butane	Y = 9435X – 151 (0.999)	Y = 9382X – 120	Y = 9215X	Y = 9360X
n-pentane	Y = 10916X – 29 (0.999)	Y = 10960X – 72.5	Y = 10671X	Y = 10853X
i-pentane	Y = 12829X – 437 (0.999)	Y = 12667X – 165	Y = 11345X	Y = 11759X
ethene	Y = 3890X + 129 (0.999)	Y = 3916X – 33	Y = 3919X	Y = 3930X
propene	Y = 6228X – 1.19 (1)	Y = 6319X – 260	Y = 6215X	Y = 6366X
1-butene	Y = 6729X + 2402 (0.98)	Y = 6661X + 2112	Y = 7418X	Y = 7424X
1,3 butadiene	Y = 7721X – 234 (0.999)	Y = 7680X – 103	Y = 7599X	Y = 7606X
benzene	Y = 6852X – 368 (0.999)	Y = 6740X + 73	Y = 6757X	Y = 6827X
acetylene	Y = 3090X – 151 (1)	Y = 3073X - 8	Y = 3072X	Y = 3087X

1 estimated using "valve open time"
2 estimated using 5 fold manual dilution of NIST standard
3 estimated from 1 point calibration of online system as standard
4 estimated from 1-point calibration using tedlar sampling vessels

Table 4.4 Summary of regression equations and correlation coefficients (R^2 for 4 point calibration only, for all other calibration procedures $R^2 = 1$)

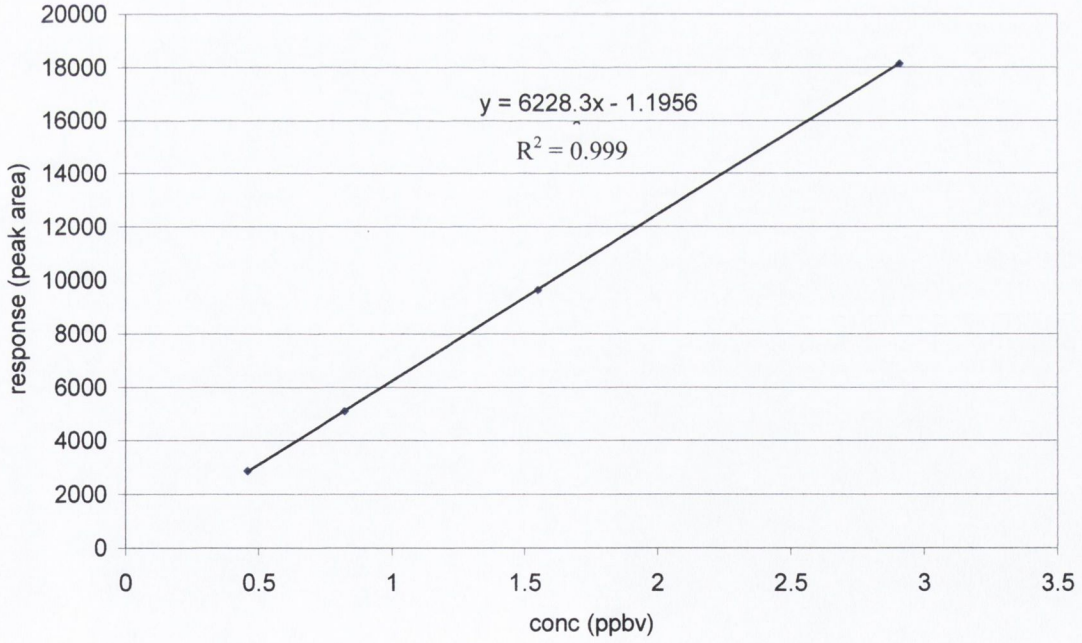


Figure 4.7 Calibration plot for propene demonstrating linearity of system response with increase in analyte concentration

Although the correlation co-efficients offer a very practical way of evaluating linearity data, they are not true measures of linearity (Green, 1996). These parameters, taken by themselves can be misleading and should be used in conjunction with separate techniques verifying linearity. One such approach is to examine the deviation of response factors over the concentration range. Response factors are determined by dividing the peak area by the concentration.

Two separate criteria were examined, the first as stated by Green (1996), that response factors calculated at each concentration level shall not differ from the average response factor by more than 10%.

The second criteria is given by EPA method 602 (USEPA,1984) , that response factors should be constant over the working range, if an rsd<10% is achieved then linearity can be assumed. The relative standard deviation is the standard deviation of the series divided by the mean of the series, expressed as a percent.

	ethane	propane	n-butane	i-butane	n-pentane	i-pentane	ethene	propene	1-butene	1,3 butadiene	benzene	acetylene
Lev 1 (% diff. from mean Rf)	0.7	0.4	0.6	3.4	2.6	1.3	0.2	0.8	15.6	1.7	0.8	1.2
Lev 2 (% diff. from mean Rf)	1.4	2.4	8.7	4.5	4.2	6.6	0.3	0.6	4.1	1.7	5.6	0.6
Lev 3 (% diff. from mean Rf)	2.3	2.3	4.6	3.9	1.3	0.1	2.4	0.1	0.1	1.7	2.0	0.1
Lev 4 (% diff. from mean Rf)	0.1	0.5	4.7	4.0	0.4	7.8	2.4	0.1	19.8	1.7	2.8	1.7
% rsd for Rf values over entire range (epa 602)	1.6	1.9	6.3	4.6	3.0	5.9	1.9	0.6	14.7	1.9	3.8	1.2

Rf = response factor (peak area / concentration)

Table 4.5 Difference from mean response factors (%) for each concentration level and relative standard deviation for response factors obtained over entire range (EPA method 602)

Table 4.5 summarizes the differences for both criteria and approaches. In rows 2-5 only average response factors for 1-butene deviated from the mean response factor by more than 10%. Row 6 verifies this deviation from linearity, as the relative standard deviation for response factors aver the entire investigated range deviated by more than 10%.

The analysis above shows that only 1-butene does not exhibit the required linearity, an R^2 value of 0.98, a relatively large y-intercept and significant deviations in response factors all confirm this.

Two point calibration

To verify the "open valve time" method used to demonstrate linearity, a five fold manual dilution of the traceable standard gas mix was carried out, using the procedure and setup outlined in appendix G. Using the mobile sampling method, seven, 1 litre Tedlar vessels were filled with this diluted standard mix by attaching the sample inlet of the mobile method to one of the stainless steel sample inlets on the 5 litre Tedlar bag, the standard gas contained in the 5 litre vessel was then sampled for between 5 and 10 minutes using the mobile method.

These seven samples were then analysed on the P-E system, with a normal "valve open" time of 40 minutes (i.e the time an ambient sample would be run for). The results of the first six analyses together with those obtained for the highest calibration level, where valve open time was also 40 minutes (no effective dilution), were evaluated and the regression equations presented in Table 4.4 were obtained. Both approaches gave very similar results for all compounds.

The average response factors for each compound at the 5 fold manual dilution concentration were also calculated. These were compared to the average response factor obtained from the 4 point calibration in Table 4.6.

The percentage difference between the response factors is minimal for all compounds except 1-butene, for which the difference of 12% is once again greater than the criterion outlined by Green (1996). Hence, the linearity of response to analyte concentrations is confirmed for both approaches, for all compounds, except 1-butene.

	Average response factor[1] : 4 point calibration[2]	Average response factor[1]: manually diluted concentration[3]	% difference[4]
ethane	4321	4358	1%
propane	6239	6251	1%
n-butane	9952	10163	2%
i-butane	8885	8686	2%
n-pentane	10825	10536	3%
i-pentane	11593	11835	2%
ethene	3999	3864	3%
propene	6232	5873	6%
1-butene	9228	10368	12%
1,3 butadiene	7529	7547	1%
benzene	6578	6836	4%
acetylene	3021	3067	2%

1 calculated from chromatogram peak area divided by concentration
2 based on six replicants at each concentration level
3 based on six replicants at the 5 fold diluted concentration
4 percent difference between 5 fold dilution response factor and average 4 point calibration response factor (Green, 1996: criterion, <10%)

Table 4.6 Comparison of average response factors obtained with 4 point calibration and manual dilution

Both approaches are seen to compare very well, however the time consuming and tedious nature of the manual dilution method makes the "valve open time" approach more practical. Limited expertise is required to perform the dilutions and the method of doing so is not associated with the kind of difficulties and errors associated with the manual dilution procedure outlined in Appendix G.

Ideally, a second traceable standard mix at a lower concentration could be used in conjunction with the current mix to obtain multi-point calibrations without the need for dilution. However, due to the expense of purchasing such standards it was not possible to do so during this research project.

Comparison with 1-point calibrations.

In EPA methods TO-14A and TO-15, multi-point calibration is optional, hence it is useful to investigate if a 1 point calibration of the mobile sampling method would suffice.

To this end, the regression equations from the 4 point and 2 point calibrations using Tedlar vessels were compared to those obtained from:

(i) calibration of the online system run as standard, using a 1 point calibration of the undiluted NIST standard, sampled from the calibrant cylinder through the dedicated stainless steel calibration line for the online system, and

(ii) a 1 point calibration using the undiluted calibrant gas sampled into a tedlar vessel using the mobile method and sampled as per section 4.1.2 (valve open time of 40 minutes).The average response of six replicate analysis were used to asses linearity. The relevant regression equations are shown in Table 4.4.

For 1 point calibrations the regression line is assumed to pass through the origin, hence the intercept value of 0. For nearly all compounds considered, the 1,2 and 4 point calibrations with Tedlar vessels, and the 1 point calibration from the online system calibrated as standard gave similar regression equations. The exception is 1-butene, which displays large Y-intercepts in the 2 and 4 point calibrations.

Table 4.7 compares the average response factors obtained for the standard 1 point calibration of the online system with those obtained for the 1, 2 and 4 point calibrations using Tedlar vessels. All average response factors compare very well with the 4 calibration procedures, the exception being 1-butene, with a large variation in linearity calling into question its ability to be quantified accurately and precisely over the required concentration range using the mobile sampling method.

From the procedures carried out we can see that as in EPA method TO-14A and TO-15, it is not routinely necessary to carry out a multi-point calibration as all average response factors and regression equations are similar for 1 (undiluted),2(manual dilution) and 4("valve open" time) point calibrations.

A multi point calibration should be carried out if analytical problems are encountered with the P-E system (i,e change of equipment or analytical method conditions).

	Average response factors[1]			
	4 point calibration[2]	2 point calibration[3]	1 point calibration[4] (online system)	1 point calibration[5] (Tedlar vessels)
ethane	4322	4337	4270	4294
propane	6239	6261	6411	6339
n-butane	9952	10292	9757	10230
i-butane	8885	8965	9215	9360
n-pentane	10825	10702	10761	10853
i-pentane	11593	12168	11345	11759
ethene	3999	3885	3919	3930
propene	6232	6051	6215	6366
1-butene	9228	8885	7419	7425
1,3 butadiene	7529	7600	7599	7606
benzene	6578	6798	6757	6828
acetylene	3021	3069	3073	3087

1 calculated from chromatogram peak area divided by concentration
2 calculated from 4 point calibration using "valve open time"
3 calculated from manual dilution calibration
4 calculated from 1 point calibration using online system as standard
5 calculated from 1 point calibration using tedlar vessels

Table 4.7 Average response factors for1, 2 and 4 point calibrations using tedlar vessels and 1 point using online system run as standard

Number of compounds required in the calibration mix

The data acquired for linearity studies was used to investigate the number of compounds required in a standard mix in order to calibrate the system. Multi-component standards (possibly with as many components as measured) are necessary as primary standards. They allow the carbon responses of individual hydrocarbons to be checked for a particular FID under particular conditions. Depending on the type of FID and working conditions, carbon responses can vary significantly among individual hydrocarbons.

A certified multi-component standard can be used to determine whether measured hydrocarbons can be quantified using a one mean carbon response or carbon responses for hydrocarbon groups (e.g. alkanes, alkenes, alkynes and aromatics), or if individual carbon responses are required.

As FID response is dictated in the main by the number of carbon atoms in a molecule, it might be anticipated that at least a three compound mix is necessary: one compound for each

column, i.e propane and benzene as recommended by USEPA (1998c), and an individual response for acetylene.

Figure 4.8 shows a plot of concentration versus (peak area response / carbon number), for all compounds on the PLOT column (excluding 1-butene due to the limited linearity seen). It is clear that more than one standardised compound is required to calibrate all compounds on this column.

The responses of the pentanes and acetylene is not based solely on a per carbon basis hence these compounds must be calibrated separately (Figures 4.9 and 4.10), and any standard mix used to calibrate the system must incorporate either iso-pentane or n-pentane and acetylene. When these 3 compounds are removed, the linear graph shown in Figure 4.11 is obtained, with an R^2 value of 0.99 and a y-intercept not significantly different to 0.

Hence, any one of these compounds could be used to calibrate the others, as their responses are seen to be solely dependant on their carbon number. As benzene is analysed on the separate BP1 column, a standardised concentration of this compound is necessary in any standard gas mix. This implies that a 4 compound standard mix is the minimum required to calibrate the system.

This will make future purchases of NIST traceable standardised gas mixes cheaper, allowing additional funds to be allocated to other areas of interest within the particular project.

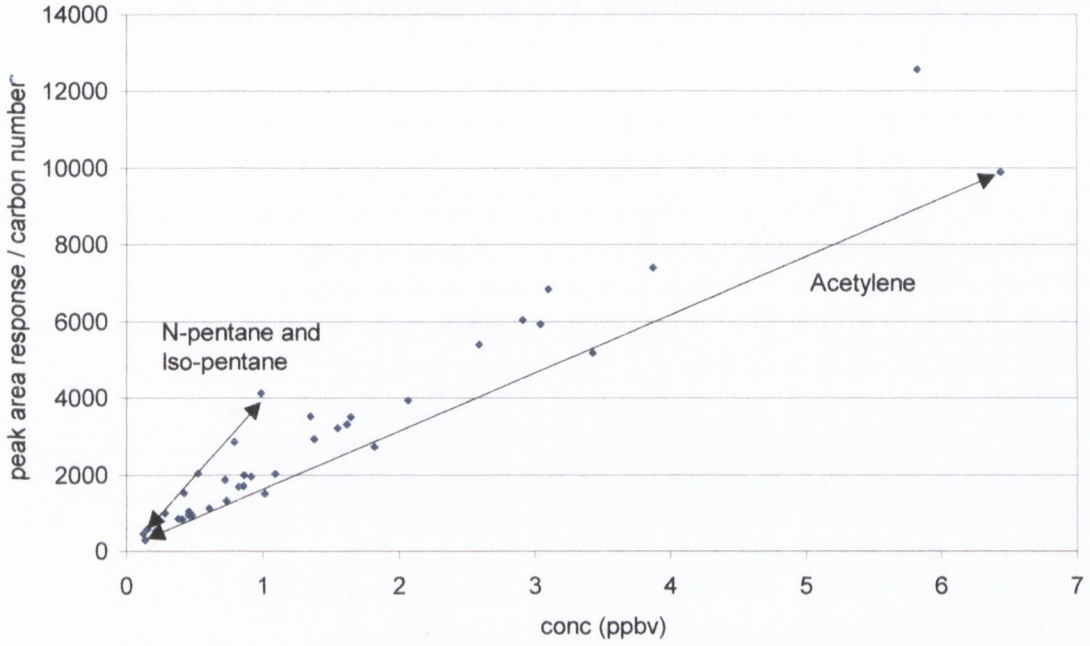


Figure 4.8 Peak area response on a per carbon basis for all calibration levels for PLOT column

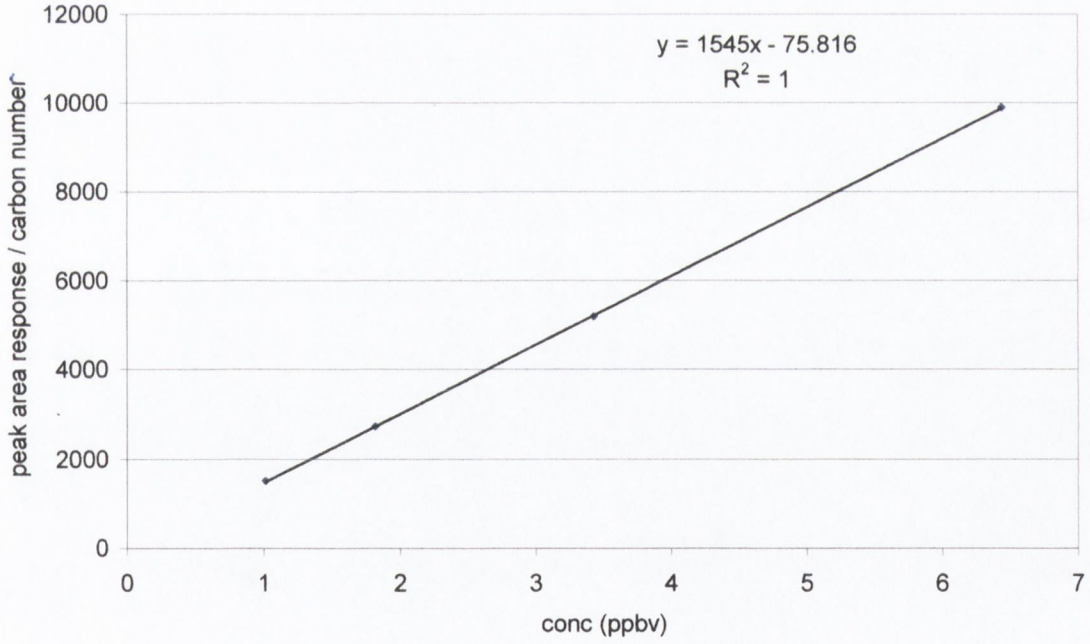


Figure 4.9 Peak area response on a per carbon basis for acetylene for all calibration level

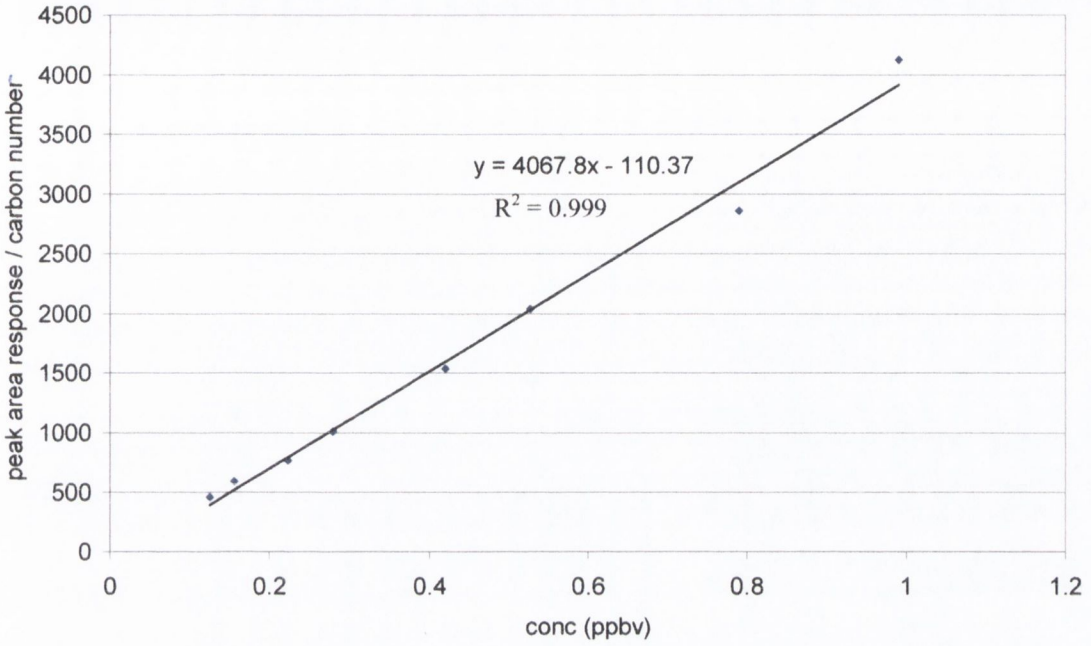


Figure 4.10 Peak area response on a per carbon basis for iso-pentane and n-pentane for all calibration levels

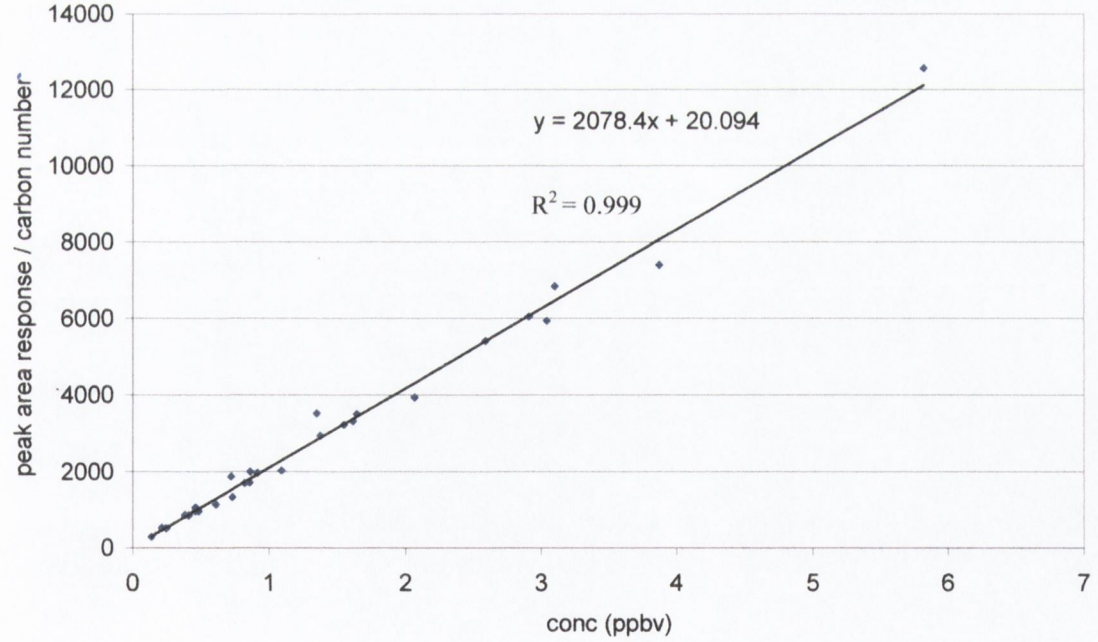


Figure 4.11 Peak area response on a per carbon basis for ethane, propane, n-butane, iso-butane, ethene, propene and 1,3 butadiene for all calibration levels (4 point calibration data)

4.2.5 Method detection limits

The detection limit of a method can be defined as '*The lowest content that can be measured with reasonable statistical certainty.*' (AOAC – PVMC, 1993).

According to the USEPA method for detection limit determination (40CFR part 136 Appendix B), the method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

The approach outlined in this USEPA guide was used to estimate the method detection limit for our sampling method. The MDL procedure was designed to be applicable to a broad variety of physical and chemical methods, so is device and instrument independent.

To ascertain the detection limits, seven replicant analysis were carried out on low concentration calibration samples. The results obtained in the 5 fold manual dilution case (section 4.2.4) were employed. For each compound, the standard deviation of the results of these seven analyses were used to calculate the MDL according to equation (4.1):

$$MDL = t_{\alpha, n-1} (S.D), \quad \text{(40 CFR 136, Appendix B)} \qquad (4.1)$$

Where t is the student's t-value at a given confidence (α) for n-1 degrees of freedom. A confidence level of 99% is required, at 6 degrees of freedom, giving a t-value value of 3.1.

S.D is the standard deviation of the concentrations determined in the seven replicate analyses for the hydrocarbon of interest.

The MDL values obtained for each hydrocarbon are presented in Table 4.8.

According to Appendix B of 40 CFR 136, the low concentration standard used, should be between approximately 5 and 10 times the MDL. We can see that the majority of MDL's are approximately 5 times the lower standard used and all MDL's are less than 10 times the standard used to quantify the limits.

Excellent method detection limits were obtained for all compounds other than 1-butene for which a relatively high value of 0.42ppbv was observed. All other compounds showed method detection limits of 0.2 ppbv or less. This gives added confidence that the method can be applied to a wide variety of sampling situations, where very low hydrocarbon concentrations are anticipated.

Although specific quantitative concentrations are presented for method detection limits, the limits should be thought of more as a guide, where measured concentrations at or near these values should be reported with care.

The only compound whose MDL approaches the concentrations expected to be encountered in everyday ambient sampling, is 1,3 butadiene. This is not so much an indictment on the sampling method, but more a comment on the generally very low levels of 1,3 butadiene observed in ambient Dublin samples (Chapters 5,6,7 and 8).

	Replicate analysis concentrations (ppbv)							Mean (ppbv)	Standard deviation (ppbv)	**MDL (ppbv)**
	1	2	3	4	5	6	7			
ethane	1.12	1.18	1.15	1.17	1.15	1.24	1.13	1.16	0.04	**0.12**
propane	0.50	0.53	0.52	0.52	0.51	0.55	0.50	0.52	0.02	**0.06**
n-butane	0.25	0.28	0.26	0.28	0.26	0.32	0.25	0.27	0.02	**0.07**
iso-butane	0.15	0.19	0.17	0.18	0.17	0.19	0.15	0.17	0.02	**0.05**
n-pentane	0.13	0.17	0.16	0.16	0.18	0.16	0.14	0.16	0.02	**0.05**
iso-pentane	0.18	0.21	0.20	0.20	0.19	0.22	0.19	0.20	0.02	**0.05**
ethene	0.55	0.63	0.62	0.62	0.60	0.64	0.59	0.61	0.03	**0.09**
propene	0.54	0.61	0.59	0.60	0.56	0.62	0.55	0.58	0.03	**0.09**
1-butene	0.48	0.64	0.56	0.58	0.54	0.81	0.38	0.57	0.13	**0.41**
1,3 butadiene	0.74	0.79	0.78	0.78	0.77	0.81	0.75	0.77	0.02	**0.07**
benzene	0.74	0.78	0.76	0.76	0.75	0.82	0.75	0.77	0.03	**0.09**
acetylene	1.19	1.34	1.26	1.30	1.25	1.37	1.25	1.28	0.06	**0.19**

Table 4.8 Method detection limits for mobile sampling method

4.2.6 Accuracy

Accuracy is defined by IUPAC as the 'Ability of a measuring instrument to give responses close to a true value' (Inczedy, *et al.*, 1998).

ISO defines accuracy and bias as *'The difference between the expectation of the test results and an accepted reference value.* Note: Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.' (ISO 3534-1, 1993).

The accuracy of an analytical method is the extent to which test results generated by the method and the true value agree. The true value for accuracy assessment can be obtained in several ways, one alternative being to compare results with those obtained from an established reference method (Huber, 1998). A second common approach is to analyse results obtained using a traceable calibration standard.

In this study, a comparison with an established reference method was made. This approach ensured that any effects due to compounds not present in the NIST calibration mix but present in ambient samples would be reflected in the assessment of accuracy. This provides a better measure of the accuracy of the mobile sampling method in "real world" sampling conditions.

The established reference method used for determining the accuracy of the mobile sampling method was the P-E online system run as standard, (i.e sampling ambient air through the sampling manifold from the inlet on the trailer roof, Appendix E, Figure E.1). The comparison was made by locating the mobile sampler in the vicinity of the online sampling inlet, and sampling into Tedlar vessels for the same period of time (40 minutes) as the online system. The sampled air in the Tedlar bag was analysed as in section 4.1.2, following the sample carried out by the online system run as standard.

Although it is only necessary to analyse and compare 10 samples (Eurachem, 1998), this procedure was repeated approximately 40 times to compare accuracy data over as wide a concentration range as possible. To facilitate this, samples were taken during peak time traffic

flow periods (07:00-10:00 and 17:00-20:00) on days with low wind speeds, and during off-peak times (23:00-01:00) with relatively turbulent atmospheric conditions. A comparison of the results obtained for both methods gives a measure of accuracy of the bag sampling method relative to that of the online system run as standard.

Initial investigations into accuracy were conducted using an approach outlined in EPA method TO-14A, which compares the "true value" to the experimental value and expresses the difference as a percentage. The criterion, as outlined in this method is an accuracy of ±10%. The relative accuracy is determined according to equation (4.2).

$$\text{Relative Accuracy (\%)} = \frac{\text{True value} - \text{experimental value}}{\text{True value}} \times 100 \qquad (4.2)$$

In the EPA method, the true value is a traceable known standard concentration, in our comparison the true value is that obtained for the P-E system run as standard. The results are presented in Table 4.9.

The compound which most frequently displayed a relative accuracy (%) greater than ±10% (on 78% of occasions), was 1-butene for which the highest deviation observed between the two methods had an associated relative accuracy of -96%. For all other compounds, the frequency with which the 10 % relative accuracy criterion as laid down by EPA Method TO-14A was exceeded, varied between 2 and 12 %. The highest percent accuracy observed for each compound and the Pearson correlation co-efficients are also shown in Table 4.9.

It is clear that the criterion outlined in method EPA method TO-14A are too restrictive for the mobile sampling method as all compounds other than 1-butene displayed maximum relative accuracies between 11 and 20%. However, the relative accuracy for all compounds would likely improve if only 10 sample comparisons had been analysed as per Eurachem (1998). The Pearson's correlation coefficients obtained also provide evidence of the relative accuracy of the mobile method, with an r value of 0.99 obtained for all compounds except 1-butene.

Compound and concentration range (true value in ppbv)	% of times relative accuracy exceeded EPA method to-14a criterion (± 10%)	Highest % relative accuracy observed	Pearsons co-efficient (r)	Average relative accuracy %
ethane (0.2 - 7.0 ppbv)	3%	-13%	0.99	2%
propane (0.2 – 3.9 ppbv)	10%	-19%	0.99	-1%
n-butane (0.2 – 6.1 ppbv)	10%	-19%	0.99	-1%
i-butane (0.1 – 4.6 ppbv)	12%	-20%	0.99	-1%
n-pentane (0.1 – 2.0 ppbv)	10%	-20%	0.99	4%
i-pentane (0.2 – 5.7 ppbv)	5%	-20%	0.99	1%
ethene (0.5 – 9.4 ppbv)	3%	-17%	0.99	-1%
propene (0.1 – 3.5 ppbv)	8%	-19%	0.99	-1%
1-butene (0.2 – 1.7 ppbv)	78%	-96%	0.91	-19%
1,3 but (0.1 – 0.7 ppbv)	8%	-20%	0.99	-2%
benzene (0.1 – 2.6 ppbv)	3%	-11%	0.99	1%
acetylene (0.3 – 9.5 ppbv)	5%	-18%	0.99	2%

Table 4.9 Summary of accuracy data for mobile method relative to standard online method

The fact that all the largest relative accuracy values were negative is an indication that the difference between the two methods on these occasions was possibly due to contamination in the Tedlar bags, as the experimental values obtained on these occasions were greater than the "true value".

However, the occasions on which the criterion set out in EPA Method TO-14a was exceeded, were, in general associated with the lower concentrations. To illustrate this, Figures 4.14 and 4.15 present the relative accuracies for propene and benzene against peak area (concentration) obtained for the online system (true value). The trend observed for both compounds is similar, where an increase in the amount of scatter is observed as concentration (peak area) decreases. For all compounds, the relative accuracy is poorer at the very low concentrations examined, but the criterion established for the mobile method (±20%) are not exceeded.

Only for 1-butene, is the criterion exceeded over a very wide concentration range (Figure 4.17). For all other compounds, the average relative accuracy (for all values, Table 4.9) is very close to zero. This indicates that over a large number of measurements (n = 40), very little additional systematic error is observed, relative to the online system run as standard. Graphically in Figures 4.12 and 4.15, we can observe the % relative accuracy for benzene

against both measurement number and peak area (concentration), and see there is no obvious systematic trend, with relative accuracies distributed randomly both positively and negatively, suggesting random error is the main cause of the differences in the results.

This is quite probable when the method of determining accuracy is considered. Measurements were taken on the roof of the trailer where small random variations due to turbulence, in the micro-environment between the mobile sampler and the sample inlet of the online-system are likely to affect the results obtained, resulting in the random spread observed.

For comparison purposes, the percent relative accuracy was calculated and plotted for toluene (Figures 4.13 and 4.16), a compound with known systematic bias in the mobile sampling method due to tedlar bag contamination (section 4.1.3). The effects of this systematic bias are clear, as nearly all values in Figure 4.13 are negative due to contamination in the Tedlar vessels (not random distribution). An average relative accuracy of -46% is observed for toluene, as opposed to –1% for benzene.

Figure 4.16 shows how the relative accuracy deviates systematically with concentration, where Tedlar bag contamination has a much greater effect at low concentrations, but its impact lessens with increasing concentration. The relative accuracy is seen to be negligible above a peak area of 40000 (approximately 4.5ppbv), due to the high concentrations observed relative to the contamination concentration of toluene in the vessels.

In addition, the poor relative accuracy observed for 1-butene is outlined in Figure 4.17, where large differences are observed between the two methods over the entire concentration range investigated. The scatter plots shown in Figures 4.18 and 4.19 for benzene and 1-butene illustrate the difference in relative accuracies of the two compounds. For benzene, both methods agree very well, with a slope of almost 1, and y intercept not significantly different to 0. In contrast, 1-butene has a slope of 1.27, a significantly different y intercept to 0, allied to a relatively poor R^2 value.

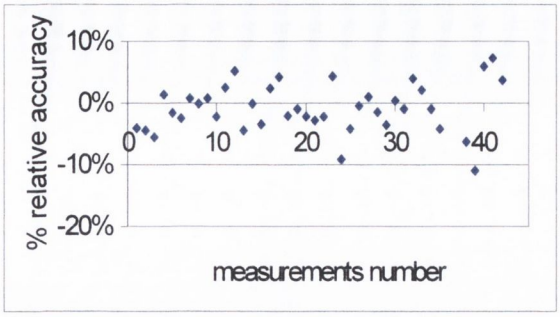


Figure 4.12 Relative accuracy. for benzene

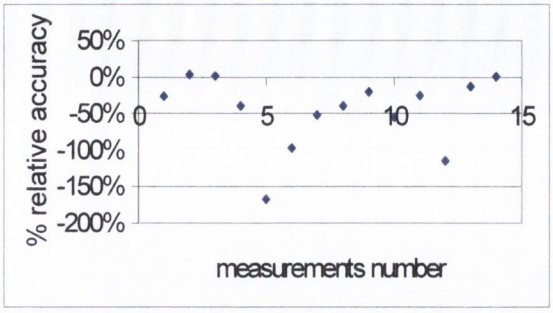


Figure 4.13 Relative accuracy for toluene

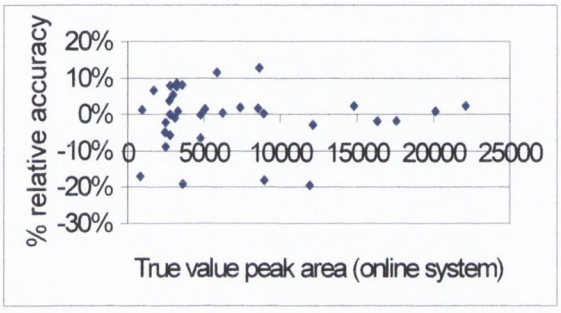


Figure 4.14 Relative accuracy for propene against area.

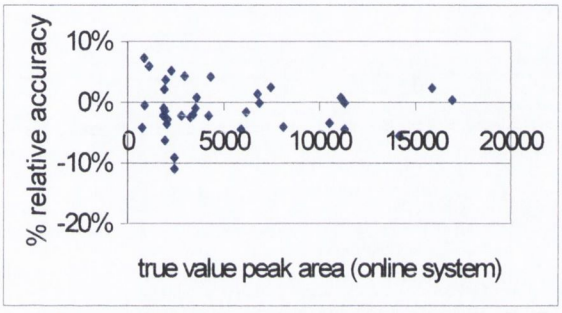


Figure 4.15 Rel. acc., benzene against area

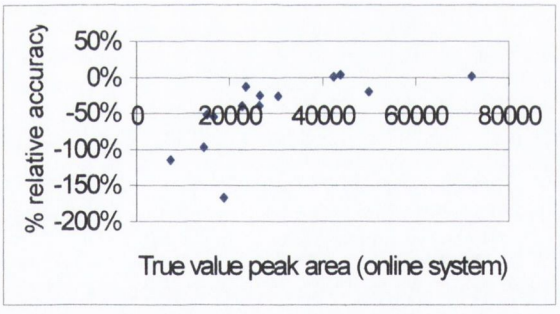


Figure 4.16 Rel.acc., toluene against area.

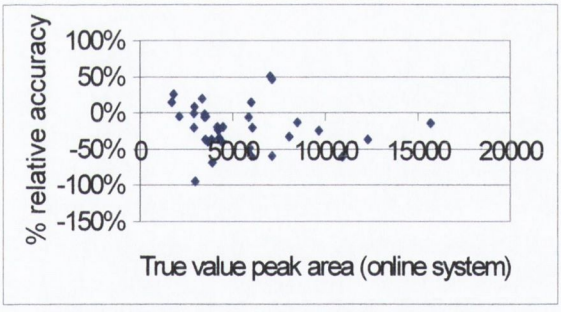


Figure 4.17 Rel.acc., 1-butene against area

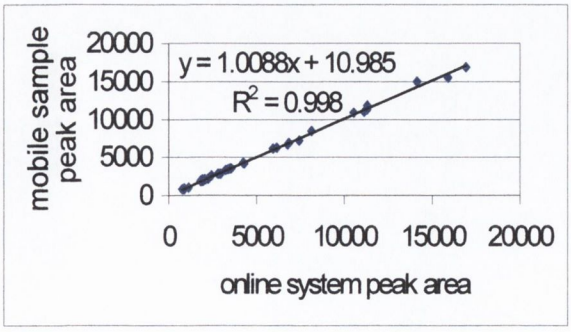


Figure 4.18 Scatter plot for benzene

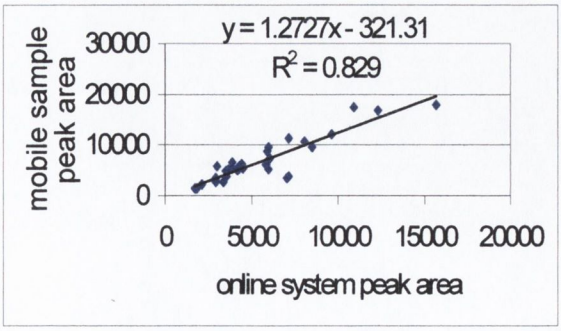


Figure 4.19 Scatter plot for 1-butene

4.2.7 Precision

Precision can be defined as '*A measure for the reproducibility of measurements within a set, that is, of the scatter or dispersion of a set about its central value.*' (McNaught and Wilkinson, 1997).

Precision can therefore be thought of as the degree of scatter between a series of measurements obtained from multiple samples of the same homogeneous sample under prescribed conditions. The most common precision measurement is repeatability, which should be determined over both short (daily) and long term (weekly) intervals. Short term repeatability analyses a method's precision and will give the smallest expected precision. It will give an idea of the sort of variability to be expected when a method is performed by a single analyst on one piece of equipment over a short time-scale, i.e. the sort of variability to be expected between results when a sample is analyzed in duplicate (Eurachem, 1998). Long term or intermediate precision takes into account intra-laboratory variations such as different days and different reagants (although the latter is not as relevant for our study).

Precision is usually expressed in terms of standard deviation or relative standard deviation. Both short term and long term repeatability are generally dependent on analyte concentration, and so should be determined at a number of concentrations and if relevant, the relationship between precision and analyte concentration should be established. Relative standard deviation may be more useful in this case as it should remain largely constant over a reasonable range of interest (Eurachem, 1998).

According to Handley and Adlard (2001), both long and short term precision should be estimated using a minimum of nine determinations over the prescribed range ; for example using three replicates at three concentration levels. For short term precision analysis of the mobile sampling method, 3 replicant standards at four concentration levels were analysed (12 samples). The procedure for linearity and calibration curve determinations (4 point calibration) described in section 4.2.4 was followed.

For long term precision, 3 replicant standards were examined at each concentration level on 2 separate days, 3 weeks apart. For environmental analysis a wide range of acceptability criteria

applies, where relative standard deviations of anywhere between 2% and 20% are observed. EPA Method TO-15, measures replicate precision and calculates it as the absolute value of the difference between replicate measurements of a sample divided by the average value and expressed as a percentage. This approach was altered to accommodate the 3 replicant samples at each of the 4 calibration levels considered in this study, by applying the EPA approach to the 2 values which differed by the greatest amount.

For long term estimates, the largest difference at each calibration level between the 2 separate days of analysis was employed. The results obtained are summarized in Tables 4.10 and 4.11, along with the relative standard deviation observed in each set of three measurements at each concentration level.

The short-term intra day precision results in Table 4.10, show that all compounds meet the criterion set out in EPA Method TO-15. The results shown represent a conservative measure of precision, as the smallest and largest values obtained in each set were used in its determination. The relative standard deviation (RSD) observed for all 3 analyses at each concentration level is probably a more representative measure of the scatter of results and hence, precision. The vast majority of the RSD values presented in Table 4.10 are less than 5 % at all concentration levels, the exception being iso-pentane, whose RSD is always less than 10%. These values indicate excellent intra day, short term precision over all concentration levels.

As expected, relative measures of precision increase over a longer time period. The results for inter-day precision in Table 4.11 summarize the trend observed. Only 1-butene exceeded the EPA TO-15 criterion of 25%, with a replicate precision of 32.5 % observed at the lowest concentration level. The relative standard deviations observed over the longer time period, are all less than 10%, except those for 1-butene.

These data suggest the mobile method displays adequate short and long term precision. Additional analysis to confirm this findings and to ascertain replicate precision over a wider concentration range was carried out. For this, a 5 litre Tedlar bag was employed as a larger sample reservoir, housing the air to be analysed. Air was sampled into the 5 litre vessel using

the universal pump's exhaust port, at various times of the day to ensure a wide concentration range. This air was subsequently sampled from the 5 litre vessel using the mobile sampler, which was attached using teflon and tygon tubing as shown in Figure H.1, Appendix H. Duplicate samples were obtained at 5 different concentration levels (Five seperate 5 litre samples taken at different times of the day and diluted with zero air if necessary, to obtain a wide concentration range). The use of the 5 litre bag allowed the duplicate samples to be taken from a homogenous ambient air sample, on which replicate precision analysis could be performed over a wide concentration range. Replicate precision results calculated as per EPA method TO-15 are presented in Table 4.12.

Figures 4.20 to 4.25 illustrate graphically the increase in replicate precision with decreasing concentration but even the lowest concentrations investigated (near the detection limits) do not exceed the 25% criteria. The requisite replicate precision of less than 25% is achieved over a wide concentration range for all compounds except 1-butene, where the replicate precision is greater than 25% over the entire concentration range investigated.

These results verify the precision of the mobile sampling method over a wide concentration range, encompassing the concentrations likely to be encountered in ambient sampling applications.

	Std level 1		Std level 2		Std level 3		Std level 4	
	(i) % rep. prec. (n=2)	(ii) % rsd (n=3)	(i) % rep. prec. (n=2)	(ii) % rsd (n=3)	(i) % rep. prec. (n=2)	(ii) % rsd (n=3)	(i) % rep. prec. (n=2)	(ii) % rsd (n=3)
ethane	0.5%	1.0%	1.5%	0.8%	0.5%	1.0%	1.7%	0.9%
propane	3.3%	1.8%	1.0%	0.2%	0.5%	1.0%	5.8%	2.9%
n-butane	6.5%	3.3%	2.6%	1.4%	3.7%	2.0%	2.6%	1.3%
i-butane	5.0%	2.8%	1.0%	0.2%	9.2%	4.9%	9.3%	4.9%
n-pent	5.9%	2.9%	4.3%	2.2%	3.9%	1.9%	5.5%	3.0%
i-pent	10.5%	5.4%	19.1%	9.6%	5.5%	2.8%	3.6%	2.0%
ethene	5.7%	3.0%	4.1%	2.1%	3.6%	1.8%	6.7%	3.8%
propene	3.4%	1.7%	3.1%	1.6%	3.5%	1.8%	4.6%	2.4%
1-butene	6.4%	3.2%	6.4%	3.7%	3.1%	1.7%	3.2%	1.7%
1,3 but	2.8%	1.5%	4.9%	2.7%	2.2%	1.2%	1.0%	0.5%
benzene	1.7%	1.0%	9.6%	5.3%	6.9%	3.5%	5.5%	2.8%
acetylene	6.4%	3.2%	1.6%	0.8%	1.1%	0.6%	4.5%	2.3%

Table 4.10 Short term, intra day precision results for : (i) amended EPA method to-15 and (ii) relative standard deviation for all 3 replicants at each calibration level

	Std level 1		Std level 2		Std level 3		Std level 4	
	% rep. prec. (n=2) (epa to-15)	% rsd n=6	% rep. prec. (n=2) (epa to-15)	% rsd n=6	% rep. prec. (n=2) (epa to-15)	% rsd n=6	% rep. prec. (n=2) (epa to-15)	% rsd n=6
ethane	2.2%	0.9%	6.0%	3.0%	1.4%	0.5%	6.3%	2.4%
propane	8.8%	3.2%	4.8%	2.1%	3.2%	1.4%	6.4%	2.5%
n-butane	14.9%	5.4%	7.3%	3.2%	11.7%	5.8%	17.8%	6.7%
i-butane	14.8%	5.7%	24.2%	10.0%	16.2%	5.3%	18.6%	7.9%
n-pent	9.0%	3.4%	9.2%	4.3%	7.0%	2.8%	13.6%	5.6%
i-pent	15.0%	5.3%	24.9%	9.5%	13.6%	5.2%	10.5%	3.8%
ethene	9.8%	3.2%	7.4%	3.1%	9.9%	3.4%	9.9%	4.0%
propene	8.3%	3.1%	3.7%	1.9%	6.2%	2.5%	8.3%	3.5%
1-butene	32.5%	14.0%	24.7%	12.8%	15.0%	6.9%	5.6%	2.2%
1,3 but	6.5%	2.1%	6.8%	3.1%	3.6%	1.2%	4.9%	1.8%
benzene	5.5%	2.0%	12.2%	5.5%	10.5%	3.5%	9.2%	3.6%
acetylene	11.2%	4.0%	7.4%	3.3%	4.2%	1.7%	9.0%	3.2%

Table 4.11 Long term, inter day precision showing results obtained for the altered approach outlined in epa method to-15 and also the relative standard deviation for all 6 replicants at each calibration level

Compound and mean concentration range (n=2 for each conc level) (ppbv)	% rep prec for lowest conc level	% rep prec for 2nd lowest conc level	%rep prec for middle conc level	% rep prec for 2nd highest conc level	% rep prec for highest conc level
Ethane (0.2 - 4.1)	14%	3%	1%	1%	1%
Propane (0.1 – 1.8)	25%	3%	1%	1%	1%
n-butane (0.2 – 7.3)	1%	3%	1%	1%	1%
i-butane (0.9 - 4.6)	24%	1%	1%	9%	1%
n-pentane (0.1 - 2.8)	8%	5%	2%	4%	1%
i-pentane (0.2 - 7.7)	2%	3%	2%	6%	1%
Ethene (0.4 – 9.6)	2%	4%	1%	5%	5%
Propene (0.3 – 3.2)	13%	2%	9%	1%	1%
1-butene (0.2-2.6)	29%	19%	17%	46%	30%
1,3 butadiene (0.1 – 0.6)	18%	8%	1%	4%	2%
Benzene (0.2 – 2.6)	7%	6%	1%	4%	1%
Acetylene (0.2 – 4.9)	14%	5%	5%	5%	3%
AVERAGE % rep prec	13%	5%	4%	7%	4%

Table 4.12 Replicate precision analysis of ambient samples over a wide concentration range

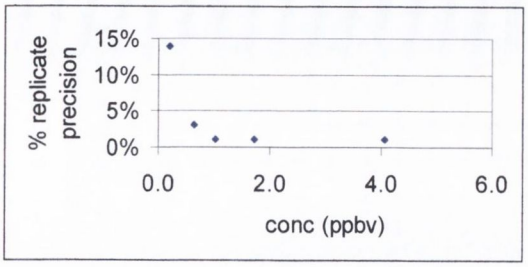


Figure 4.20 Replicate precision against conc for ethane

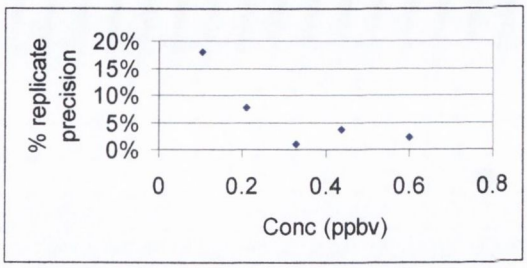


Figure 4.21 Replicate precision against conc for 1,3 butadiene

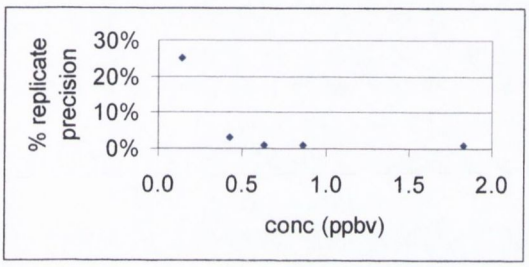


Figure 4.22 Replicate precision against conc for propane

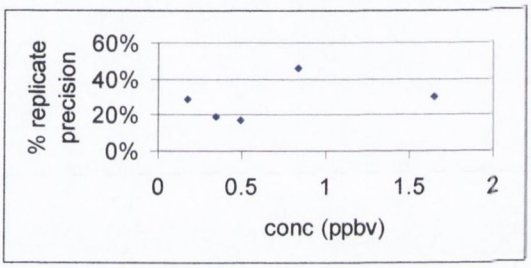


Figure 4.23 Replicate precision against conc for 1-butene

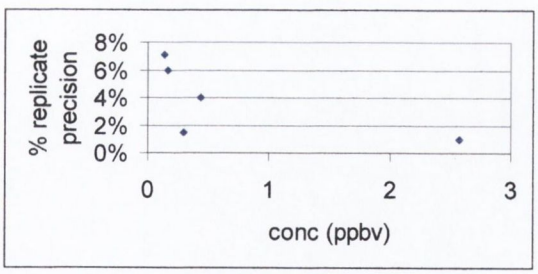


Figure 4.24 replicate precision against conc for benzene

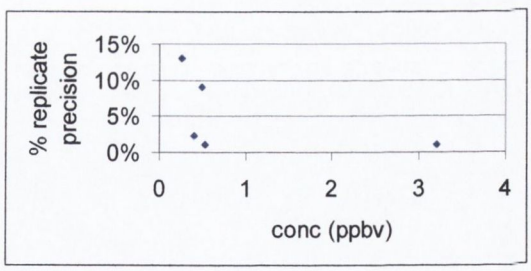


Figure 4.25 replicate precision against conc for propene

4.2.8 Robustness

According to the ICH '*The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage.*' (ICH , 1995).

A measure of an effective method is how well its performance stands up to less than perfect implementation (Eurachem, 1998). Within any method there are likely to be certain stages which, if not carried out with enough care, will have a severe effect on method performance. These stages should be identified, and if possible, their influence on method performance evaluated using 'robustness tests'. This process demonstrates that operator error will not effect results to a significant degree. This involves making deliberate variations to the method, and investigating the subsequent effect on performance. Robustness tests are normally applied to investigate the effect on either precision or accuracy (Eurachem, 1998).

For the mobile sampling method, the factors which were most likely to affect our method performance were anticipated to revolve around the sampling stage, in particular the extent to which the sampling vessel was filled and the length of time over which the sample was taken (flow rate). The effect of changes in these parameters on relative accuracy were ascertained, through comparison of equivalent results obtained with the P-E online system. For a comparison of sample flow rate, it was important to confirm that a change in this parameter had no significant effect on the accuracy of results obtained. For this, a technique was required which allowed the P-E system run as standard (sampling for the normal 40 minutes) to be directly compared with mobile samples, both taken from the same homogenous sample reservoir, over time periods between 5 minutes and 40 minutes for the mobile method. To this end, a dual stainless steel port 5 litre Tedlar bag was employed. This enabled simultaneous sampling from the 5 litre vessel to both the online system (sampling for 40 minutes) and the mobile sampling method (sampling for various times by employing different flow rates). This sampling setup is shown in Appendix I, Figure I.1. The 5 litre vessel was filled with ambient air prior to sampling by connecting one sample inlet to the exhaust on the SKC universal pump. This was carried out at different times of the day to obtain as wide a concentration range as practical. This air was then sampled from the 5 litre vessel using the mobile method as per section 4.1.1. This sample was analyzed immediately proceeding the online

measurement by disconnecting the 5 litre vessel from the online system and attaching the sampled 1 litre vessel, as per section 4.1.2.

In addition to changes in sampling time for the mobile method, the effect of sample volume on accuracy was also examined. It was anticipated that once sufficient sample volume was present in the 1 litre sample vessel (approx 400cm^3, P-E system samples for 40 minutes at 10 mls / min), no further increase in this volume would affect the relative accuracy of the results.

This assumption was investigated by ensuring that sample volumes in the above investigations were (approximately), 500mls, 750mls or 900 mls. This was achieved by setting the flow rate to the approximate values outlined in Table 4.13. The flow from the sampling pump exhaust was measured using a digital flow meter.

Five analysis were carried out at the two extreme sample times (5 and 40 minutes), with three samples analyzed for each of the two intermediary sampling periods (10 and 20 minutes, Table 4.13). The sample volume was also varied more for the 2 extreme sampling times. Table 4.14 presents the Pearson's correlation coefficients between the results of the mobile sampling and online method's for each sampling time period.

These values suggest that only the relative accuracy of 1-butene is affected by changes in flow rate and sample volume. As it is envisaged that a large proportion of ambient sampling with the mobile method will be carried out over sampling times between 5 and 10 minutes, this unacceptable feature makes sampling of this compound ill-advised.

Using the same approach, as in section 4.2.6 to evaluate the relative accuracy (EPA method TO-14a) for each sampling time, we obtain similar relative accuracies as those obtained in section 4.2.6, where only 1-butene exceeds the criteria established in section 4.2.6 of ±20%. The highest observed relative accuracy noted for 1-butene was –59%.

Scatter plots comparing the benzene and 1,3 butadiene peak area response for the P-E system run as standard against that for the mobile sampling method are presented in Figures 4.26 and 4.27 respectively. The data shown cover all the sample times and volumes investigated. The

slopes of almost 1, allied to the excellent correlations and y-intercepts not significantly different from 0, verify the limited effect changes in flow rate and sampled volume have on relative accuracies obtained.

Flow rate (mls / min)	Sample time (minutes)	volume (cm^3)
180	5	900
150	5	750
100	5	500
150	5	750
180	5	900
90	10	900
50	10	500
90	10	900
45	20	900
25	20	500
45	20	900
23	40	900
19	40	750
13	40	500
19	40	750
23	40	900

Table 4.13 Changes in flow rate, sample time and volume applied to mobile sampling method to investigate method robustness

Sample time(mins)	ethane	propane	n-butane	i-butane	n-pentane	i-pentane	ethene	propene	1-butene	1,3 butadiene	benzene	acetylene
5	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.68	0.99	0.99	0.99
10	1	0.99	1	0.99	0.99	1	0.99	1	0.78	1	1	1
20	0.99	0.99	0.99	0.98	0.99	0.99	0.99	0.99	0.99	1	0.99	0.99
40	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.96	0.99	0.99	0.99

Table 4.14 Pearson's correlation coefficients for peak area response between both methods for differing mobile method sampling times (flow rate) and sample volume

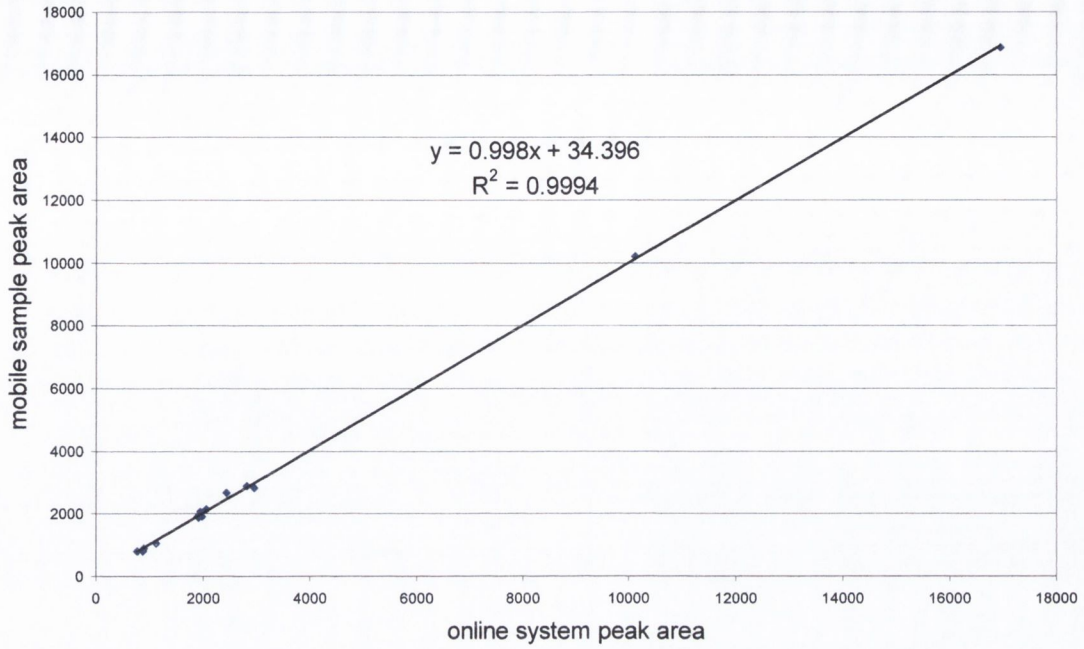


Figure 4.26 Scatter plot of benzene peak area response for online system against mobile sampled values for changes in mobile sampling flow rate and sample volume

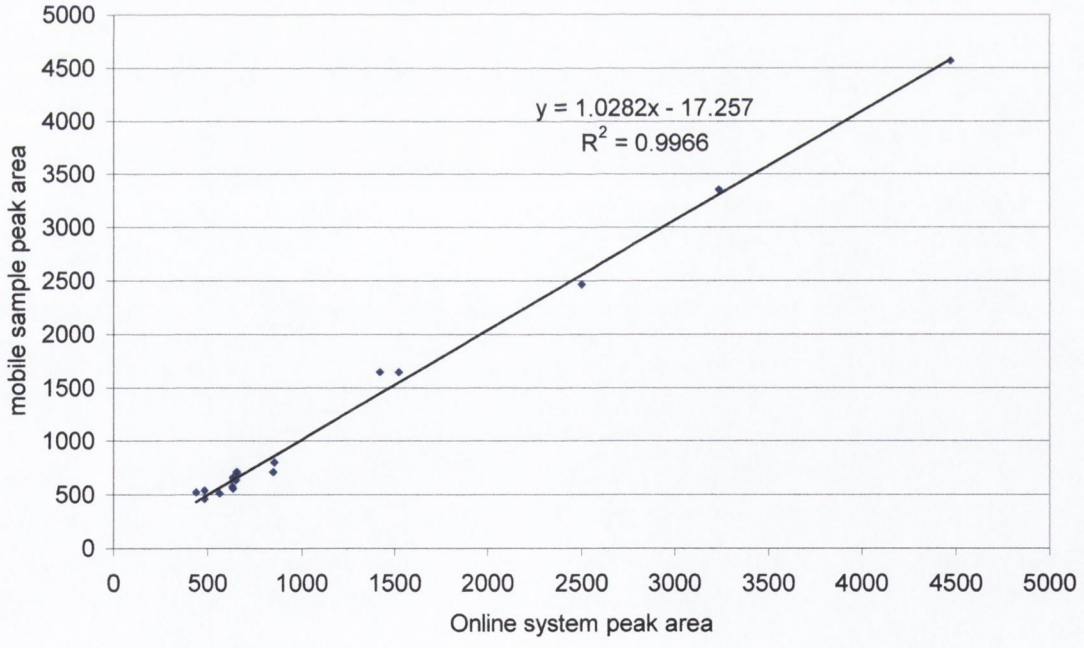


Figure 4.27 Scatter plot of 1,3 butadiene peak area response for online system against mobile sampled values for changes in mobile sampling flow rate and volume

4.2.9 Range

The range of an analytical method is the interval between the upper and lower levels (including these levels) that have been demonstrated to be determined with precision, accuracy and linearity using the method as written (Huber, 1998). The range is normally expressed in the same units as the test results (e.g. percentage, parts per million) obtained by the analytical method. In this study, parts per billion volume is used.

Linearity

Table 4.3 outlines the concentration range over which linearity has been demonstrated for all compounds. However, for the seven compounds which showed a response based solely on carbon number (ethane, propane, n-butane, iso-butane, ethene, propene and 1,3 butadiene), this range can be extended significantly.

As shown in Figure 4.11, the responses of these seven compounds vary in direct proportion to one another, hence any one of these compounds could be used to calibrate the other six. This behaviour can be used to extend the demonstrated linear range for each of the seven compounds by relating the lowest per carbon number peak area response and the highest per carbon number peak area response for all seven compounds to each of the seven individually.

For example, from the level 1 calibration concentrations, we can see that iso-butane has the lowest per carbon number peak area response of 291 (1162 divided by 4 carbons). This value, multiplied by the carbon number of each compound and divided by the average response factor for each compound (from the 4 point calibration procedure, Table 4.6) gives the lowest concentration in the range for each of the seven compounds.

This procedure was also applied to the highest per carbon response obtained (ethane in calibration level 4, 25112 divided by 2), to obtain upper values on the linear concentration range for each of the seven compounds. The extended linear ranges for these seven compounds, along with the linear ranges for the other 5 compounds are presented in Table 4.15.

	Lowest concentration (ppbv)	Highest concentration (ppbv)
ethane*	0.13	5.81
propane*	0.14	6.04
n-butane*	0.12	5.05
iso-butane*	0.13	5.66
n-pentane	0.12	0.79
i-pentane	0.16	0.99
ethene*	0.15	6.28
propene*	0.14	6.05
1-butene	0.45	2.85
1,3 butadiene*	0.15	6.67
benzene	0.60	3.83
acetylene	1.01	6.44

* compounds whose response was based on a purely per carbon basis

Table 4.15 Concentration ranges over which linearity is demonstrated

It has been shown in section 4.2.5 that the linearity of 1-butene is relatively unacceptable and the associated range for this compound is only shown for comparison purposes.

Benzene is the only compound for which the lowest concentration at which linearity has been determined may be too high. It is anticipated that background levels will in the main be less than 0.6 ppbv, the lowest concentration on the linearity curve.

However, the linearity of response over a very wide concentration range for the P-E online system run as standard has been well documented for the compounds being investigated (benzene included), using thousands of hours of sampled data from online systems (USEPA, 1999d) taking part in the AIRS program. As the precision and relative accuracy of the mobile method are both very low for this compound at low concentrations, it is unlikely that its response deviates from linearity at the low concentrations anticipated during ambient sampling.

For all other compounds, the linear range demonstrated is anticipated to encompass those levels anticipated during normal ambient sampling. The concentrations in the NIST traceable standard calibration gas mix, did not allow the system to be calibrated at the high concentration levels which may be encountered during episodes of elevated concentrations associated with highly stable atmospheric conditions.

In an attempt to verify the linearity at these very high concentrations, an additional experiment was carried out using the 5 litre Tedlar bag as a sample reservoir.

Air was sampled into the 5 litre Tedlar vessel using the exhaust of the universal pump at a roadside where very slow moving traffic was observed, a location where elevated HC concentrations were anticipated to be encountered. This air was then sampled in duplicate using the mobile sampling method as in section 4.2.7 (precision).

The first sample was then attached and analyzed on the P-E system as per section 4.1.2 (sample procedure), the data pertaining to this analysis was examined and the amount of dilution of the sample required to reduce all HC concentrations to within the pre-determined linear range was determined.

The duplicate sample taken from the 5 litre reservoir was diluted using the "valve open time" procedure (section 4.2.5). A valve open time of 5 minutes was used, which equates to a dilution factor of 6.35 when the excess sample volume analysed was taken into account, (i.e, 1.3 minutes equivalent excess sampling time at a flow of 10mls/min, added to 5 minutes open valve time, gives 6.3 minutes, which divided by 40 minutes implies a dilution factor of 6.35).

If the response remains linear at the higher concentrations, then the results of the analysis of the first sample (with no dilution) should be similar to those obtained by multiplying the duplicate (diluted) sample results by the dilution factor of 6.35. The results obtained are presented in Table 4.16. The small percentage differences shown in the last column suggest that linearity was preserved in the undiluted sample.

This shows that the detector response is linear above the highest concentration for which the range of linearity was established using formal procedures. As the sample investigated had exceptionally high HC concentrations, it is not anticipated that samples will be encountered on a regular basis where response deviates from the determined linearity.

	Undiluted sample		Diluted sample			% difference between undiluted and diluted samples
	peak area response	conc (ppbv)	peak area response[1]	Corrected peak area response[2]	Corrected conc (ppbv)	
ethane	30364	7.0	4615	29305	6.8	-4%
propane	22246	3.6	3415	21683	3.5	-3%
n-butane	61046	6.1	10121	64268	6.5	5%
iso-butane	31770	3.6	5355	34004	3.8	7%
n-pentane	20370	1.9	3363	21357	2.0	5%
i-pentane	65830	5.7	10818	68696	5.9	4%
ethene	36070	9.0	5503	34943	8.7	-3%
propene	17576	2.8	2819	17903	2.9	2%
1-butene	8502	0.9	1594	10123	1.1	16%
1,3 butadiene	3860	0.5	634	4026	0.5	4%
benzene	14153	2.2	2353	14940	2.3	5%
acetylene	28836	9.5	4367	27728	9.2	-4%

1 "valve open time" of 5 mins
2 Diluted peak area response multiplied by dilution factor of 6.35

Table 4.16 Comparison of diluted and undiluted ambient sample for undiluted concentrations outside the linear calibration range

Accuracy and precision

Accuracy and precision were determined over the wide concentration range summarized in Table 4.17. The fact that the majority of these estimations were carried out using ambient samples, where the sample matrix is unknown, adds to confidence in the mobile method's performance with regard to accuracy and precision when sampling "real world" samples.

The response for the mobile method does not deviate from linearity over the anticipated required concentration range within which both accurate and precise results are anticipated.

	Concentration range for which accuracy has been determined (ppbv)	Concentration range for which precision has been determined (ppbv)
ethane	0.2 – 7.0 ppbv	0.2 – 4.1 ppbv
propane	0.2 – 3.9 ppbv	0.1 – 1.8 ppbv
n-butane	0.2 – 6.1 ppbv	0.2 – 7.3 ppbv
Iso-butane	0.1 – 4.6 ppbv	0.9 – 4.6 ppbv
n-pentane	0.1 – 2.0 ppbv	0.1– 2.8 ppbv
i-pentane	0.2 – 5.7 ppbv	0.2 – 7.7 ppbv
ethene	0.5 – 9.4 ppbv	0.4 – 9.6 ppbv
propene	0.1 – 3.5 ppbv	0.3 – 3.2 ppbv
1-butene	0.2 – 1.7 ppbv	0.2 – 2.6 ppbv
1,3 butadiene	0.1 – 0.7 ppbv	0.1 – 0.6 ppbv
benzene	0.1 – 2.6 ppbv	0.2 – 2.6 ppbv
acetylene	0.3 – 9.5 ppbv	0.2 – 4.9 ppbv

Table 4.17 Concentration ranges for which accuracy and precision have been determined for the mobile sampling method

4.3 SAMPLE STABILITY

When using Tedlar sampling bags, it is generally advised that samples be analyzed within 48 hours (SKC, 2004). However, Shikiya *et al.*, (1984) showed that benzene samples stored in Tedlar bags at relatively low concentrations (10-50ppbv), only degraded by 1 % after 72 hours.

In this study it was intended to analyze all samples on the day of sampling, hence validation of sample stability within the Tedlar vessel over a 24 hour period was required. To do this, the sampling procedure used for accuracy determination in section 4.2.6 was employed.

For the stability examination, five online and mobile samples were analysed. The analysis of the mobile samples was delayed for 24 hours and compared to the P-E online samples analyzed the previous day. The relative accuracies of the results should remain within ± 20% if the storage of samples for 24 hours does not have an adverse affect on Tedlar samples.

The results presented in table 4.18 for the five sample analysis carried out, show that with the exception of 1-butene, all compounds have relative accuracies of less than ±20%. The relative accuracy results in Table 4.18 show a significant improvement on those presented in section 4.2.6 (accuracy), as only 5 analysis were determined for stability. This illustrates how the

section 4.2.6 presents a conservative estimation of accuracy for the mobile method, due to the relatively large number of sample comparisons made (approximately 40).

	Analysis 1 (% relative accuracy)	Analysis 2 (% relative accuracy)	Analysis 3 (% relative accuracy)	Analysis 4 (% relative accuracy)	Analysis 5 (% relative accuracy)
ethane	10	-2	4	8	7
propane	-7	-4	-3	3	3
n-butane	9	-1	1	3	6
iso-butane	-4	-7	-5	5	4
n-pentane	1	7	-6	4	4
i-pentane	10	2	2	6	9
ethene	2	3	1	3	9
propene	-9	-2	-3	2	1
1-butene	-25	-36	-32	-15	-21
1,3 butadiene	-8	-4	1	-4	-3
benzene	-4	1	-3	2	4
acetylene	1	4	-6	8	6

Table 4.18 Relative accuracies obtained after a delay in analysis of mobile samples for 24 hours (stability analysis for Tedlar vessels)

4.4 SUMMARY

A summary of the validated method parameters are shown in Table 4.19.

	Linear range (ppbv)	Method detection limits (ppbv)	Accuracy range (ppbv)	Precision range (ppbv)
Ethane	0.13 – 5.81	0.12	0.2 – 7.0	0.2 – 4.1
Propane	0.14 – 6.04	0.06	0.2 – 3.9	0.1 – 1.8
n-butane	0.12 – 5.05	0.07	0.2 – 6.1	0.2 – 7.3
Iso-butane	0.13 – 5.66	0.05	0.1 – 4.6	0.9 – 4.6
n-pentane	0.12 – 0.79	0.05	0.1 – 2.0	0.1– 2.8
i-pentane	0.16 – 0.99	0.05	0.2 – 5.7	0.2 – 7.7
Ethene	0.15 – 6.28	0.09	0.5 – 9.4	0.4 – 9.6
Propene	0.14 – 6.05	0.09	0.1 – 3.5	0.3 – 3.2
1-butene	0.45 – 2.85	0.41	0.2 – 1.7	0.2 – 2.6
1,3 butadiene	0.15 – 6.67	0.07	0.1 – 0.7	0.1 – 0.6
Benzene	0.60 – 3.83	0.09	0.1 – 2.6	0.2 – 2.6
Acetylene	1.01 – 6.44	0.19	0.3 – 9.5	0.2 – 4.9

Table 4.19 summary of validated method parameters

In addition, the mobile method sampling method was seen to be selective relative to the P-E online system run as standard, and the sampling method was shown to be robust to minor deviations in the mobile sampling procedure anticipated when sampling "real world" samples. Appendix J outlines the Quality Control procedures which should be followed to ensure the mobile sampling procedure and online system are both operating as expected, thus ensuring accurate and precise results.

4.5 PILOT MOBILE SAMPLING STUDY

4.5.1 Objectives

The primary objective of this pilot study was to examine the practicality of the newly validated sampling method and note any physical impediments associated with its use. Bearing this in mind, a sampling study was undertaken which required frequent changes of tedlar bag sampling vessels and was associated with non-stationary sampling, potentially the most ambitious application of the method. This pilot study was undertaken as an undergraduate final year project, with additional assistance received from Laurence Gill, of the Dept. Civil, Structural and Environmental Engineering, TCD, in regard to sampling and project planning. As no previous research has been undertaken in Dublin city into comparing exposure of commuters to hydrocarbon concentrations for various modes of transport, a secondary objective was to quantify the average HC concentrations experienced by bicycle and bus commuters travelling on the same route at similar times.

4.5.2 Route map and sampling details

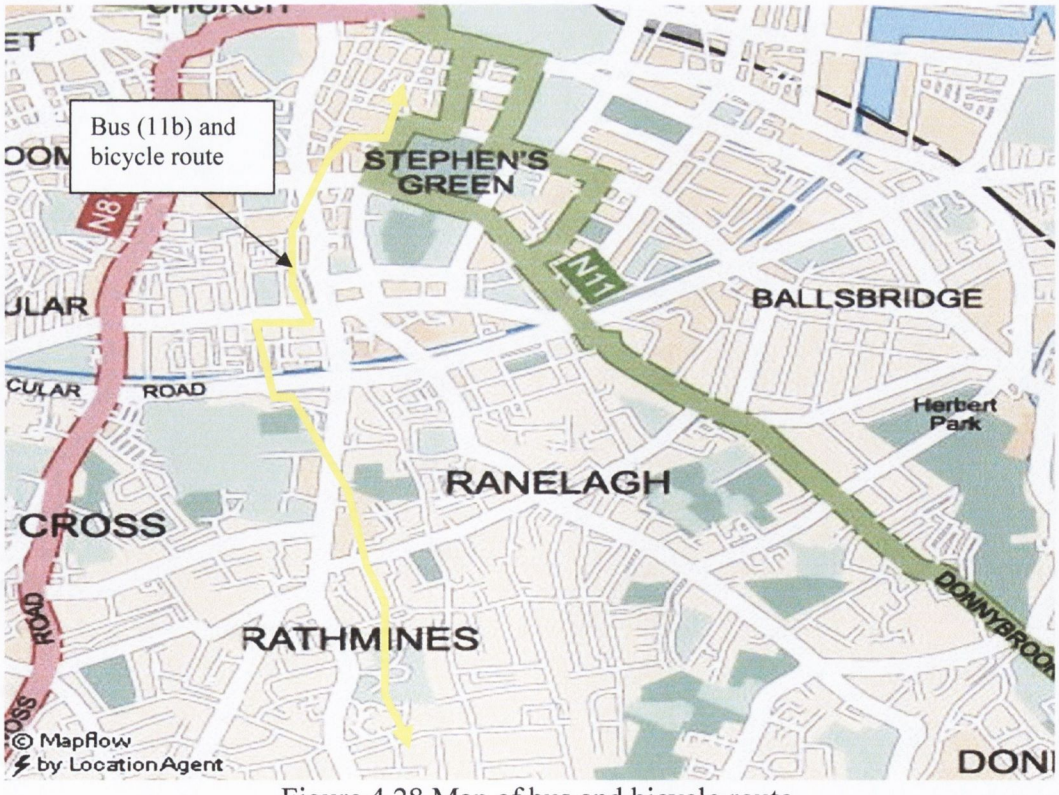


Figure 4.28 Map of bus and bicycle route

In all 14 bus and 14 bicycle samples were taken over a 2 week period. For both modes of transport, seven samples were taken in each direction, either to or from Dublin city.
For convenience of sampling, the bus route taken by the 11b from Palmerstown Road to Nassau Street was investigated (Figure 4.28).

The cycling route followed this bus route to enable a direct comparison of the concentrations obtained. The average bus journey took 20 minutes as opposed to 14 minutes for the cyclist and the total distance for each journey was approximately 3.5kms.

For bus sampling, seating location was taken at random in an attempt to simulate average exposure experienced by commuters on this mode of transport. The sample inlet of the mobile sampler was located at head height, and the air was sampled from the start to the end of the bus journey.

For cycle sampling, an adapted carrier bag was used to house the sampling case while travelling. Approximately 30cm of teflon tubing was connected to the sample chamber and the resultant extended sampling inlet was placed as near as possible to the cyclists head.

Due to the pilot nature of the study and the relatively minimal sampling pool obtained, only limited analysis has been carried out on values obtained. The important results have been extracted and are presented and discussed in the following sections.

4.5.3 Results

Average values

Table 4.20 shows that with the exception of ethane, the average concentrations experienced by the bus commuter are higher than those experienced by the cyclist. For ethane and propane, the concentration difference between both modes is very small probably due to their weak association with road traffic emissions.

For the other nine hydrocarbons monitored, the bus concentrations are on average 1.47 times those obtained for cycling. The effects of these higher concentrations will be compounded by the fact that the bus journey is on average 6 minutes longer than the cycling trip.

The most important observation to be noted from Table 4.20, is the relatively high levels of 1,3 butadiene and benzene sampled for both modes of transport. In section 4.6.7, these are discussed in terms of air quality standards and comparisons with similar studies.

	Mean (ppbv)		st. deviation (ppbv)		rel. st. dev (%)		Median (ppbv)		98^{th} percentile (ppbv)	
	cycle	bus	cycle	bus	cycle	bus	cycle	bus	cycle	bus
Ethane	8.58	7.85	4.51	4.25	53%	54%	6.86	6.29	18.00	17.79
Propane	5.16	5.89	4.30	5.11	83%	87%	3.68	4.65	14.73	18.32
n-but	5.45	7.87	2.60	4.93	48%	63%	4.60	7.84	10.62	16.75
i-but	2.53	3.71	1.19	2.30	47%	62%	2.22	3.34	4.91	7.76
n-pent	1.45	2.01	0.64	1.21	44%	60%	1.21	1.58	2.40	4.26
i-pent	3.29	4.73	1.35	2.76	41%	58%	2.98	4.38	5.38	9.63
Ethene	7.77	11.92	3.98	6.92	51%	58%	6.00	10.41	14.02	25.13
Propene	2.48	3.99	1.28	2.02	52%	51%	2.02	3.29	4.50	8.45
1,3 but	0.47	0.78	0.19	0.34	40%	44%	0.45	0.74	0.80	1.46
Benzene	1.62	2.21	0.75	1.36	46%	61%	1.60	1.88	2.81	4.93
Acet	5.60	7.92	2.50	4.77	45%	60%	4.85	7.25	9.87	18.03

n-but = n-butane, i-but = iso-butane, n-pent = n-pentane, i-pent = iso-pentane, 1,3 but = 1,3 butadiene, acet = acetylene, st. deviation = standard deviation, rel. st. dev = relative standard deviation.

Table 4.20 Average bicycle and bus concentrations obtained over 2 week study for hydrocarbons validated in section 4.2

Correlation matrices

Correlation matrices of individual compound concentrations for both modes of transport are presented in Tables 4.21 and 4.22. In general, the compounds can be segregated into 3 main groups, the first comprising, ethane and propane, the second comprising, iso-butane and n-butane and the third comprising the remaining 7 compounds. Ethane and propane are seen to correlate reasonably well with only the butanes, while the butanes correlate quite well with the remaining 7 HC compounds. The highest correlations are seen between these 7 compounds (iso-pentane, n-pentane, ethene, propene, 1,3-butadiene, acetylene and benzene), two of which, ethene and acetylene are known markers for road traffic emissions. For both bicycle and bus journeys the high correlations seen between these 7 compounds leads us to conclude that road traffic emissions are the major source for HC compounds being monitored. This is to be expected for the cyclist but the similar correlations observed for the interior of the bus suggest that external sources (in the form of road traffic) are also the main cause of the high concentrations observed in the bus.

	eth	prop	n-but	i-but	n-pent	i-pent	ethene	prope	1,3 bu	benz	acet
ethane	1.00	0.50	0.68	0.71	0.63	0.60	0.71	0.68	0.59	0.72	0.54
propane	0.50	1.00	0.82	0.80	0.58	0.50	0.51	0.42	0.54	0.43	0.75
n-butane	0.68	0.82	1.00	1.00	0.90	0.86	0.83	0.77	0.83	0.77	0.95
i-butane	0.71	0.80	1.00	1.00	0.91	0.87	0.85	0.80	0.86	0.80	0.95
n-pentane	0.63	0.58	0.90	0.91	1.00	0.99	0.96	0.94	0.94	0.91	0.92
i-pentane	0.60	0.50	0.86	0.87	0.99	1.00	0.96	0.96	0.94	0.92	0.89
ethene	0.71	0.51	0.83	0.85	0.96	0.96	1.00	0.99	0.94	0.97	0.85
propene	0.68	0.42	0.77	0.80	0.94	0.96	0.99	1.00	0.95	0.98	0.80
1,3 butad	0.59	0.54	0.83	0.86	0.94	0.94	0.94	0.95	1.00	0.91	0.87
benzene	0.72	0.43	0.77	0.80	0.91	0.92	0.97	0.98	0.91	1.00	0.83
acetyl.	0.54	0.75	0.95	0.95	0.92	0.89	0.85	0.80	0.87	0.83	1.00

1,3 bu = 1,3 butadiene, acetyl = acetylene

Table 4.21 Correlation matrix for bicycle journeys

	eth	prop	n-but	i-but	n-pent	i-pent	ethene	prope	1,3 bu	benz	acet
ethane	1.00	0.59	0.60	0.61	0.65	0.67	0.69	0.67	0.68	0.68	0.74
propane	0.59	1.00	0.77	0.72	0.42	0.44	0.47	0.42	0.50	0.36	0.40
n-butane	0.60	0.77	1.00	0.99	0.82	0.84	0.78	0.75	0.79	0.75	0.70
i-butane	0.61	0.72	0.99	1.00	0.84	0.87	0.78	0.74	0.79	0.74	0.72
n-pentane	0.65	0.42	0.82	0.84	1.00	0.98	0.92	0.91	0.91	0.91	0.93
i-pentane	0.67	0.44	0.84	0.87	0.98	1.00	0.90	0.88	0.88	0.91	0.88
ethene	0.69	0.47	0.78	0.78	0.92	0.90	1.00	0.98	0.98	0.95	0.93
propene	0.67	0.42	0.75	0.74	0.91	0.88	0.98	1.00	0.98	0.97	0.89
1,3 butad	0.68	0.50	0.79	0.79	0.91	0.88	0.98	0.98	1.00	0.92	0.92
benzene	0.68	0.36	0.75	0.74	0.91	0.91	0.95	0.97	0.92	1.00	0.82
acetyl	0.74	0.40	0.70	0.72	0.93	0.88	0.93	0.89	0.92	0.82	1.00

1,3 butad = 1,3 butadiene, acetyl = acetylene

Table 4.22 Correlation matrix for bus journeys

4.5.4 Meteorological effects

Regional hourly wind speed and temperature covering the period of study was obtained from the synoptic meteorological station situated at Dublin airport and maintained by Met Eireann. The effects of wind speed on the ethene concentrations obtained for both modes of transport are shown in Figures 4.29 and 4.30.

As discussed in greater detail in proceeding chapters, wind speed is an indicator of atmospheric dilution and dispersion. With all other variables effecting ambient levels constant, higher wind speeds lead to proportionally lower ambient concentrations. This is clearly seen in Figure 4.29 for the concentrations experienced by the cyclist but Figure 4.30 suggests that

wind speed has a lesser impact on concentrations experienced within the vehicle. This is in agreement with the findings of Duffy and Nelson (1997).

For this study, due to the limited sampling pool, wind speed cannot be considered in isolation, as periods with low wind speeds were on several occasions also associated with very low temperatures. This would have a significant effect on the proportion of catalytic converters working to their optimum due to cold starts (Heeb *et al.*, 2003).

However, it is not possible to directly ascertain the effects of temperature in this study, as all the sampling periods of colder weather occurred during morning peak time traffic flow. The effects of low wind speed, low temperature and a resulting increase in cold starts are clear from Table 4.23, which shows the concentrations obtained during morning peak traffic time for both modes of transport on the 14/02/03.

Both samples were taken between 08:00 and 09:00 when the temperature was –0.5°C and the regional wind speed was less than 2 m/s. Concentrations for all hydrocarbons are significantly higher on the bus, except for ethane and propane. The bus concentrations for benzene and 1,3 butadiene and the cyclist concentrations for benzene are above the air quality standards of 1.5 and 1.0 ppbv respectively.

	bicycle concentrations sampled between 08:00-09:00 on 14/02/03 (ppbv)	bus concentrations sampled between 08:00-09:00 on 14/02/03 (ppbv)
ethane	19.1	9.7
propane	7.3	6.1
n-butane	9.3	15.1
i-butane	4.2	7.5
n-pentane	2.4	4.2
i-pentane	5.3	10.0
ethene	14.3	18.3
propene	4.3	5.9
1,3 butad	0.6	1.03
benzene	2.9	4.0
acetylene	8.7	12.0

Table 4.23 Concentrations for both modes of transport obtained on 14/02/03

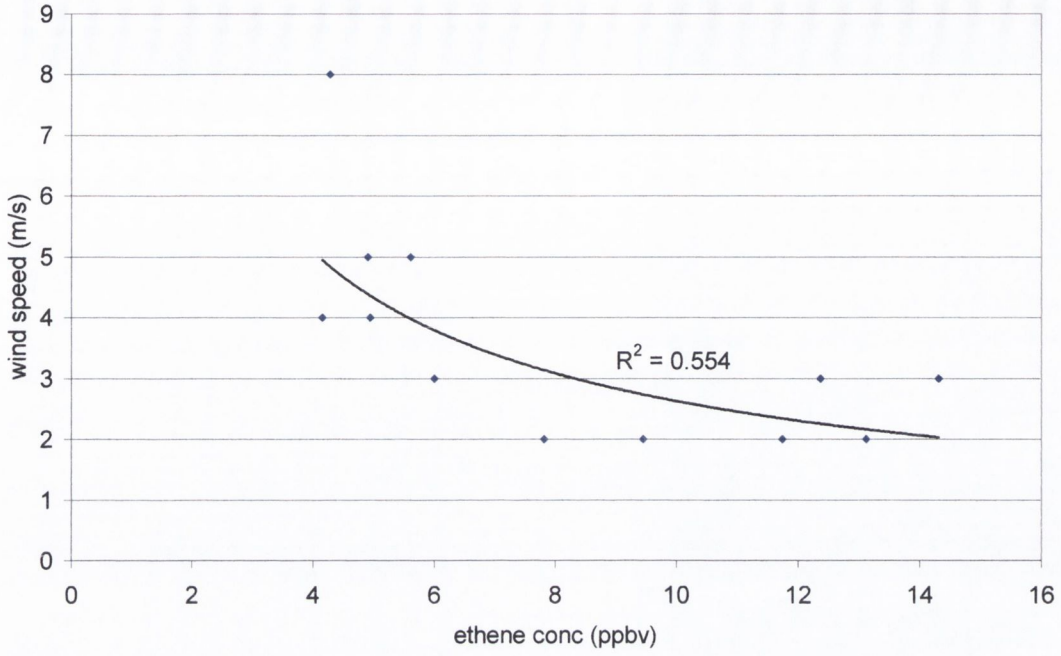


Figure 4.29 Scatter plot of ethene concentration against wind speed for the bicycle commuter

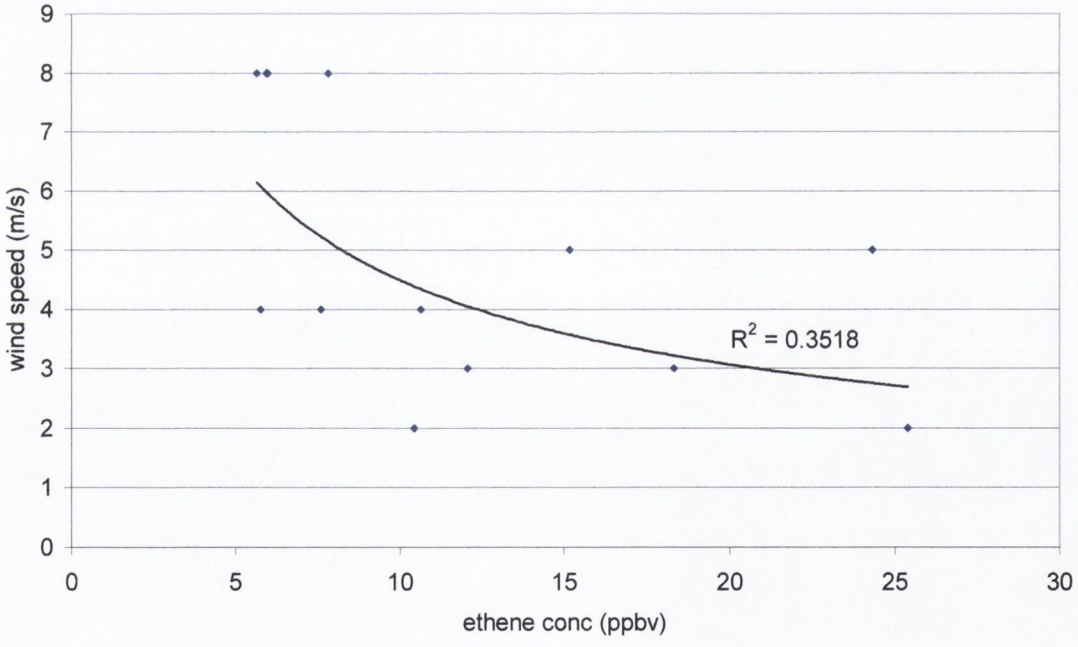


Figure 4.30 Scatter plot of ethene concentration against wind speed for the bus commuter

4.5.5 Temporal trends for both modes of transport

Figure 4.31 shows the average daily trends of 1,3 butadiene exposure for both modes of transport. A similar number of journeys in and out of the city were made for both modes within each time period shown. The trend observed for bicycle concentrations is similar to that observed with roadside monitors (Chapters 5 and 7), where a morning peak is followed by a mid-day trough and a subsequent evening peak.

The trend observed for bus concentrations is markedly different, where a much higher morning peak is followed by successive decreases in average hourly concentrations. This may be due to the slower average speeds during the morning trips: the average morning trip took 25 minutes as opposed to 19 minutes in the evening rush hour.

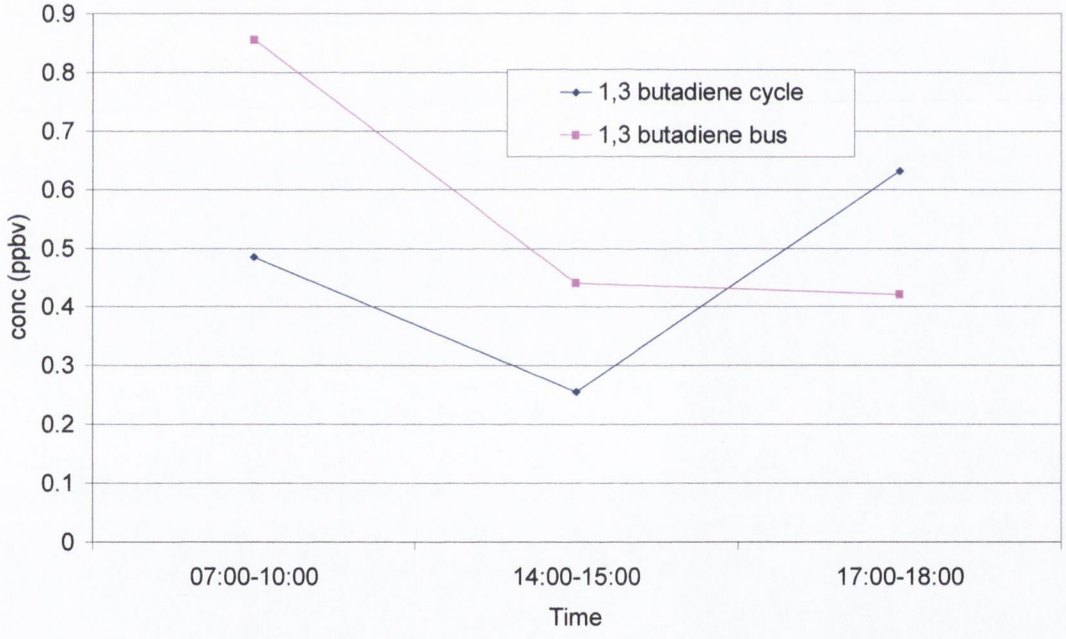


Figure 4.31 Average daily trend of 1,3 butadiene for both modes of transport

4.5.6 Comparisons with other studies

As no air quality standards exist for the short term exposure of any hydrocarbon compounds monitored, it is difficult to assess the impact of the concentrations observed for both modes of transport.

If long term, yearly average air quality limits are used as a guide, average benzene concentrations in Table 4.20 for both modes of transport are above the EU 2010 limit value of 1.5ppbv. Neither mode of transport exceeds the recommended UK air quality standard of 1.0ppbv for 1,3 butadiene.

The average results observed for benzene bus concentrations compare well with those found by Batterman *et al.* (2002), where benzene levels of 1.5ppbv were observed. The bus concentrations observed during this Detroit study were cited as being very similar to other US and Canadian studies but much lower than European and Asian studies, as illustrated by concentrations observed by Lee and Jo (2002), where average benzene levels of 6.7ppb were observed during urban Korean bus commutes and Kim *et al.* (2001) observed concentrations of 6.1ppb in Birmingham. Results for Dublin bus concentrations were also significantly lower than those observed in a similar study by Nelson and Duffy (1997), where benzene and 1,3 butadiene concentrations were evaluated at different times of the day in buses with and without air-conditioning. In general, the concentration trends cited in other studies, comparing bus and bicycle transport modes are similar to those observed in Dublin, where exposure levels are higher for bus than bicycle commuting (Taylor and Ferguson,1999). The ratio of bicycle to bus concentrations observed in Dublin, for the 7 compounds strongly related to traffic emissions compares very well to those reported by Taylor and Ferguson (1999), where a Dublin average ratio of 1.5 relates well to the overall average ratio of between 1 and 2 for a number of studies examined by Taylor and Ferguson.

4.5.7 Summing up

Both the primary and secondary objectives of the pilot study were completed. Namely, the recently validated sampling method was applied to a real world sampling application and no insurmountable obstacles were encountered. The method's ease of use was noticeable, and mobile sampling was carried out with relative ease. The secondary objective of quantifying the hydrocarbon exposure of different commuters in Dublin City was made relatively uncomplicated due to the practicality of the sampling method employed. Following this successful pilot study, the sampling method was employed in more varied and rigorous sampling and analysis studies. These are discussed in Chapters 6 and 8.

5. ONLINE HC MONITORING AT A SUBURBAN MOTORWAY SITE

5.1 OBJECTIVES AND MONITORING DETAILS

The primary objective of this monitoring campaign was to ascertain the extent of road traffic emissions associated with a sub-urban Motorway (M4). Different analysis techniques are employed in an attempt to isolate the Motorway source effect.

5.1.1 Site description and map

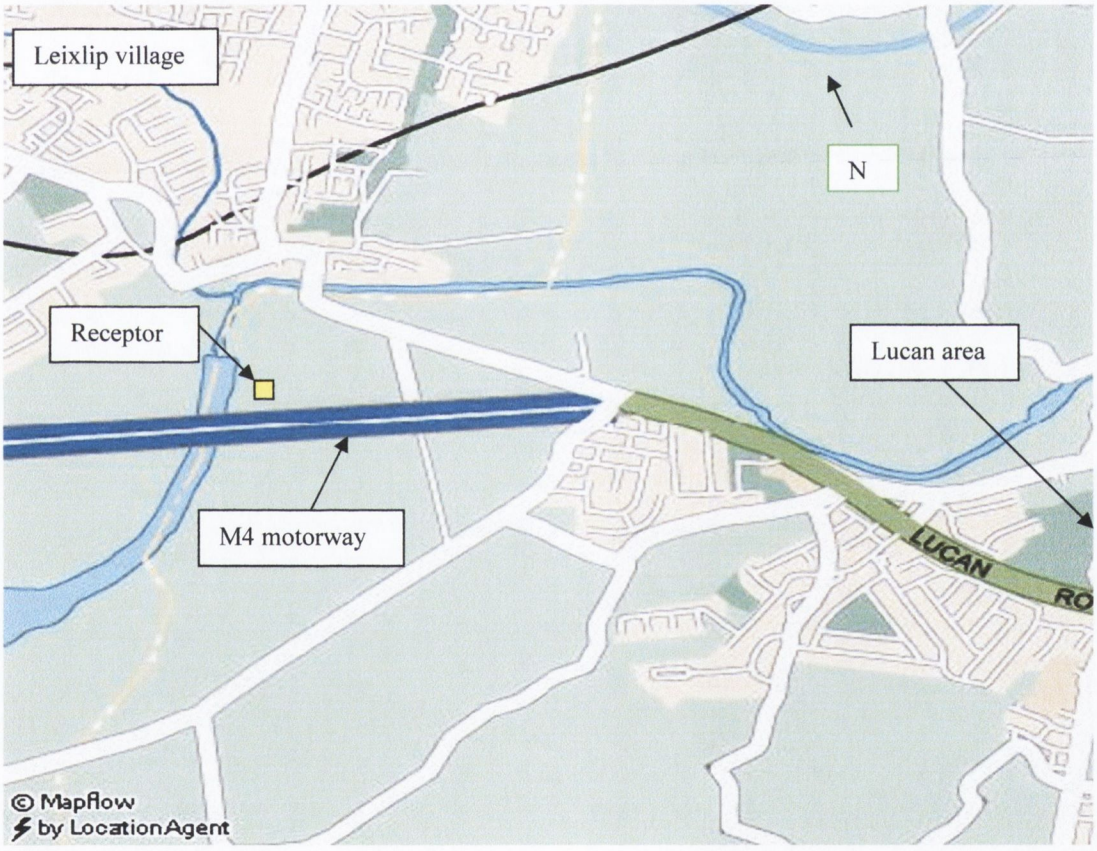


Figure 5.1 Site map of Leixlip monitoring location

The Leixlip monitoring site (Figure 5.1) is a free flowing motorway site (M4) located 10 miles west of Dublin, on the main Dublin to Galway (west of Ireland) route, at an altitude of 50 metres. The motorway consists of two lanes running in approximately east –west directions. The receptor is located 20 metres North of the nearest kerbside.

5.1.2 Monitoring period and breakdowns

The on-line system was first put into use for this project on the 22nd of November 2001. Various teething and initialisation problems were encountered over the initial 2 months, central to which were carrier gas helium leaks and a lack of calibration gas, making the quantification of compounds impossible.

Smaller problems such as the GC intermittently shutting itself on and off (due to overheating) were also encountered, all of which had to be remedied before the monitoring programme could start in earnest.

The monitoring period ranged from 8th February 2002 to the 23rd September 2002. Various problems were encountered during this 8 month period which resulted in 3096 hours out of a possible 5450 being sampled (57%). Examples of some of the problems overcome are illustrated below.

Methods associated with the Turbochrom software required re-writing. Problems were encountered with analytical column switching on the GC (deans switch), resulting in heavier HC compounds being sent to the PLOT column, a scenario highly undesirable due to the difficulties associated with removing these compounds from this analytical column.

The ATD400 sporadically gave "bus errors", the solution to which involved obtaining new internal processor boards for the instrument (this particular complication resulted in no data being obtained for July and the first half of August).

Additional problems were encountered with the zero air generator, which developed several leaks with continued use. Finally, difficulties associated with the mass flow controler had to be resolved, to ensure a reproducible volume of air was being sampled.

5.2 METEOROLOGICAL DATA

5.2.1 Local wind direction and windspeed

Meteorological data is only analysed for those hours in which hydrocarbon data was obtained. The frequency of occurrence of average hourly local wind direction for each 15° sector is plotted in Figure 5.2. The sectors with the highest rate of occurrence in Figure 5.1 relate to wind directions approximately parallel (105-180°) and perpendicular (180-240°) to the M4 motorway.

Of these the wind directions near parallel to the M4 in an easterly direction have the highest frequency. The wind direction of 90-165° also relates to the greater Lucan area which has a population of 41,330 (CSO,1996), and surrounding heavily trafficked roads in the distance (approximately 2 miles). The sector 0-90° shows by far the lowest levels of incidence in the main due to the shielding effect of a nearby building.

The local hourly wind speed data obtained during the monitoring period is shown in Figure 5.3. The main trend which can be observed in Figure 5.3 is the overall decrease in hourly wind speeds from the Winter/Spring to Summer months. Average hourly wind speeds for each 15° wind sector can be seen in Figure 5.4. From this we can see the wind direction sector 15-90° has by far the lowest average wind speeds.

The highest average speeds are seen approximately perpendicular (180°) to the M4 and parallel in a Westerly direction (285°). Comparing the frequency of wind direction (Figure 5.2) to average wind speeds for different wind directions (Figure 5.4), we can see easterly wind direction (105°), parallel to the M4 has both the highest frequency of occurrence and lower average wind speed relative to the perpendicular or westerly wind directions.

The extreme difference in average wind speeds for the sector 15-90° is again most probably down to the shielding effect of the nearby building.

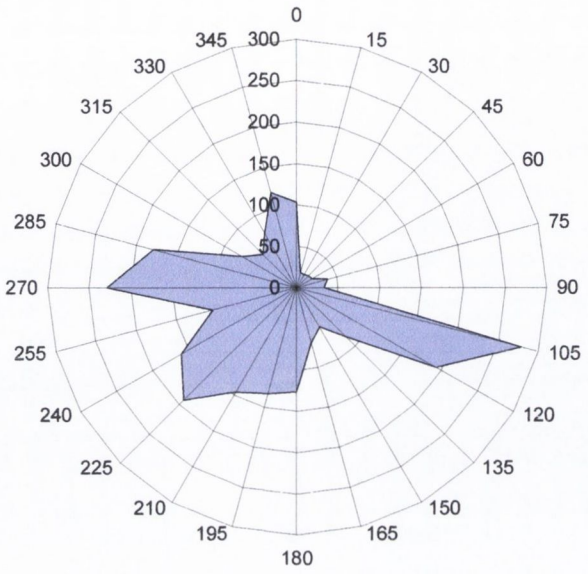


Figure 5.2 Wind direction frequency rose for all data

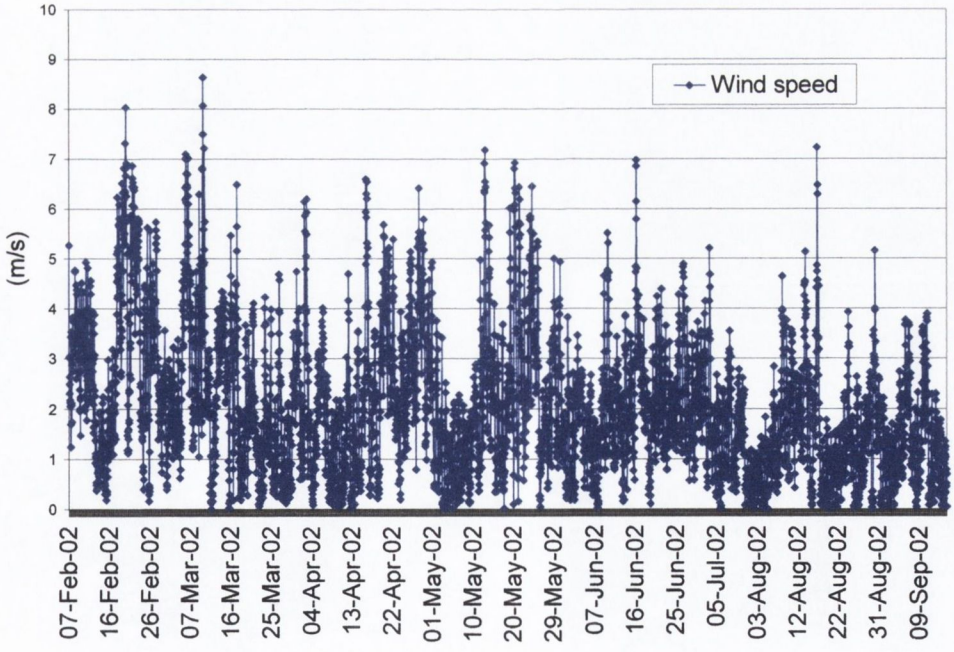


Figure 5.3 Local hourly wind speed over entire monitoring period

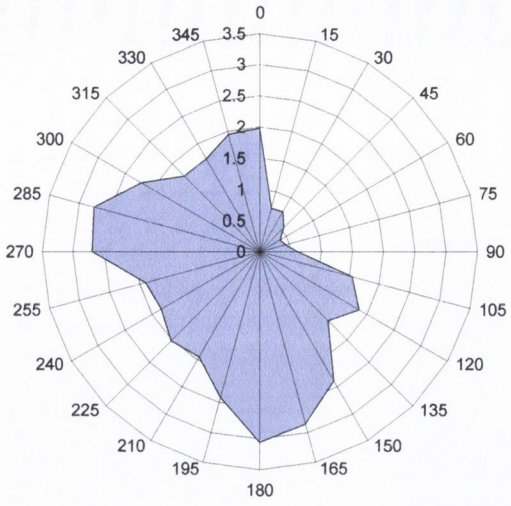


Figure 5.4 Average wind speed rose (m/s)

5.2.2 Temperature.

The variation in hourly local temperature over the duration of the monitoring period is shown in Figure 5.5. As expected the trend is a positive one (red line), with hourly temperature rising from Winter to Summer.

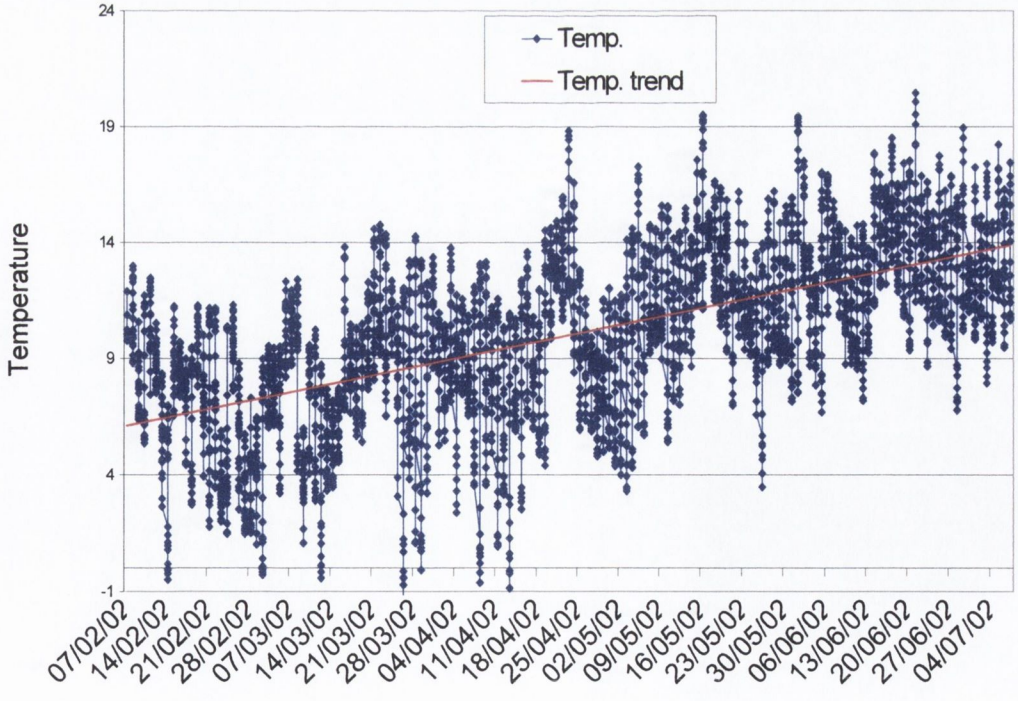


Figure 5.5 Hourly local temperature over the entire monitoring period

5.2.3 Regional stability data

Hourly regional stability class was obtained from Met Eireann for the nearby Casement Aerodrome (approximately 1Km South). This data was used to see the relative occurrence of stable (stability class A to D) and unstable (stability class E to G) atmospheric conditions within each 15° wind sector. The frequency rose in Figure 5.6 shows that the incidence for unstable air class (A to D) in each 15° sector is very similar to that obtained for all stability classes (A to G).

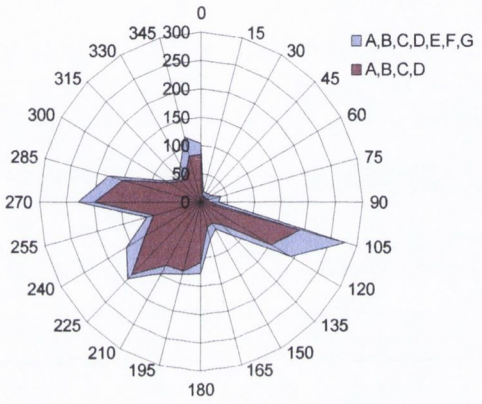


Figure 5.6 Rose plot of unstable atmospheric conditions (stabilities A-D) and all atmospheric conditions (stabilities A-G)

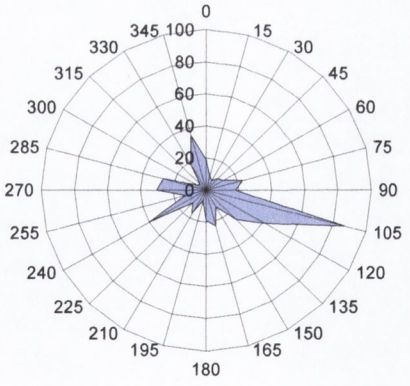


Figure 5.7 Rose plot of frequency of incidence of stable air (stabilities E,F,G)

Figure 5.7 shows the frequency of stable air (stabilities E-G) within each 15° wind direction sector. By far the highest incidence of stable air was seen to emanate from the 105° wind direction sector.

The effect of stability classes on measured hydrocarbon concentrations is examined in detail in later sections. In addition to obtaining regional stability class data from Met Eireann, additional regional wind direction and wind speed data for the nearby Casement aerodrome was acquired.

As the casement regional meteorological station is relatively nearby, correlation's between the two sets of data can be used to validate the local measurements obtained from the onboard local meteorological station.

5.2.4 Regional versus local wind direction

It was anticipated that the nearby building would have an effect on correlations obtained for regional versus local wind directions. In an attempt to quantify this effect we grouped the regional wind direction data was grouped into two wind direction sectors, 0°-80° anticipated to be affected by the building, and 90-360°, not expected to be affected by building shielding and funnelling.

Wind directions 0-80°: When a scatter plot of local versus regional wind directions is plotted for this regional wind direction sector (0-80°), the buildings effect on locally obtained wind directions becomes apparent. (Figure 5.8)

Whenever the regional wind direction emanated from the 0-80° sector, a local wind direction within one of two well-defined bands was obtained (Figure 5.8). These local wind direction bands occurred in the main between 100-160° and 320-350°. This phenomena is due to air masses travelling in a direction between 0°- 80°, coming into contact with the nearby building and being funnelled around the obstacle giving an impression of a local wind direction associated with either 100-160° or 320-350°. As a result of this, regional wind directions between 0°and 80° might appear to be near-parallel to the M4 motorway, and thus contribute to a less accurate quantification of a source effect from the motorway at the receptor.

As the local and regional 0-80° wind directions do not correlate well, the validity of any results associated with a local wind direction between 0° and 80° is questionable.

As a result, hourly hydrocarbon concentrations associated with local or regional wind directions in the sector 0-80° are omitted in later analysis. This reduced our data set by less than 5%, and does not compromise the primary objective of the monitoring programme, namely to estimate the source effect from the M4 motorway, expected to be associated with wind directions 105-285° relative to the receptor.

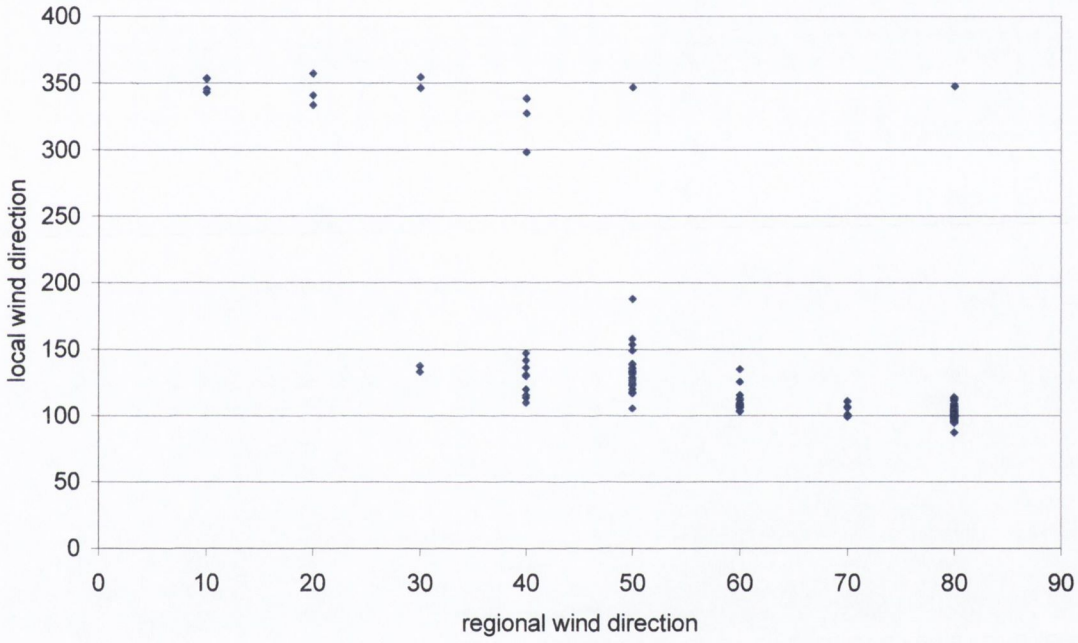


Figure 5.8 Scatter plot of local versus regional wind direction for regional 0-80°

Wind direction 90-360°: The correlation between local and regional wind directions for the remaining wind direction sectors were seen to correlate reasonably well, with an R^2 value of 0.77 obtained (Figure 5.9). This correlation suggests that, a high degree of confidence should be associated with local wind directions from this wind direction sector.

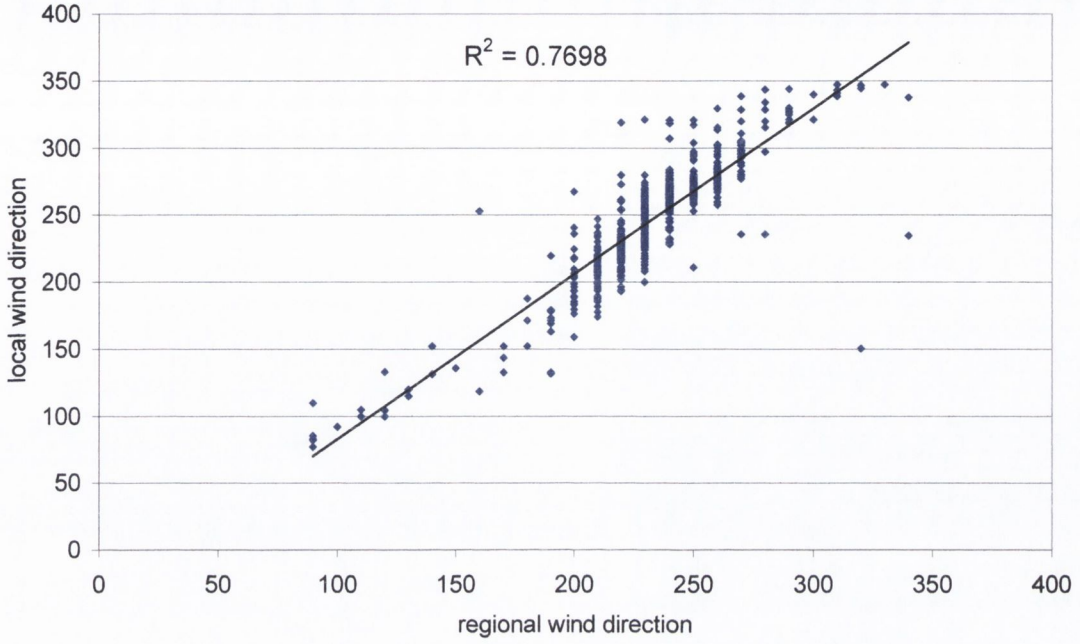


Figure 5.9 Scatter plot of local versus regional wind direction, for wind directions 90-360°

5.2.5 Regional versus local wind speed

The local and regional wind speeds were seen to correlate very well (Figure 5.10), with the regional wind speeds at casement aerodrome consistently higher due to the difference in height between the regional and local anemometers. The wind speed at Casement is measured at 10 metres as opposed to 3 metres at the receptor.

The slope of the regression line in Figure 5.10 is 0.21, indicating that the wind speed measured at 10metres in casement aerodrome is almost 5 times that measured for a height of 3 metres at the receptor.

Using the power law described in section 2.6.4, which outlines the logarithmic increase in wind speed with height due to limited surface drag, we obtain an exponent value (p) of 1.29. An expected value of between 0.1 and 0.4 is expected depending on the atmospheric stability, surface roughness and depth of the mixing height (Boubel *et al.*, 1994).

The large difference between the observed and theoretical exponents is possibly due to difference in topography between the two sites, the aerodrome is located 94 metres (www.meteireann.ie) above sea level as opposed to 50 metres for the receptor.

In addition, it should be noted that the power law wind profiles do not necessarily represent the data well, the behaviour of which is site dependant (Irwin, 1979).

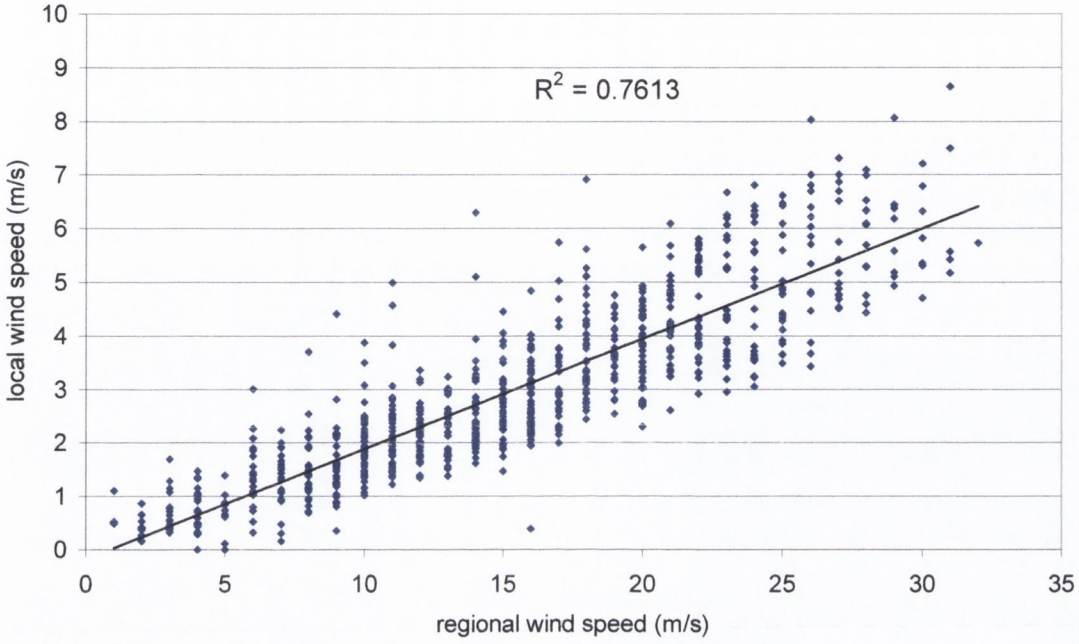


Figure 5.10 Scatter plot of local versus regional wind speed

5.3 TRAFFIC DATA

Traffic flow on the M4 motorway was constantly monitored during the sampling period. Induction loops located between interchanges to the East and West of the air monitoring site were used for this purpose. The loops were installed and maintained by the National Roads Authority, who made the data available for this project.

The total flow of vehicles per hour was used to correlate traffic activity with the hydrocarbon concentrations obtained. Similar to the meteorological data, hourly traffic flow data was only used where corresponding hydrocarbon data was obtained. As a relatively limited amount of weekend hydrocarbon data was obtained (140 hours of data over 7 weekends), due to the inability of the online system to run unattended for more than 24 hours, only weekday traffic was considered.

A plot of average weekday diurnal traffic flow is shown in Figure 5.11. The morning peak can be seen from 07:00-10:00, with a peak traffic volume of 2000 vehicles per hour. The later evening peak is seen to extend over a longer period of 16:00 to 20:00, with a higher average peak volume of 2700 vehicles per hour.

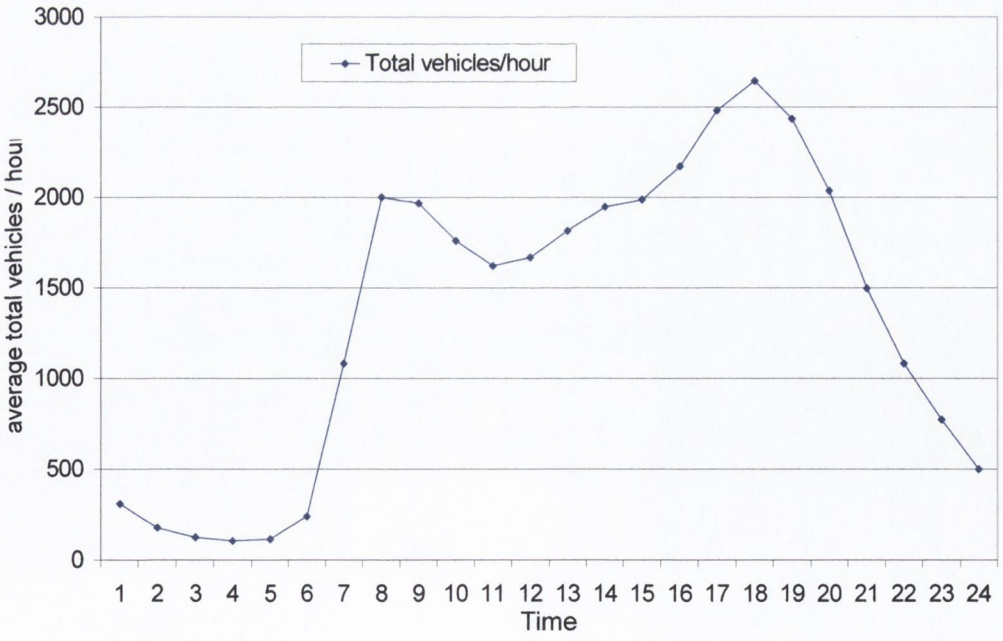


Figure 5.11 Average diurnal weekday traffic flow on the M4 Motorway

5.4 MEASURED HYDROCARBON CONCENTRATIONS

Summarised statistical data for the M4 monitoring period are presented in Table 5.1 below.

	Max (ppbv)	Mean (ppbv)	Std deviation (ppbv)	Relative Std dev. (%)	98th percentile (ppbv)	50th percentile (ppbv)
ethane	6.98	1.43	0.86	60.50	3.72	1.44
propane	8.59	0.72	0.68	94.76	2.65	0.56
n-butane	4.41	0.46	0.53	114.89	2.09	0.28
isobutane	3.12	0.28	0.33	119.48	1.29	0.17
isopentane	3.35	0.28	0.34	120.41	1.42	0.16
ethene	7.25	0.78	0.85	109.14	3.43	0.49
propene	1.59	0.22	0.21	91.80	0.92	0.15
1-butene	0.53	0.12	0.06	51.93	0.34	0.11
1,3 butadiene	0.71	0.24	0.13	53.51	0.54	0.21
trans-2-but	0.31	0.10	0.05	46.79	0.21	0.09
cis-2 butene	0.20	0.05	0.02	45.93	0.12	0.05
trans-2 pent	0.29	0.06	0.04	68.77	0.17	0.05
cis-2 pentene	0.13	0.04	0.02	58.21	0.10	0.04
toluene	6.83	0.31	0.45	145.47	1.67	0.16
o-xylene	1.58	0.11	0.12	113.17	0.48	0.07
m+p xylene	4.35	0.21	0.28	134.31	1.04	0.12
benzene	2.09	0.16	0.15	89.63	0.65	0.12
ethylbenzene	1.15	0.09	0.09	98.54	0.38	0.07
acetylene	4.01	0.52	0.43	82.08	1.98	0.41

Table 5.1 Summary statistics for hydrocarbons monitored

The compound with by far the highest mean was seen to be ethane, which can most probably be primarily related to natural gas leakage (Derwent *et al.*, 2000). The second highest average is seen from ethene, a compound synonymous with road traffic emissions (Wadden *et al.*, 1986; Lewis *et al.*, 1993; Tanaka *et al.*, 2001). While the mean and median (50th percentile) concentrations of ethane are very similar, the mean ethene concentration is much greater than the median for that compound. In Table 5.1 the mean and median values of all other compounds are seen to behave in a manner similar to either ethane or ethene. It is possible that

compounds with a much higher mean than median value are associated with a relatively greater local source effect, raising the mean relative to the median. Also associated with these compounds is a higher relative standard deviation (%) due to a larger relative concentration range. In contrast, if background hydrocarbon concentrations are monitored (far away from any local source contributions), the mean and median values would be anticipated to be very similar, for all compounds.

The evidence as to which compounds show a definite local source effect, specifically the M4 motorway, is examined in greater detail in sections 5.6 to 5.8.

Table 5.2 presents a Pearson correlation matrix for the concentrations of all compounds monitored. This is a useful tool in estimating which compounds possibly emanate from a common or similar source. However, caution must be exercised as correlation must not be interpreted as causation (mac Bertheoux and Brown, 1994).

A correlation co-efficient close to 1 indicates a very strong correlation, while a value close to 0 is indicative of a weak one. In the main the compounds which showed the greatest difference between mean and median values showed the strongest correlation between their hourly concentrations, again suggesting contributions from a similar local source.

As ethene and acetylene correlate well with most of these compounds and both are known markers for road traffic tail-pipe emissions (Barletta *et al.*, 2002), it suggests that road traffic emissions are possibly the single most significant local source monitored at the receptor. This is examined in more detail in sections 5.6 to 5.8.

	eth	prop	n-b	i-b	i-p	ethe	pro	1-bu	1,3b	t2b	c2b	t2p	c2p	tol	o-xy	m+p	benz	eben	acet
ethan	1.00	0.71	0.69	0.69	0.59	0.59	0.54	0.46	0.39	0.46	0.50	0.48	0.27	0.55	0.55	0.46	0.58	0.56	0.63
prop	0.71	1.00	0.88	0.86	0.76	0.75	0.71	0.56	0.20	0.33	0.50	0.63	0.46	0.71	0.66	0.61	0.75	0.64	0.81
n-but	0.69	0.88	1.00	0.97	0.92	0.83	0.82	0.71	0.21	0.36	0.59	0.81	0.60	0.84	0.78	0.75	0.84	0.75	0.85
i-but	0.69	0.86	0.97	1.00	0.88	0.83	0.79	0.69	0.24	0.40	0.64	0.75	0.54	0.80	0.72	0.70	0.80	0.70	0.85
i-pen	0.59	0.76	0.92	0.88	1.00	0.81	0.85	0.79	0.21	0.33	0.59	0.79	0.69	0.90	0.86	0.83	0.84	0.82	0.78
eth	0.59	0.75	0.83	0.83	0.81	1.00	0.91	0.74	0.29	0.40	0.64	0.71	0.52	0.80	0.70	0.71	0.85	0.69	0.89
pro	0.54	0.71	0.82	0.79	0.85	0.91	1.00	0.84	0.27	0.38	0.65	0.81	0.64	0.88	0.83	0.82	0.89	0.81	0.82
1-but	0.46	0.56	0.71	0.69	0.79	0.74	0.84	1.00	0.38	0.48	0.65	0.78	0.67	0.81	0.82	0.78	0.76	0.78	0.68
1,3 b	0.39	0.20	0.21	0.24	0.21	0.29	0.27	0.38	1.00	0.90	0.60	0.39	0.34	0.20	0.31	0.16	0.20	0.33	0.28
t-2-b	0.46	0.33	0.36	0.40	0.33	0.40	0.38	0.48	0.90	1.00	0.72	0.45	0.45	0.31	0.40	0.25	0.31	0.41	0.41
c-2-b	0.50	0.50	0.59	0.64	0.59	0.64	0.65	0.65	0.60	0.72	1.00	0.71	0.60	0.59	0.63	0.54	0.58	0.62	0.60
t-2-p	0.48	0.63	0.81	0.75	0.79	0.71	0.81	0.78	0.39	0.45	0.71	1.00	0.73	0.84	0.77	0.79	0.81	0.78	0.72
c-2-p	0.27	0.46	0.60	0.54	0.69	0.52	0.64	0.67	0.34	0.45	0.60	0.73	1.00	0.72	0.72	0.70	0.65	0.69	0.49
tol	0.55	0.71	0.84	0.80	0.90	0.80	0.88	0.81	0.20	0.31	0.59	0.84	0.72	1.00	0.89	0.88	0.86	0.87	0.77
o-xyl	0.55	0.66	0.78	0.72	0.86	0.70	0.83	0.82	0.31	0.40	0.63	0.77	0.72	0.89	1.00	0.92	0.85	0.91	0.67
m+p	0.46	0.61	0.75	0.70	0.83	0.71	0.82	0.78	0.16	0.25	0.54	0.79	0.70	0.88	0.92	1.00	0.81	0.96	0.65
benz	0.58	0.75	0.84	0.80	0.84	0.85	0.89	0.76	0.20	0.31	0.58	0.81	0.65	0.86	0.85	0.81	1.00	0.82	0.82
ethb	0.56	0.64	0.75	0.70	0.82	0.69	0.81	0.78	0.33	0.41	0.62	0.78	0.69	0.87	0.91	0.96	0.82	1.00	0.66
acet	0.63	0.81	0.85	0.85	0.78	0.89	0.82	0.68	0.28	0.41	0.60	0.72	0.49	0.77	0.67	0.65	0.82	0.66	1.00

Table 5.2 Correlation matrix for hourly hydrocarbon concentrations

5.5 ANALYSIS OF RESULTS

5.5.1 Entire data set

For the analysis of Hydrocarbon data, compounds monitored were grouped into 4 different chemical classifications as per Table 5.3

COMPOUND	CLASSIFICATION
ethane	Alkane
propane	Alkane
n-butane	Alkane
iso-butane	Alkane
iso-pentane	Alkane
ethene	Alkene (Olefin)
propene	Alkene
1-butene	Alkene
trans-2-Butene	Alkene
cis-2-Butene	Alkene
1,3 butadiene	Alkene
trans-2-Pentene	Alkene
cis-2-Pentene	Alkene
benzene	Aromatic
toluene	Aromatic
o-xylene	Aromatic
m+p-Xylene	Aromatic
ethylbenzene	Aromatic
ethyne (Acetylene)	Alkyne

Table 5.3 Compounds monitored and chemical classifications

Figure 5.12 shows the variation in the average daily concentrations of acetylene over the course of the monitoring period. Other compounds in all four classifications behaved in a similar manner, exhibiting similar graphical trends. Toluene was the only compound to deviate from the observed trend, where the maximum value obtained was seen in September. Apart from this single hourly value the overall trend was similar to that presented for acetylene.

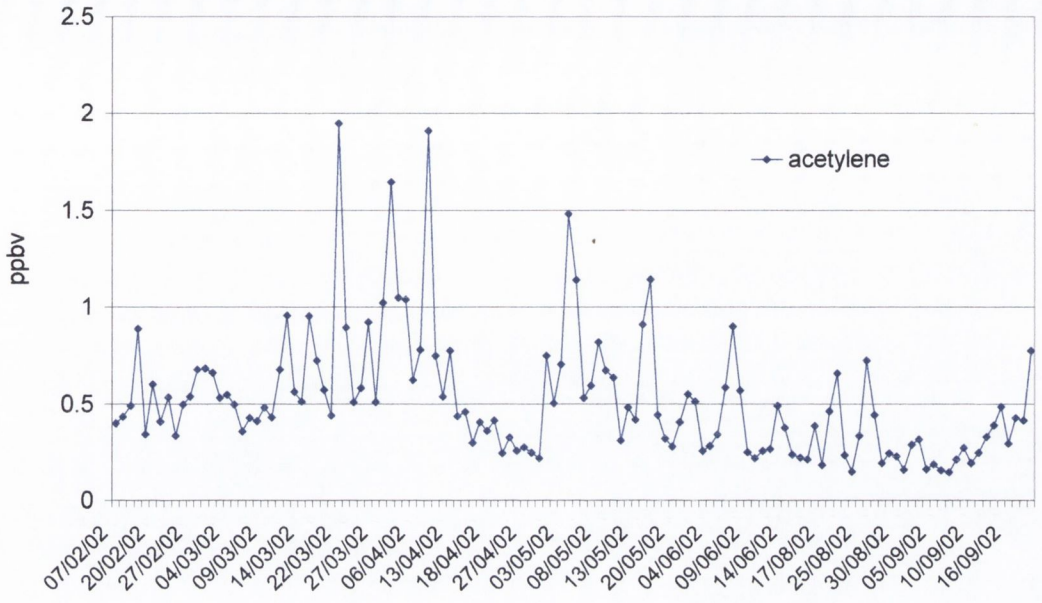


Figure 5.12 Average daily acetylene concentrations over monitoring period

It is clear that peaks obtained in the Summer are relatively lower than those obtained in the Winter months. This can be attributed to increased Summertime atmospheric mixing from an extended boundary layer (elevated mixing height), in conjunction with greater photochemical activity, reducing Summertime ambient concentrations of the monitored compounds (Chan, 2002; Hsieh *et al.*, 2003).

The four peak average daily values seen from the end of March to the beginning of May are due to meteorological episodes of stable air yielding night-time atmospheric inversions and low day-time wind speeds. The corresponding lack of atmospheric dispersion and dilution associated with these conditions, elevates the ambient hydrocarbon concentrations of all compounds being monitored (Barletta *et al.*, 2002).

This is a clear indication of the strong effect certain meteorological conditions can have on monitored concentrations. Wind speed is also a good indicator as to the level of atmospheric mixing and atmospheric dilution (Skov *et al.*, 2001). The scatter plot in Figure 5.13 of measured acetylene concentration versus wind speed illustrates the effect of low wind speeds on monitored values.

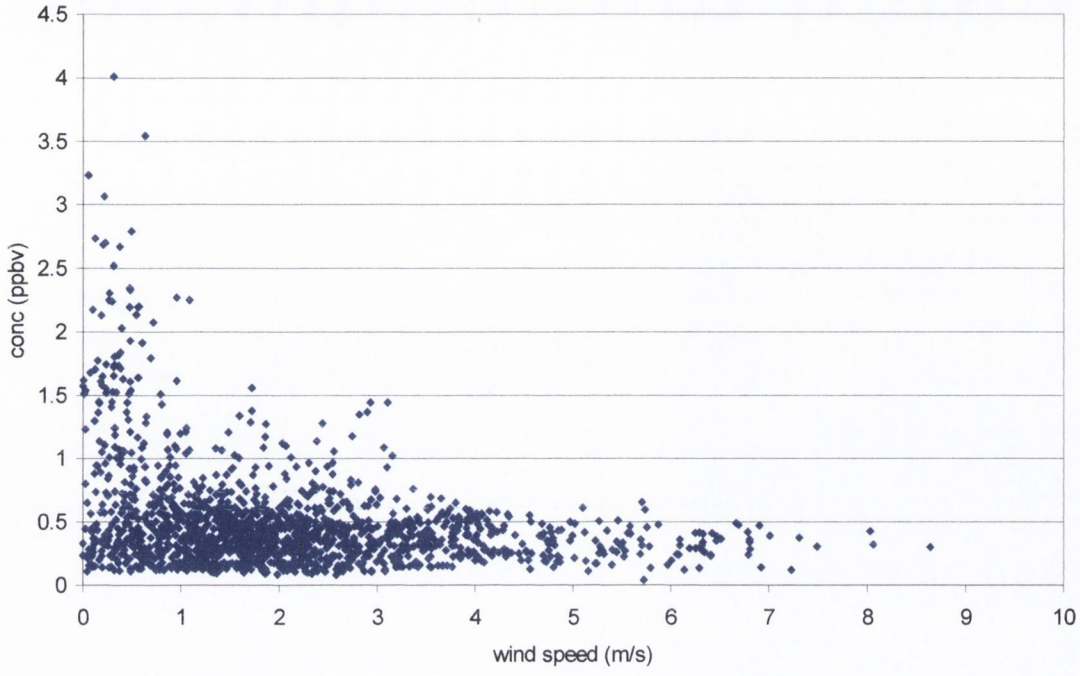


Figure 5.13 Scatter plot of wind speed versus acetylene concentration

The vast majority of acetylene concentrations above 1.5 ppbv are seen to occur at wind speeds below 1 m/s. At no time was an acetylene concentration of 1.5 ppbv exceeded when the local wind speed was greater than 2 m/s.

This illustrates how the majority of low acetylene concentrations are associated with higher wind speeds, which in turn relates to more turbulent atmospheric conditions. Other measured compounds displayed similar concentration / wind speed relationships.

Diurnal trends

In a preliminary attempt to correlate HC concentrations with traffic flow on the M4, the average hourly concentrations throughout the day were plotted for all compounds. The aim was to eliminate compounds which showed little or no correlation to the diurnal traffic flow profile shown in Figure 5.14. None of the alkanes monitored displayed a strong diurnal profile. Very slight morning peaks could be observed for n-butane, iso-butane and iso-pentane between 07:00 and 10:00, correlating with peak time morning traffic. Figure 5.14, shows two

plots for iso-pentane and iso-butane, which are representative of all three compounds. The remaining alkanes, ethane and propane did not show any signs of a morning traffic related peak.

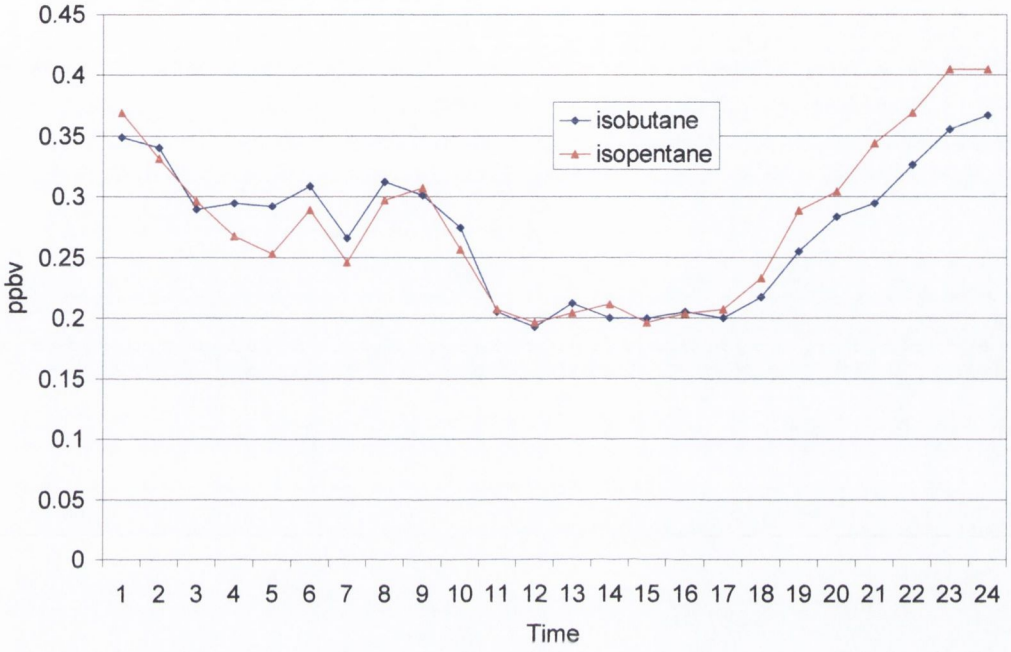


Figure 5.14 Average 24 hr concentrations for iso-butane and iso-pentane

For the alkenes, Figure 5.15 shows four compounds which exhibit a diurnal trend to a greater or lesser degree. Morning peaks are observable between 07:00 to 10:00 and the evening rise in concentrations begins at 16:00, correlating well with morning and evening traffic flow.

Figure 5.15 shows relatively little deviation over 24 hours for the compound 1,3 butadiene. This is a compound expected to be strongly related to road traffic emissions (Dollard *et al.*, 2001). However, if an alternate significant local source exists, this could have the effect of masking road traffic emissions. This is explored further in section 5.8, where the 1,3 butadiene / propene ratio is examined, to investigate the extent of 1,3 butadiene road traffic emissions.

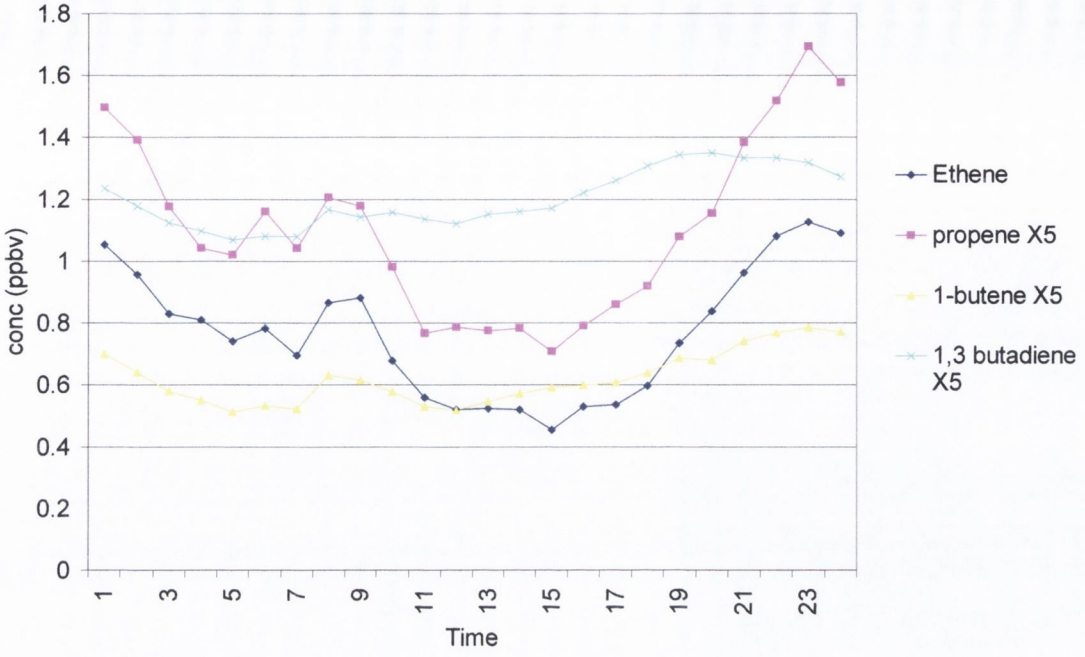


Figure 5.15 Four alkenes exhibiting diurnal profiles

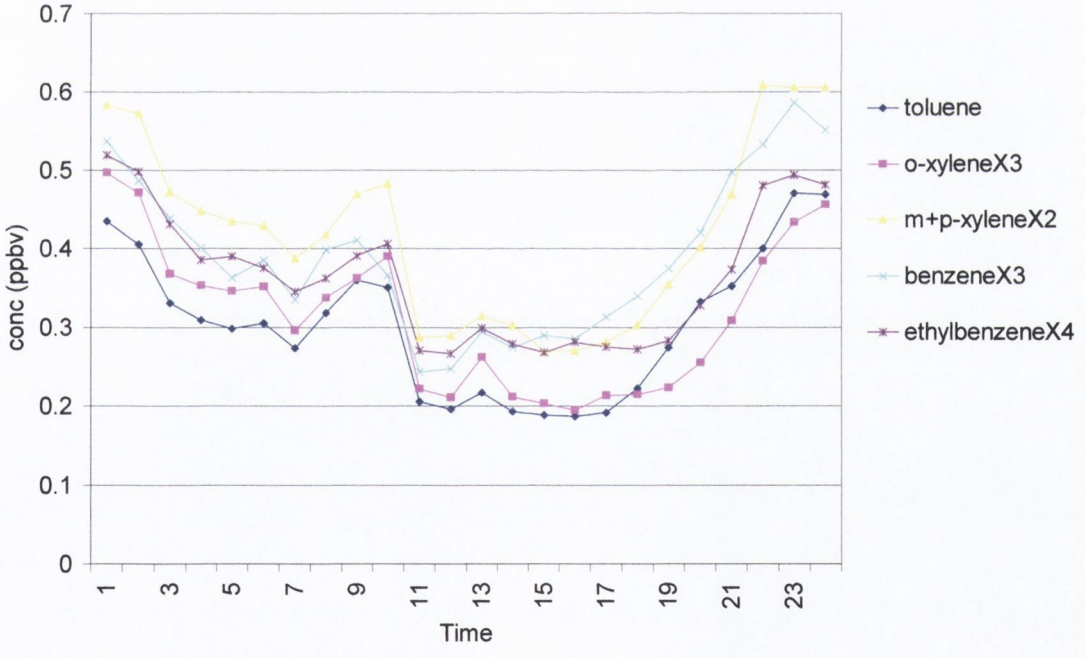


Figure 5.16 Aromatics exhibiting diurnal profile

This more curved 1,3 butadiene profile suggests gradual and slight increases and decreases, a trend more likely to be seen when monitoring background concentrations with relatively little local source contributions relative to the background value. Similar to ethane and propane, the four remaining alkenes (the butenes and pentenes), display no discernible diurnal trend.

For acetylene and all the aromatics monitored (Figure 5.16), clear morning peaks between 07:00 and 10:00 are observed, in conjunction with a rise in evening concentrations starting at 16:00. The trends seen are very similar to those shown above for ethene, a compound as previously mentioned, synonymous with road traffic emissions.

For all compounds regardless of whether they exhibit a diurnal profile or not, average night-time concentrations were higher than those obtained during daylight hours. From 22:00 to 06:00 there is relatively little traffic activity on the M4, yet the average hydrocarbon concentrations are highest for this period. It stands to reason that local traffic emissions are not the cause of these higher values, and as the phenomena affects all compounds, it is more likely to be a meteorological effect.

Local atmospheric inversions occur mainly at night where stable cold air gets trapped beneath a layer of warmer air, limiting atmospheric dilution. This process is most likely the cause of the elevated night-time concentrations observed. This process also has the effect of obscuring the evening peak concentration directly related to traffic flow.

To investigate the prevalence of such stable atmospheric conditions and to ascertain the extent to which they are a night time phenomenon, we plotted the % occurrence of stable conditions (stability class E-G) over the course of 24 hours. For the entire 8 month monitoring period no stable atmospheric conditions were observed between the main traffic active hours of 07:00 and 17:00. Figure 5.17, shows how such meteorological conditions are in the main a night time occurrence with a limited effect on expected peak time traffic emissions. The highest percent of occurrence for such stable conditions was observed between 01:00 and 02:00.

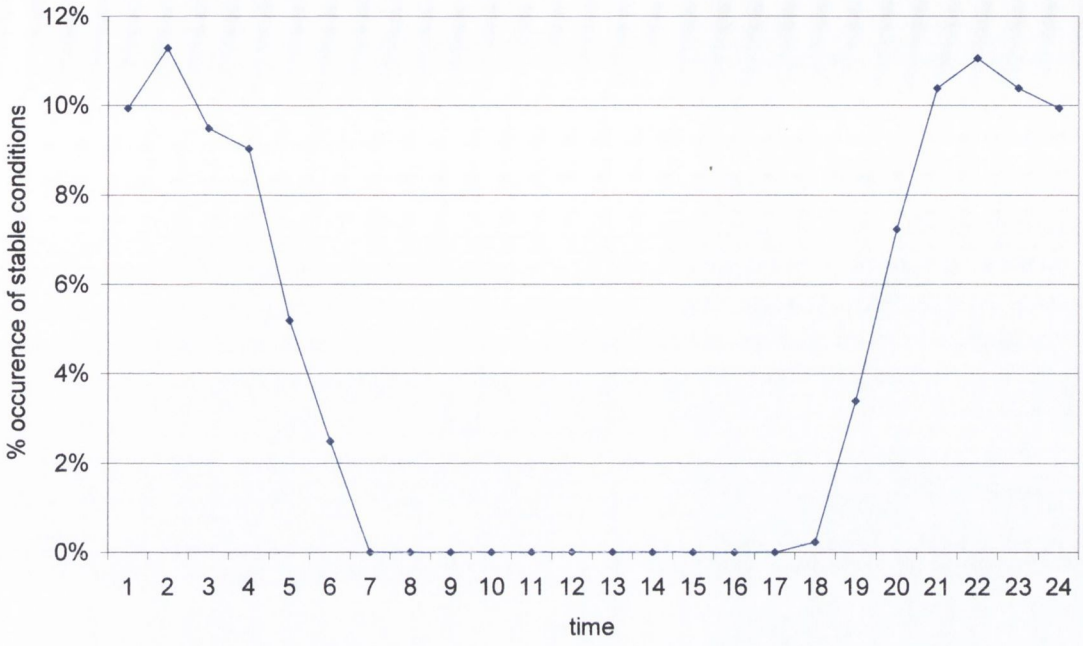


Figure 5.17 Percentage occurrence of stable atmospheric conditions

Wind roses

In conjunction with investigating the diurnal trends of the hydrocarbons monitored, the wind directions associated with the highest average concentrations were also investigated by examining the average hydrocarbon concentrations obtained for each 15° wind sector. As discussed earlier, data associated with a regional or local wind direction 0-80° were omitted from this analysis. In an attempt to remove any interference from the nearby building on the concentrations obtained, we expanded the range of directions omitted to include wind directions in the range 345-105°.

Referring to Figure 5.7, the pollution rose for the frequency of stable air with wind direction, the range 105-135° experienced the highest frequency of occurrence of stability classes E-G. Hence it could be anticipated that these wind directions would yield the highest average hydrocarbon concentrations. This is, in fact, the same for all compounds which showed a diurnal profile in the previous section. An example concentration rose plot cis-2-butene is shown in Figure 5.18 and is representative of those compounds which did not show a diurnal trend.

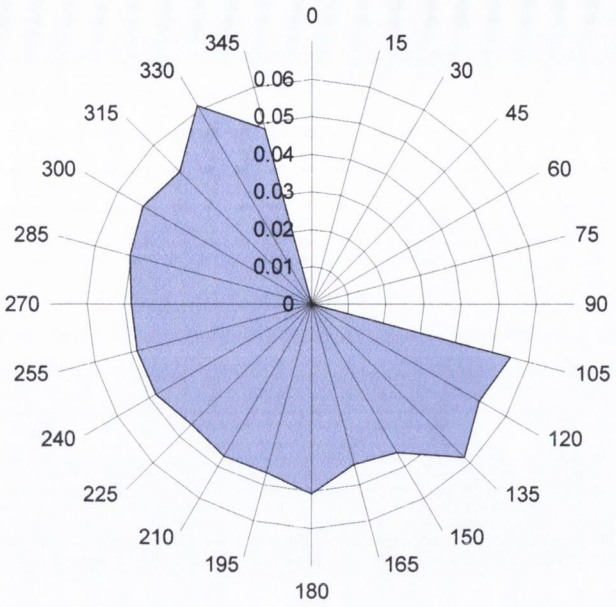


Figure 5.18 Rose plot for cis-2-butene

This plot is relatively uniform, suggesting a minor contribution to concentrations from any readily identifiable local source. The previous observation that the 1,3 Butadiene concentration levels obtained were related to background levels, with very little M4 source contributions, is substantiated by the pollution rose obtained for that compound as its shape and profile was identical to that of cis-2-butene (Figure. 5.18).

Concentration rose plots of the three alkenes which displayed diurnal trends are shown in Figure 5.19. This appears to illustrate the effect of stable air (E-G) on average measured concentrations. The highest average concentrations are seen to emanate from the wind directions most frequently associated with stable air.

However, another possible explanation is the higher concentrations associated with wind directions 105-135° are due to a source effect from the M4 when wind directions are parallel to the road, the optimum wind direction for obtaining the highest hydrocarbon concentrations. In all probability, a combination of both factors is most likely.

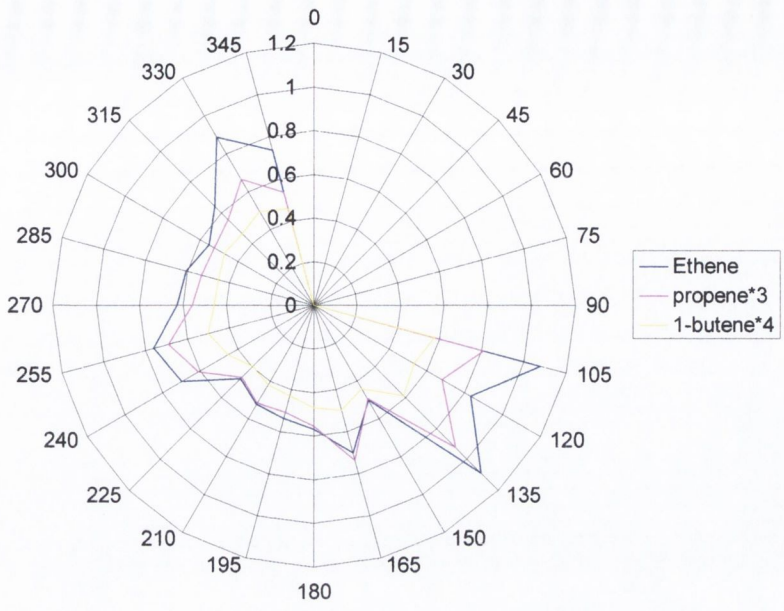


Figure 5.19 Rose plot of three alkenes which showed a diurnal trend

5.5.2 Filtered data.

In an attempt to examine in more detail the local source effect due to the M4, a form of filter was applied to all data obtained. This addressed hourly data in which either stable atmospheric conditions or slow wind speeds pertained. Stability classes E to G, occurred in the main, during night-time hours between 19:00 and 05:00, a time of minimal traffic activity.

By removing this data, occurrences of high HC concentrations not directly related to traffic activity were removed. Other hours with wind speeds less than 1 m/s, were also removed as wind directions associated with slow moving air are uncertain (Mollmann-Coers *et al.*, 2002).

Diurnal trends

After applying this data filter, the diurnal profiles for all HC compounds were examined, in the expectation that more obvious trends would be observed. The results indeed verify the observations made using 24 hour plots with non-filtered data (section 5.5.1).

The graphs for ethane and propane are representative of all alkanes (Figure 5.20). Although slight peaks occur around 09:00-10:00 and 17:00, the diurnal trend is very weak. These slight morning and evening peaks do suggest however a slight influence on ambient levels from local traffic activity.

The morning peak is seen to be the largest peak of the day, but its relative increase over other hours is minimal. With data pertaining to stable atmospheric conditions removed, the concentrations of both compounds can be seen to deviate very little over the 24 hour period, suggesting minimal local source effects.

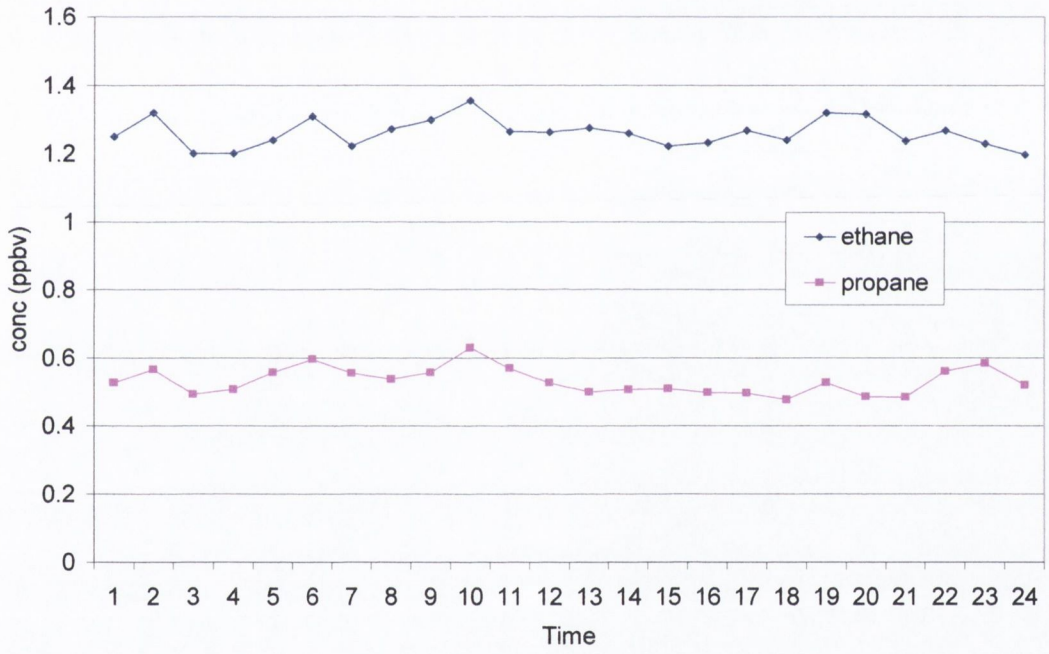


Figure 5.20 24 hour diurnal plots with filtered data for ethane and propane

The alkenes which showed only a weak diurnal trend with non-filtered data, showed a slightly stronger profile with filtered data. Two alkenes representative of those which showed only a slight diurnal profile are compared in Figure 5.21.

A very slight morning peak can be seen for both compounds but a strong evening peak is observed. This extends from 16:00 to 22:00 and correlates well with evening traffic flow.

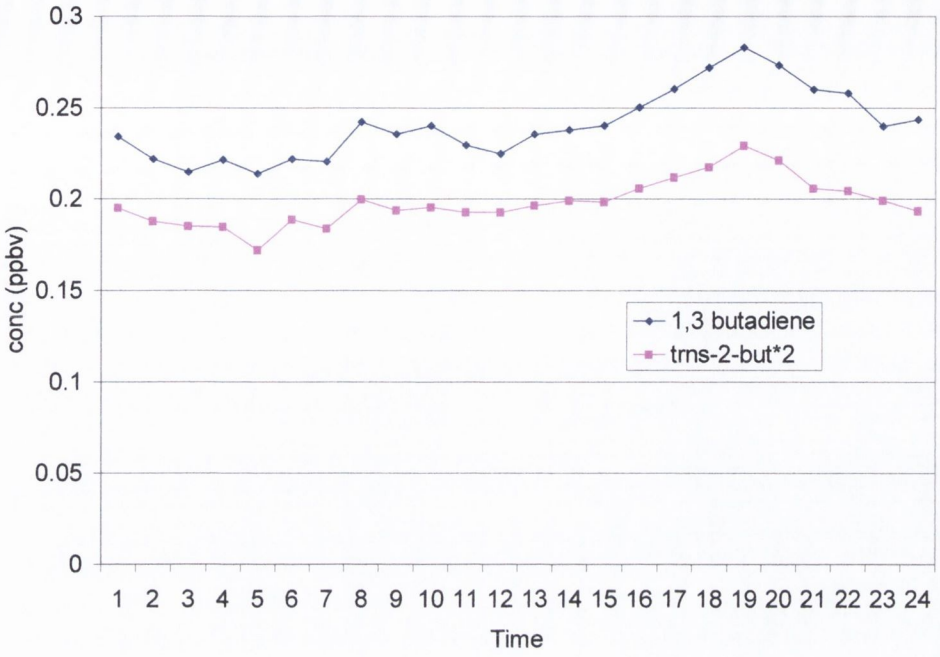


Figure 5.21 24 hour diurnal plots with filtered data for 1,3 Butadiene and trans-2-Butene (multiplied by a factor of 2)

The remaining alkenes, the aromatics and acetylene showed similar and stronger diurnal profiles with filtered data (Figures 5.22 and 5.23). Morning peaks are clearly evident between 07:00 and 10:00, as are evening peaks extending from 16:00 to 22:00. This extended evening peak reaches a maximum at approximately 19:00, all of which correlates very well with traffic flow on the M4.

The range of values observed over the course of the 24 hour period is, as expected, much greater for these compounds than for those with a relatively weak diurnal trend. The ratio of the lowest early morning concentration to the peak traffic morning concentration for 1,3 butadiene is only 1.1, however the same ratios for ethene and toluene are 2.0 and 2.2 respectively.

This again suggests that a local source affects the concentrations of some compounds to a much greater extent than others.

Figure 5.22 24 hour diurnal plot for ethene and propene (multiplied by 4)

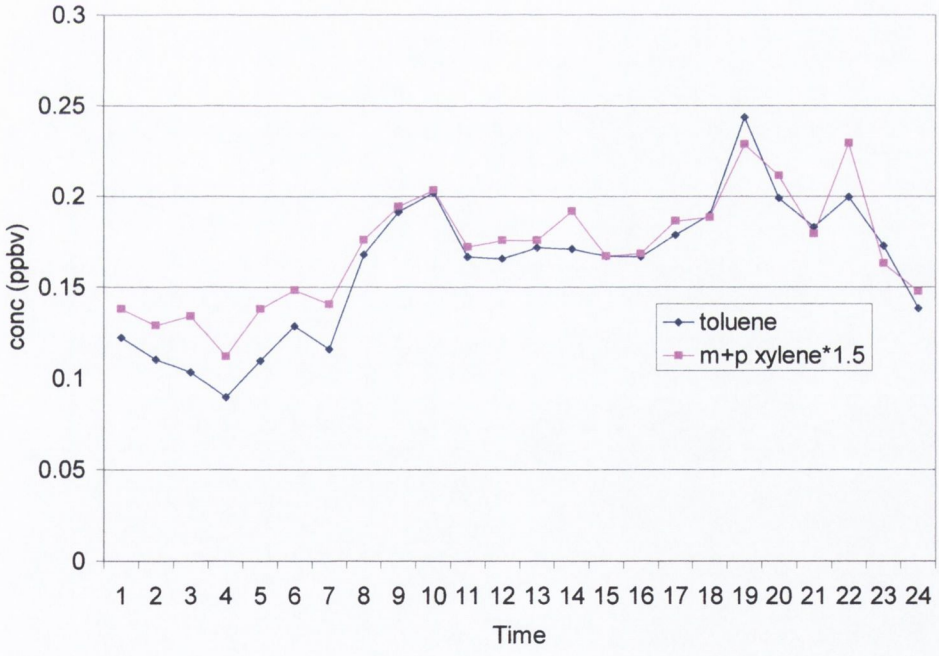


Figure 5.23 24 hour diurnal plot for toluene and m+p xylene multiplied by 1.5

Pollution roses

The filtered data, described above was used to plot pollution roses of the average HC concentrations obtained for each 15° wind direction sector.

Although all alkanes showed similar diurnal profiles for filtered data, the same cannot be said for their corresponding pollution roses. Ethane and, to a lesser extent, propane displayed similar plots to their non-filtered data pollution roses represented in Figure 5.18. Uniform concentration distributions are again obtained, showing a limited traffic related source effect.

Propane showed a slight source effect from wind direction 105° but this is very small compared to those observed in the profiles for the butanes and iso-pentane shown in Figure 5.24. This seems to suggest that there is a greater source effect for n-butane, iso-butane, iso-pentane and, to a lesser extent, propane from the easterly wind direction parallel to the M4.

This seemingly obvious source effect can not be due to slow moving, stable air, emanating from this direction (Figure 5.7), as all data associated with such conditions have been filtered from analysis. The most likely cause is road traffic emissions from the M4 relating to these wind directions. A second possible source is emissions emanating from Lucan village and surrounding roads, some 2 miles east of the receptor location.

The five alkenes which showed uniform pollution roses for non-filtered data (1,3 butadiene, cis-2-butene, trans-2-butene, cis-2-pentene, trans-2-pentene), display similar profiles with filtered data, as shown for 1,3 butadiene and trans-2-butene in Figure 5.25.

Slight source affects are apparent at 120° and 330°. The source effect related to wind direction 330° is probably Leixlip village, approximately 0.8Km distant in this general direction. The 120° peak is more than likely related to road traffic emissions from the M4.

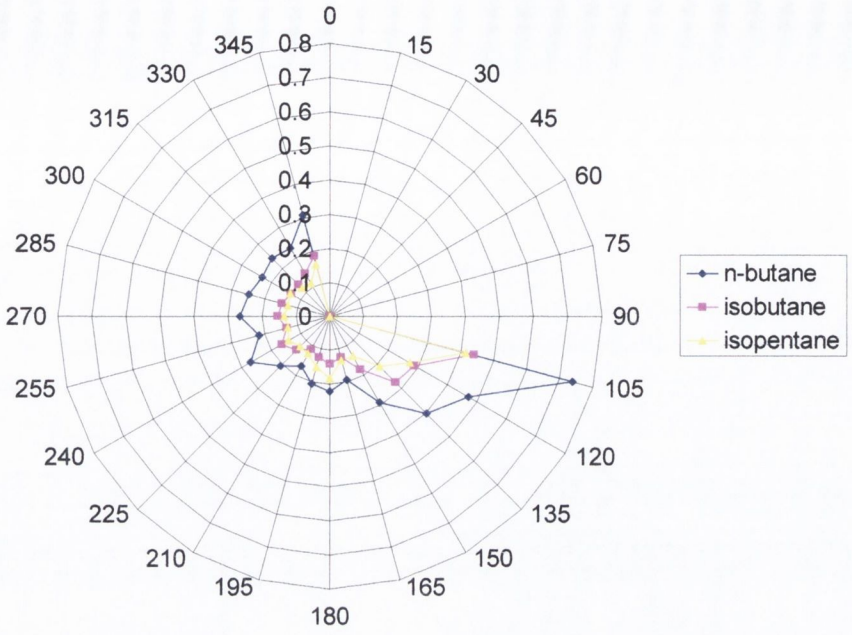


Figure 5.24 Pollution rose using filtered data for iso-butane, n-butane and iso-pentane

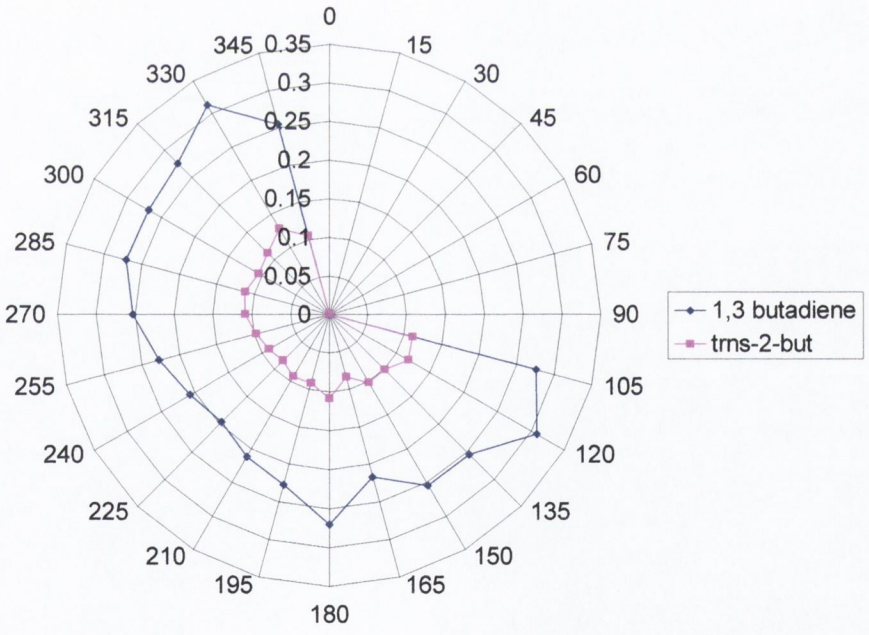


Figure 5.25 Pollution rose using filtered data for 1,3 butadiene and trans-2-butene

All remaining compounds (the aromatics, acetylene, ethene, propene, 1-butene), which showed strong diurnal trends with both non-filtered and filtered data display their highest average concentrations with wind directions between 105° and 135°. The three alkenes which showed this trend are illustrated in Figure 5.26 and the aromatics in Figure 5.27.

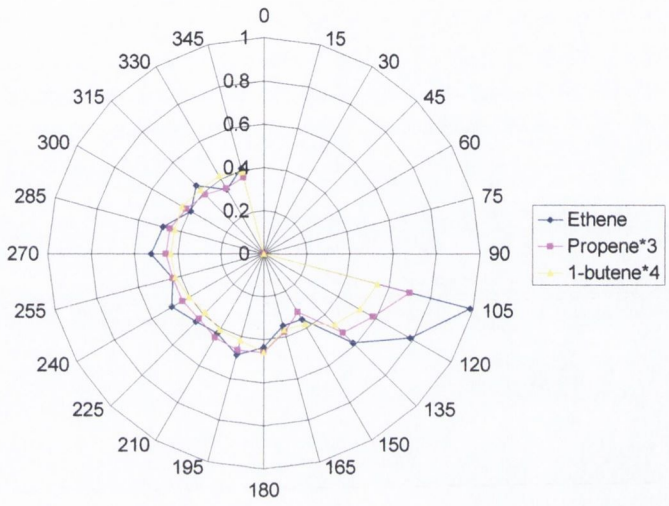


Figure 5.26 Pollution rose using filtered data for ethene, propene (X3) and 1-butene (X4)

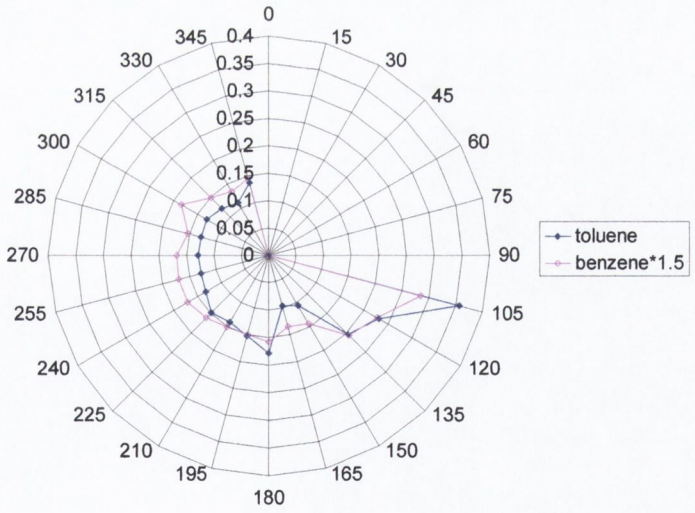


Figure 5.27 Pollution rose using filtered data for toluene and benzene (multiplied by 1.5)

As the meteorological effects which tend to elevate ambient hydrocarbon concentrations have been removed, the higher concentrations being observed from wind directions 105-135° are due to specific source effects, most likely traffic related. A similar source effect might have been expected from the near parallel wind direction 285°, however, the influence of the river Liffey passing under the M4 and the resultant local wind turbulence could impact on the dispersal of vehicular emissions associated with this wind direction, resulting in a less well defined source effect. Figure 5.28 compares the average traffic flow on the M4 junction for different wind direction sections. Surprisingly, significant variation is displayed. The wind direction of 105° has by far the highest associated average total traffic flow on the M4.While nearly all other wind directions have average traffic flows of between 1000 and 1560 vph, the wind of direction 105° is seen to have an average flow of 2413 vph. This evidence allied with the high average concentrations seen for wind direction 105° (for those compounds exhibiting a strong diurnal profile), suggests a major source effect from the M4 for most compounds monitored when the wind direction is parallel or near parallel in an easterly direction.

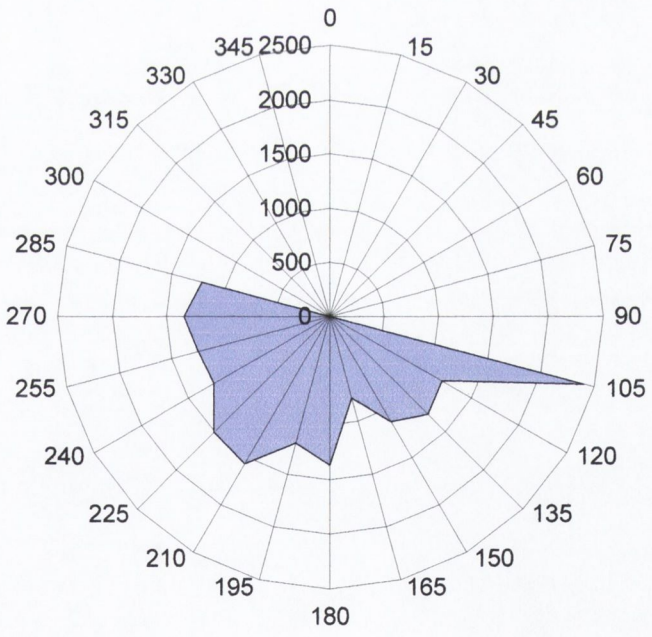


Figure 5.28 Traffic flow rose (average total vehicles per hour) for each 15°wind sector

Table 5.4 examines further the extent to which traffic flow and associated wind direction affect ethene concentrations seen in Figure 5.26. The ratio of ethene concentrations (multiplied by a factor of 1000) to traffic flow for both 15° and 45° sectors are outlined.

As expected, the highest ratios are seen at the near parallel wind directions in both easterly and westerly directions, outlining the effect the motorway orientation has on ethene concentrations, a known traffic marker.

Wind direction (°)	Vehicles per hour (vph)	Average vph per 45° sector	ethene conc. (ppbv) (Figure 3.22)	Avg ethene conc. per 45° sector (ppbv)	ethene to traffic flow ratio (ethene conc. X 1000) / vph	Avg ratio per 45° sector
105	2413	1625	0.99	0.78	0.41	0.51
120	1187		0.78		0.66	
135	1275		0.58		0.46	
150	1121	1087	0.35	0.38	0.31	0.36
165	775		0.35		0.45	
180	1364		0.43		0.32	
195	1205	1425	0.48	0.45	0.40	0.32
210	1565		0.43		0.27	
225	1505		0.44		0.30	
240	1227	1257	0.49	0.48	0.40	0.40
255	1251		0.44		0.35	
270	1336		0.52		0.39	
285	1215		0.48		0.40	

Table 5.4 Ratio of ethene concentrations to vehicle flow on the M4 for each 15° and 45° sector

Effect of wind speed with filtered data

Lower average wind speeds are an indication of reduced atmospheric dilution. Figure 5.29 plots the average wind speeds for each 15° sector, with all wind speeds of less than 1m/s omitted. The plot is very similar to that shown in Figure 5.4, in which all data was included. The lowest average wind speeds again occur at wind direction 105°. Clearly, this lower average wind speed also contributed to the elevated average concentrations measured when the wind emanated from this direction. Hence, a combination of traffic flow, wind speed and motorway orientation (wind directions of 105° to 135° are near-parallel to the M4) all contribute to a stronger source effect from 105-135°.

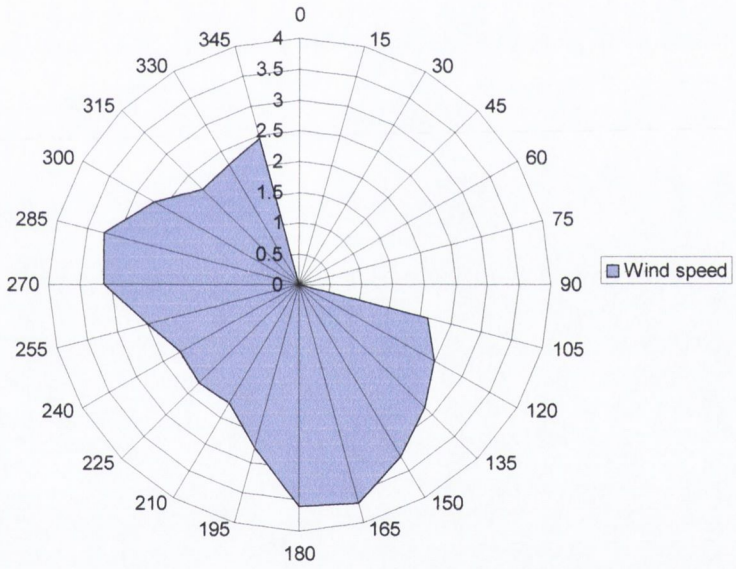


Figure 5.29 Average wind speed rose for filtered data

5.6 SECTORAL ANALYSIS

From the analysis carried out thus far it is evident that local source effects can be segregated into two separate wind direction sectors. These are the 105-285°sector, where an M4 source effect is very evident, especially easterly winds near-parallel to the M4, and the 285-345° sector where no M4 source effect should be evident and the influence of Leixlip village on concentrations obtained at the receptor can be examined.

Continuing the theme of omitting HC concentrations associated with low wind speeds (<1m/s) and stable air (stability class E-G), we analysed the data for both sectors separately. Diurnal plots were examined for both sectors, as discussed below.

5.6.1 Wind direction sector 105-285°

Figure 5.30 shows the diurnal trend in the filtered ethane and propane concentration data associated with wind directions between 105° and 285°.

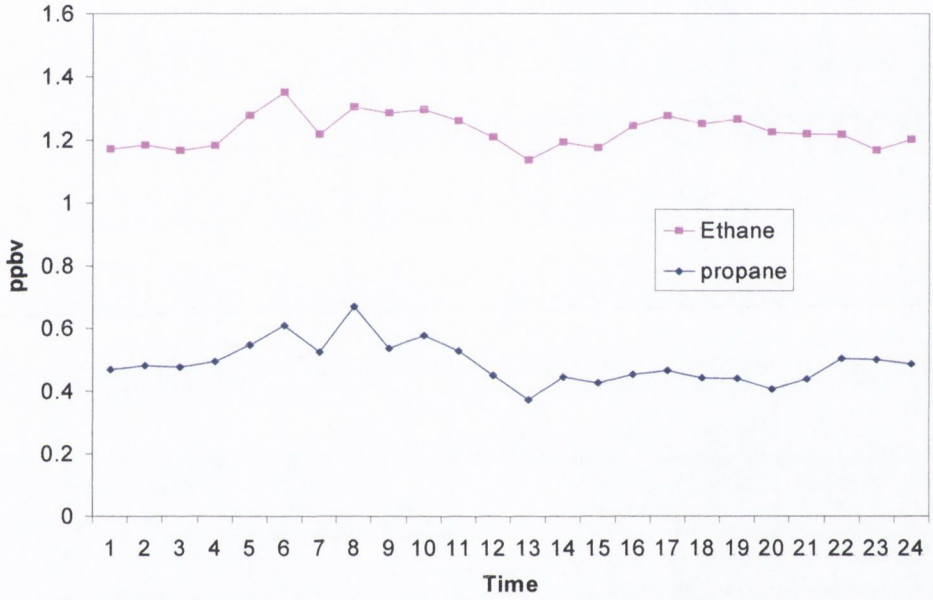


Figure 5.30 Diurnal trend for ethane and propane using filtered data for wind direction sector 105-285°

Both compounds behave in a similar way, but propane shows a 24 hour peak at 08:00 possibly relating to traffic flow on the M4. This explains the stronger source effect seen for propane (relative to ethane), discussed in the previous section on pollution roses for filtered data (section 5.5.2). No traffic related peaks are observed for ethane, with its 24 hour peak seen between 04:00 and 07:00, not correlating well with average hourly traffic activity (Figure 5.11).

In section 5.5.2, which analysed filtered data for all wind directions, it was noted that iso-butane, n-butane and iso-pentane showed a strong source effect from 105° but a weak overall

diurnal trend. The diurnal plot for filtered iso-butane concentrations for this wind direction sector is show in Figure 5.31 and is representative of all three compounds.

The evening peak seen at 17:00 does not coincide with the peak evening traffic flow which is seen to occur at around 19:00, but the morning peak extending from 07:00 to 10:00 coincides very well with the peak morning flow.

This suggests that the morning peak observed due to traffic activity is responsible for the source effect seen at 105° in the previous section on pollution roses using filtered data. The above trend is only observable when filtered data is employed in sectoral analysis.

A weak diurnal profile was again displayed by the five alkenes which showed no source effect from wind direction 105° with filtered data (Figure 5.25). The shape of the diurnal profiles for 1,3 butadiene and trans-2-pentene shown in Figure 5.32 agree well with that of the average hourly traffic flow (Figure 5.11). However, the range of average hourly values over the 24 hour period is relatively small. From these data it may be assumed that the motorway source effect for these five alkenes (1,3 butadiene, the butenes and pentenes), is relatively small.

The remaining alkenes (ethene, propene and 1-butene), the aromatics and acetylene all behave in a similar manner yet again, as illustrated by the representative diurnal plot of toluene and acetylene shown in Figure 5.33.

Both compounds follow a similar trend with clearly defined morning and evening peaks associated with peak average traffic flow. The elongated evening peak observed is due to relatively high traffic flow up until 22:00 (average of 1500 total vehicles / hour) allied to a gradual shrinkage in the boundary layer throughout the evening, leading to less atmospheric dilution and hence a more extended evening peak from 16:00 to 23:00.

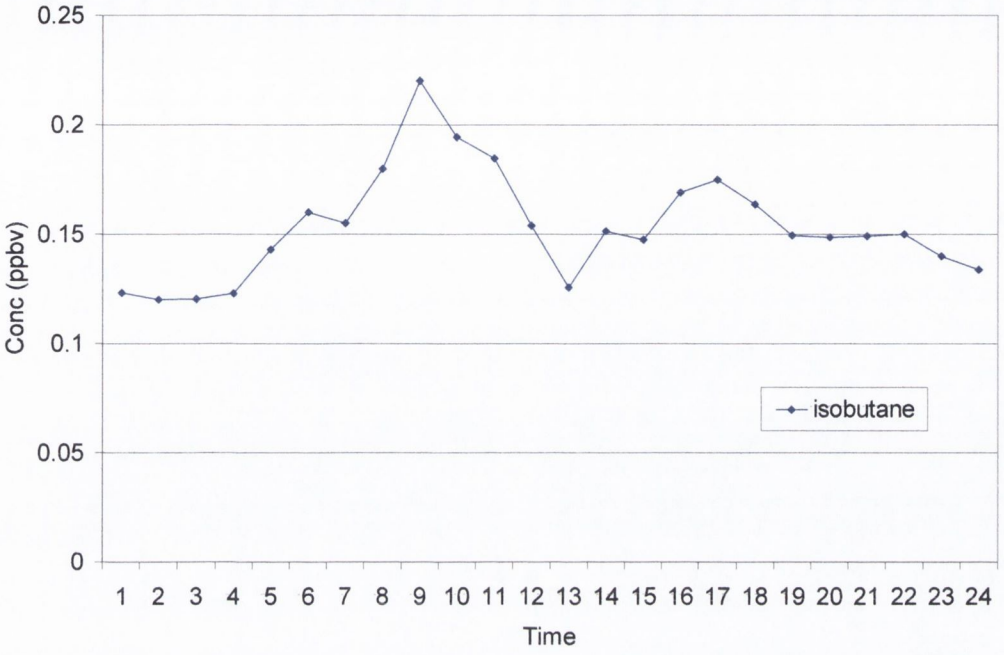


Figure 5.31 Diurnal profile for iso-butane using filtered data for wind directions between 105° and 285°

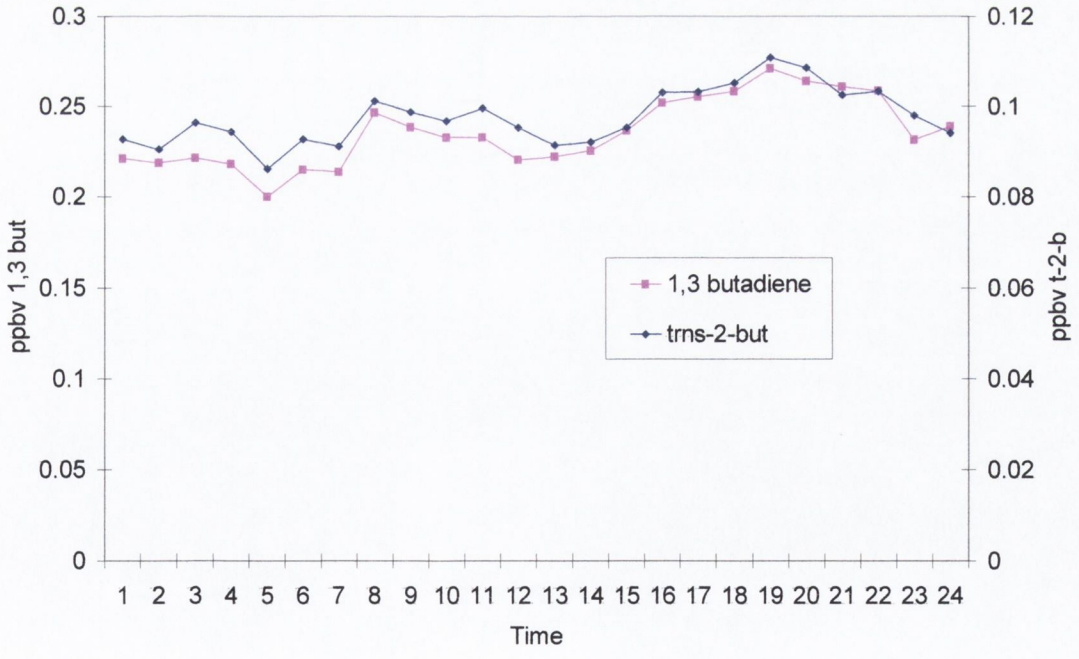


Figure 5.32 Diurnal profile for 1,3 butadiene and trans-2-butene using filtered data for wind directions between 105° and 285°

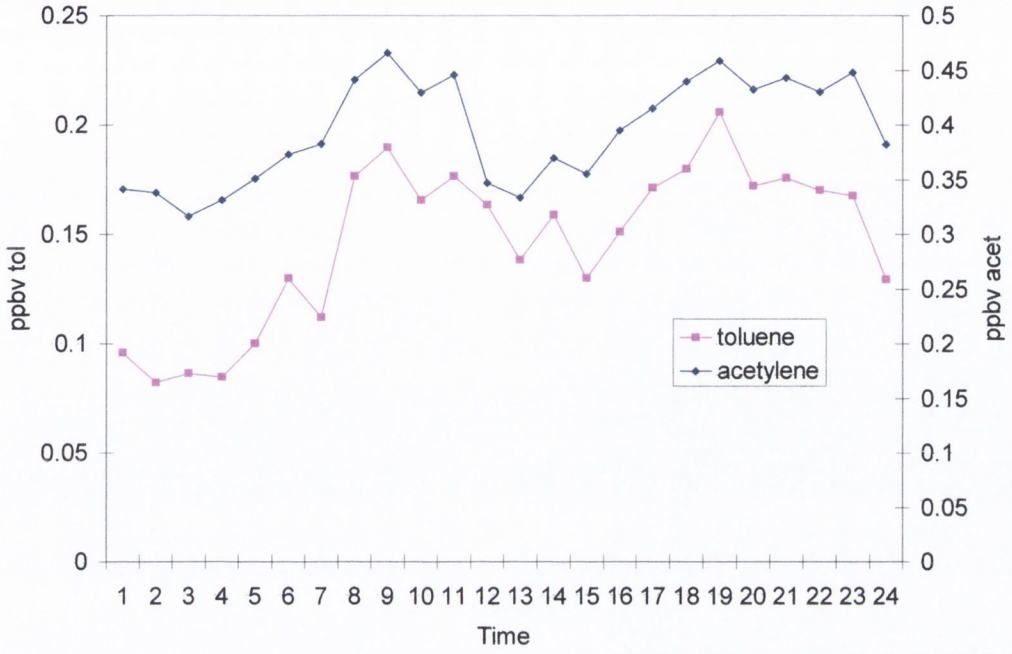


Figure 5.33 Diurnal trend for toluene and acetylene using filtered data for wind directions 105-285°

Table 5.5 attempts to quantify the morning and evening peak time M4 source effect. Using filtered data from wind directions between 105° and 285°, an approximate background concentration was estimated, by averaging the 00:00 to 04:00 concentrations for each hydrocarbon compound. These values were than subtracted from the morning peak concentrations obtained between 08:00 and 09:00 and evening peak concentrations between 18:00 and19:00, for the same data set.

The alkane concentrations are seen to deviate to the greatest extent between morning and evening peak times, the exception to this being iso-pentane for which the same background corrected concentrations were obtained for the morning and evening peak times. Similar concentrations were obtained during both peak times for the remaining three classifications of compounds.

We also calculated the relative contribution each individual HC made to its specific chemical classification of compound. This was then compared to results obtained in a Dublin City centre study by Broderick and Marnane (2002), where emissions were primarily traffic related.

In the Broderick and Marnane study, the hydrocarbon content for an "average" unleaded petrol fuel sample was also analysed in order to compare the proportion of ambient hydrocarbons to those found in petrol fuel.

The percent contributions of individual hydrocarbons to each specific chemical classification at the M4 and the city centre location are found to be very alike, this similar "fingerprint" of hydrocarbon percentages suggests that like the city centre study, the main source of these hydrocarbons is from vehicle emissions.

Similar to the 1998 study, poor agreement was seen between the alkane and alkene concentrations in air and those obtained in fuel. For alkanes, the ethane and propane sources are in the main natural gas, hence the disparity between fuel and ambient air content. For the alkenes, three compounds, ethene, propene and 1,3 butadiene have a neglible content in fuel but are present at relatively high concentrations in ambient samples as partial oxidation products (Leppard *et al.*, 1992).

The aromatic content in fuel and air are found to be generally in very good agreement. The decrease in the benzene contribution since 1998, is due to the change in benzene content in fuel from 2.9 %v/v in the "average" fuel sample in 1998 to <1% v/v in 2002. The content of benzene in the air, both in 1998 and at the M4 in 2002 is higher than its fuel percentage as benzene is also a partial oxidation product of other aromatic compounds (Hoekman, 1992; Leppard *et al.*, 1992).

From the various analyses carried out it can be concluded that the three alkanes (iso-butane, n-butane and iso-pentane), three alkenes (ethene, propene and 1-butene), acetylene and all the aromatics showed moderate to strong source effects from the M4 motorway relative to our receptor position but the contribution to ambient levels from the M4 was observed to be minimal.

These compounds relate very well to the initial hypothesis that those compounds with a large difference between mean and median concentrations may show a greater local emissions source effect. This was shown to be the case and the main local source responsible was seen to be the M4 motorway.

HC	Bkg conc (ppbv)	08:00 to 09:00 conc – bkg (ppbv)	18:00 to 19:00 conc – bkg (ppbv)	% HC per classification of compound in ambient air (bkg corrected)		% HC per class. in 1998 fuel	% HC per class. in 1998 ambient air
				08:00 – 09:00	18:00-19:00		
Alkanes							
Ethane	1.17	0.11	0.05	24%	26%	0%	29%
Propane	0.48	0.06	-0.07	12%	n/a	<1.0%	14%
n-butane	0.19	0.11	0.04	23%	20%	24%	27%
i-butane	0.12	0.10	0.03	21%	14%	7%	11%
i-pentane	0.09	0.09	0.08	20%	40%	69%	19%
Alkenes							
Ethene	0.33	0.36	0.26	75%	61%	<1.0%	68%
Propene	0.11	0.07	0.07	14%	17%	2%	20%
1-butene	0.09	0.02	0.03	4%	6%	23%	n/a
1,3 but	0.22	0.02	0.04	4%	10%	<1.0%	5%
t-2-but	0.09	0.01	0.02	1%	4%	40%	3%
c-2-but	0.04	0.01	0.01	2%	2%	35%	3%
Aromatics							
Toluene	0.09	0.10	0.08	44%	43%	46%	45%
o-xylene	0.04	0.03	0.02	13%	10%	9%	7%
m+p xyl	0.07	0.05	0.06	24%	28%	26%	20%
benzene	0.10	0.02	0.02	10%	11%	11%	22%
Ethylb	0.04	0.02	0.01	9%	7%	7%	6%
Alkyne							
Acet	0.33	0.13	0.10	n/a	n/a	<1.0%	n/a

Table 5.5 Morning and evening peak time average M4 concentrations and percent individual HC per chemical classification

5.6.2 Wind direction sector 285-345°

For the purpose of comparison with the M4 source effect, diurnal trends relating to wind directions 285-345° are also analysed. These wind directions do not come from the M4 but are associated with Leixlip village, 0.8km away.

For this wind direction sector, all compounds were seen to exhibit similar diurnal trends. This point is illustrated using two compounds already shown to behave differently with respect to road traffic emissions: propane has been seen to display very little correlation with road traffic emissions, unlike acetylene which is a known traffic emission marker.

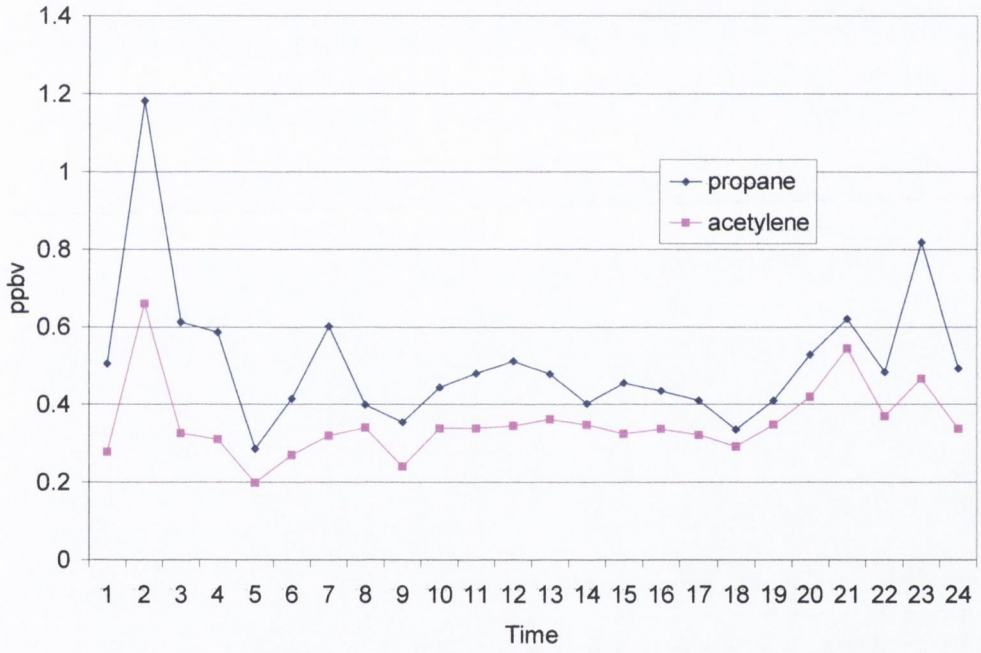


Figure 5.34 Diurnal trend for acetylene and propane using filtered data for wind directions 285-345°

Figure 5.34 shows that both compounds behave in a very similar manner over the course of the average day. The largest peaks seen do not correlate well with the times of heavy traffic activity. Some of the morning peaks displayed could relate to traffic activity in Leixlip village, but if that was the case, the acetylene peaks would be expected to be relatively larger than those for propane.

To examine the main cause of fluctuating average hourly concentrations for this wind direction sector we decided to see how meteorological effects, specifically average hourly wind speed, effect the daily profile seen. For all analysis carried out thus far, the trend for average hourly wind speed has not been seen to deviate from that shown in Figure 5.35.

A smooth graph can be seen with gradual increases and decreases over the course of the day. This trend is due to the large amount of hourly data used to construct the profile shown. Any extreme hourly wind speeds average out over the course of the monitoring period due to the large sampling pool obtained.

The average hourly wind speed over 24 hours was seen to behave in a slightly different manner for wind direction sector 285-345°. The sample size was only 10% of that for the wind direction sector 105-285°, hence a less "rounded" profile is evident. For illustration purposes, average hourly acetylene concentrations are shown on the same graph (Figure 5.36).
It is readily apparent that peak concentrations obtained are due to differences in average hourly wind speeds, indirectly an indicator of atmospheric dilution. Whenever the average hourly wind speed is seen to drop below 2 m/s, we obtain a corresponding peak acetylene concentration. The concentrations are seen to be relatively constant for wind speeds greater than 2 m/s.

As this behaviour is seen to effect compounds which are known markers for road traffic emissions (ethene, acetylene) and those not exclusive to road traffic activity (propane), we can see that atmospheric processes are the main variables in governing the hydrocarbon concentrations obtained at the receptor from wind directions 285-345°. As local source effects are seen to be negligible, we can say with a degree of fair certainty that we have monitored background hydrocarbon concentrations from these wind directions relative to the M4.

This also serves to highlight the potentially dominant effect meteorology can have in ambient hydrocarbon readings at such a rural / sub-urban environment. It also outlines the difficulty in ascertaining trends in ambient hydrocarbon concentrations without concurrent meteorological data.

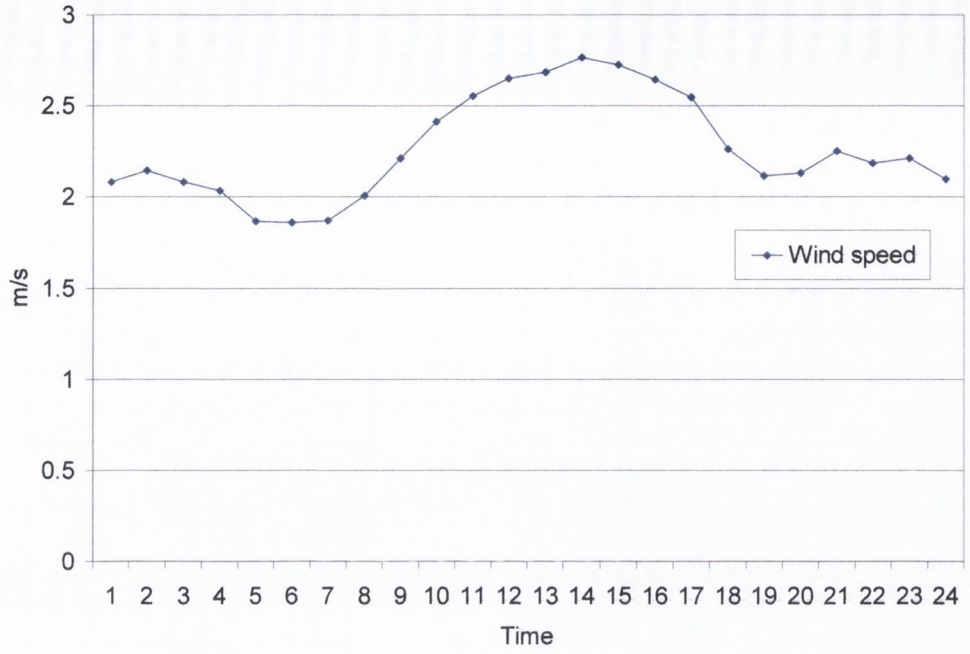


Figure 5.35 Average hourly wind speed for entire monitoring period

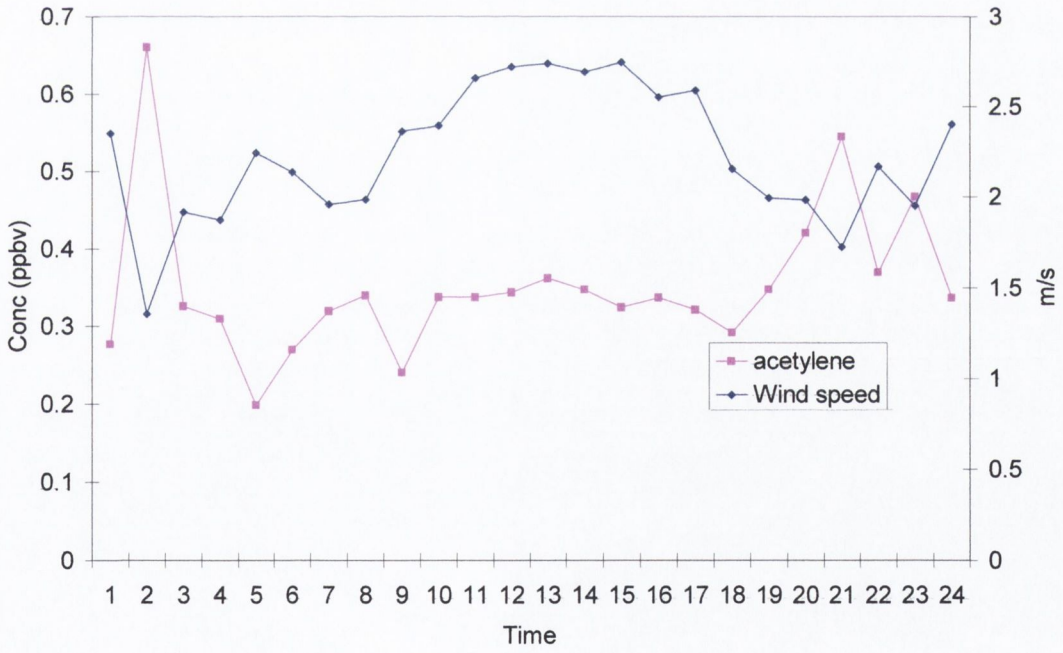


Figure 5.36 Average hourly wind speed for wind directions between 285-345° using filtered data

5.7 SOURCE AFFECT ANALYSIS USING HYDROCARBON RATIOS

5.7.1 (propene / 1,3 butadiene) ratio

The main source of 1,3 butadiene concentrations observed at the receptor was anticipated to be from the M4, as it is emitted primarily from vehicle exhaust. It can however, have significant emissions associated with its manufacture and use in industry (Dollard *et al.*, 2001). Other possible sources in the area are from off-road transport, and civil aviation sources associated with the nearby Weston and Casement Aerodromes. As the overall emissions from these sources are generally small, it is most likely that any significant emissions (other than from the M4), emanate from industrial sources.

The pollution roses observed for 1,3 butadiene and trans-2-butene are uniform in nature (Figure 5.25), and the diurnal trends observed for both show only a slight diurnal trend with filtered data from wind directions between 105° and 285° (Figure 5.32).

Ye *et al.* (1997), examined the ratio of 1,3 butadiene to propene in exhaust and roadside samples and found that where road traffic is the primary source for both compounds, a ratio of between 0.2 and 0.3 was found. Similar ratios were obtained from Dublin city centre studies in 1998 (0.24 from Marnane, 2000) and 2003 (0.27 from Chapter 7) where road traffic is the primary source for both compounds (Table 5.6). For this study, comparing similar sets of data, using ambient concentrations where no filter was applied (data from Table 5.1), a much larger ratio of 1.1 was found suggesting a significant alternate source other than the M4 for 1, 3 butadiene. As 1,3 butadiene and trans-2-butene are seen to correlate very well to each other and very poorly with all other compounds (Table 5.2), the same source is likely to emit trans-2-butene to a significant extent also.

To show the M4 source affect is being masked by this alternate, more uniform source for 1,3 butadiene, we calculated the ratio for background corrected 1,3 butadiene and propene for both morning and evening peak traffic times from wind directions between 105° and 285° (from Table 5.5). Ratios of 0.28 and 0.57 for morning and evening peaks were obtained respectively. The corrected morning peak ratio is as expected between 0.2 and 0.3. However,

the evening ratio is significantly greater, suggesting the alternate emissions increase throughout the day. This is supported by the increased content (%) of both compounds seen in Table 5.5, from morning to evening peak times. The behaviour is atypical of the alkenes, which generally stayed constant over both peak traffic periods. The ratios obtained do however, confirm the masking affect the alternate source has on the 1,3 butadiene emissions form the M4, giving the uniform pollution roses seen in Figure 5.25.

Study site	Goteburg (Sweden)	London	Sydney	Dublin city centre 1998	Dublin city centre 2003 (chapter 7)	M4 with no filters applied	M4 08:00-09:00 (bkg corrected)	M4 18:00-19:00 (bkg corrected)
Sample type	Road. air	Road. air	Tunnel air	Road. air	Road. air	Road. air	Road. air	Road. air
Ratio	0.24	0.20	0.21	0.24	0.27	1.1	0.24	0.57

Table 5.6 Ratios of 1,3 butadiene to propene in roadside air and tunnel samples

5.7.2 m+p xylene / ethylbenzene ratio

Some hydrocarbons are commonly used as indicators to assess the relative age of an air mass and also as tracers for emissions sources (Hsieh *et al.*, 2003;Monod *et al.*, 2001; Nelson and Quigley, 1983; Tanaka, 1996, Lee *et al.*, 2002). The ratios of the ambient concentrations of target hydrocarbons are assumed to be relatively constant if they originate from the same source. However, the concentrations of the more reactive species should decrease with time over daylight hours due to photochemical activity.

Nelson and Quigley (1983) have shown that the ratio of the emissions rates of m+p xylene / ethylbenzene (x/e) is constant for their principal sources such as vehicle exhaust emissions and fuel evaporation. No other hydrocarbons being monitored have this trait.

As these compounds also have relatively different atmospheric lifetimes, approximately 12 hours for m+p-xylene, compared to 1.6 days for ethylbenzene (Monod *et al.*, 2001), variations in the x/e ratio are indicative of the time in which the pollutants have resided in the sampled air. The relatively "older" the pollution in the air mass, the relatively lower the x/e ratio.

To investigate the relative age of the hydrocarbons in air masses passing over the M4, Figure 5.37 shows the average x/e ratio for each 15° wind sector from 105-285°.

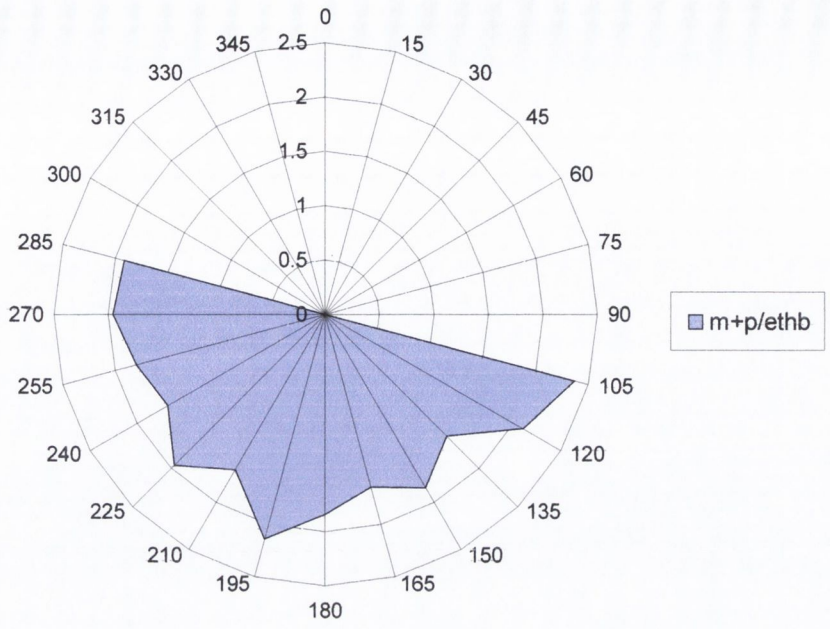


Figure 5.37 m+p xylene / ethylbenzene ratio for wind directions 105-285°

Although the distribution is fairly uniform, it is clear that, on average, the relatively youngest hydrocarbons were observed in those sampled air masses, which had emanated from the easterly wind direction of 105°, parallel to the M4. This indicates that these air masses had travelled the smallest distance between contamination and sampling points, suggesting a higher local source contribution from this wind direction than from any other.

It is also relevant to investigate how the x/e ratio deviated, if at all, over the course of the average day. Figure 5.38 shows the average diurnal profile of the x/e ratio, considering winds from the M4 motorway only.

A slight morning peak is observable, which relates well to peak morning traffic flow. This shows that the average age of the hydrocarbons in the sampled air at this time is younger than that sampled at any other time, indicating stronger local source contributions at this time. However, there is no similar evening peak, as might have been expected.

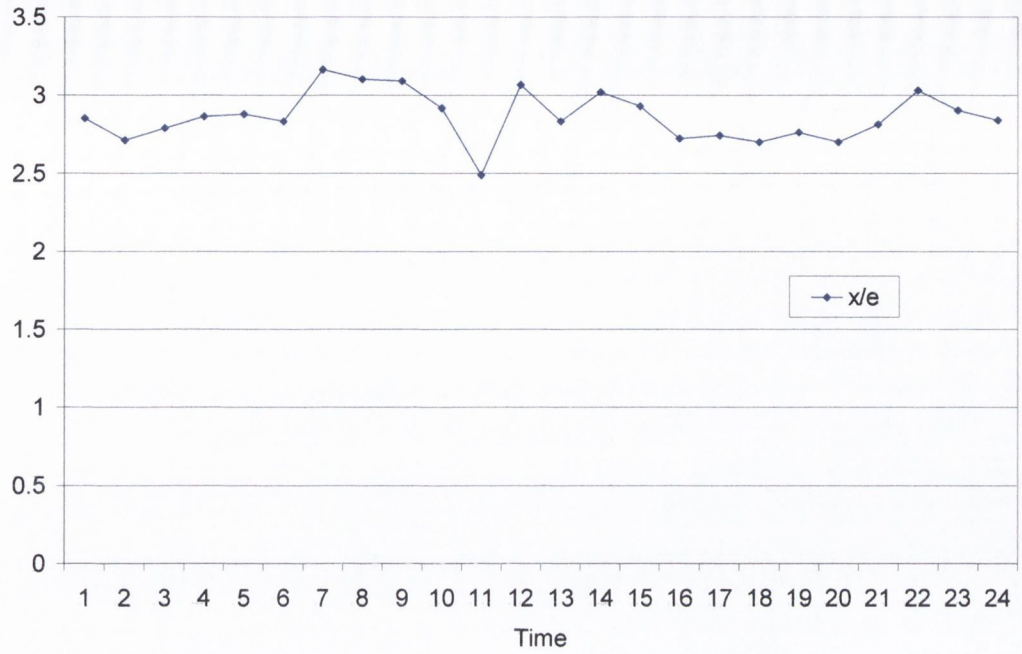


Figure 5.38 24 hour average m+p xylene / ethylbenzene ratio for wind directions 105-285°

As relatively clean air predominates at this site, local source contributions during periods of relatively high traffic activity will have a larger impact on observed x/e ratios than was observed at urban sites (Chapter 7).

5.7.3 Ethene / acetylene ratio

The ratio of ethene and acetylene concentration in exhaust gas is well known to be an indicator of the presence of a catalytic device: emissions from non-catalyst cars have a ratio close to 1 (Hockman, 1992), while catalyst equipped cars have a ratio of three or greater (Duffy and Nelson, 1996). Since the introduction of emission controls, emissions of ethene and acetylene have both decreased as a fraction of total NMHCs (Fujita *et al.*, 1994). However, the decrease is greater for acetylene because it is removed more efficiently by the catalyst (Sawyer *et al.*, 2000).

In the past, the overall values of the ratio has been determined, from which the impact of catalytic converters is deduced. In Figure 5.39, that approach is modified by calculating the diurnal profile of the ethene / acetylene ratio for wind directions relating to the M4 (105-285°).

This allows the influence of catalytic converters throughout the course of the average day to be observed.

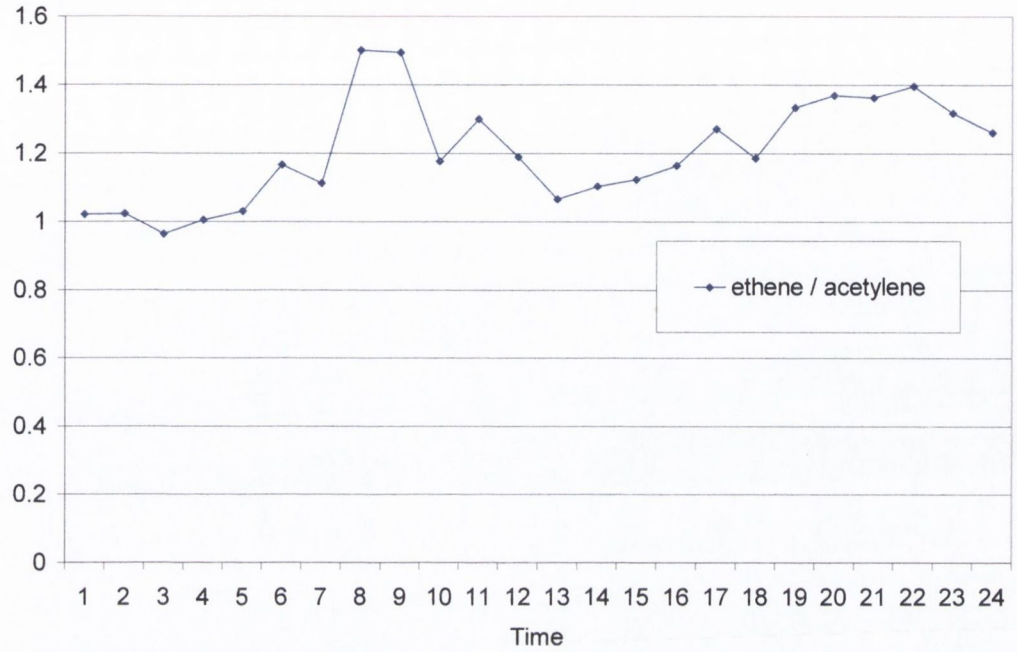


Figure 5.39 Average hourly ethene / acetylene for filtered data from 105-285°

The diurnal profile broadly follows that of the traffic flow on the motorway. The large peak seen between 07:00 and 10:00 relates very well to peak time morning traffic when a relatively high contribution from active catalytic converters could be expected. We can see from Figure 5.39 how this catalytic converter efficiency ratio can be used as an indicator of relative change in traffic activity over the course of an average 24 hour period, for an urban environment when the main local source (M4) is relatively nearby.

Figure 5.40 shows a rose diagram for catalytic converter influence as a function of wind direction. The average ethene / acetylene ratio is plotted for each 15° wind sector from 105-285° (M4 wind direction). The direction most closely related to active catalytic converters and indirectly traffic activity, again relates to easterly winds parallel to the M4. Currently, approximately 95% of petrol vehicles in the Irish traffic fleet use catalytic converter technology to reduce tail-pipe emissions (estimated from 2003 traffic fleet statistics in Chapter 6). It is therefore no surprise to see the wind direction sector previously confirmed as being

most closely related to traffic emissions from the M4, showing the strongest indication of active catalytic converters.

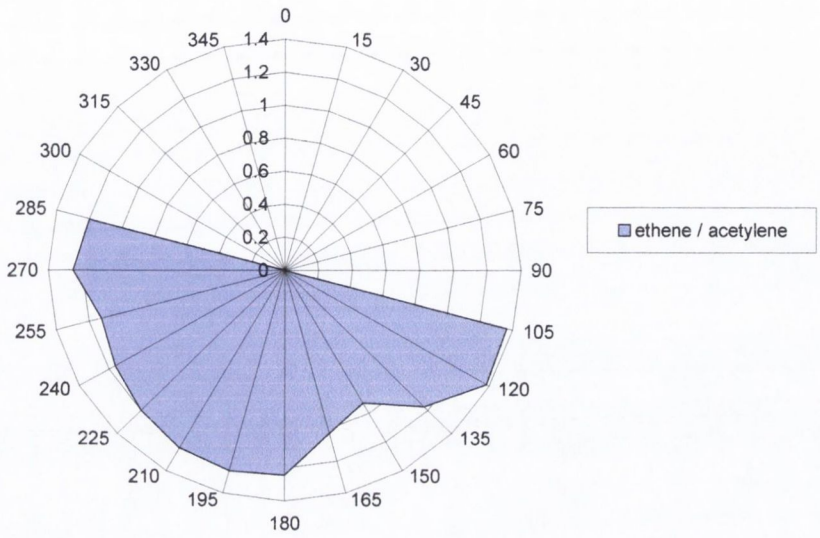


Figure 5.40 Rose diagram for ethene / acetylene ratio for filtered data for wind directions 105-285°

The average ethene / acetylene ratio, considering filtered data for wind directions 105-285° was found to be 1.2. According to Heeb (1999), this value indicates a traffic fleet with either a high percentage of inactive cats or a large proportion of emissions emanating from vehicles without catalytic converters. The relevance of ratio values 1 or 3, being indicators of non-catalytic converter activity or catalytic converter activity is explored further in the section dealing with spatial variations in hydrocarbon concentrations at a sub-urban motorway site (Chapter 6).

5.7.4 Evaporative emissions

To investigate evaporative emission trends we first looked at the correlation between hourly hydrocarbon concentration and hourly temperature (Table 5.7). All compounds which showed a positive correlation in Table 5.7 suggest they are associated with evaporative emissions. In addition to these the butanes would be expected to show evidence of evaporative behaviour (Derwent *et al.*, 2000). As acetylene, propene and ethene road traffic emissions are in the main due to tail-pipe contributions and not associated with evaporative losses (Derwent *et al.*, 2000; Borbon *et al.*, 2002: Mollmann-Coers, 2002; Barletta *et al.*, 2002.) and showed negative

correlations in Table 5.7, they were omitted from further investigation into evaporative trends over the monitoring period.

Hydrocarbon	Correlation between conc. and temperature	Hydrocarbon	Correlation between conc. and temperature
1-butene	0.45	o-xylene	-0.07
m+p xylene	0.49	ethylbenzene	0.33
iso-pentane	0.50	trans-2- pent	0.52
toluene	0.38	ethane	-0.81
cis-2-butene	0.61	n-butane	-0.58
trns-2-butene	0.25	iso-butane	-0.57
1,3 butadiene	0.19	benzene	-0.69
cis-2-pentene	0.65	propane	-0.93

Table 5.7 Correlation between hourly concentration and temperature using filtered data for wind directions 105-285°

Further analysis was carried out with the aid of a widely applied technique (Borbon *et al.*, 2003), used to investigate the extent of evaporative emissions. It involves comparing how the ratio of the measured hydrocarbon and acetylene concentrations varied with temperature. As previously cited, acetylene is a well known marker for tail-pipe emissions and due to its high vapour pressure is not associated with evaporative losses. Hence an increase in a hydrocarbon / acetylene ratio with a concurrent rise in temperature can indicate evaporative emissions of that hydrocarbon (assuming the hydrocarbon in question has no other major local source).

The average HC / acetylene ratio was calculated for each °C rise in temperature. Graphical examples of the trends observed can be seen for iso-pentane and 1-butene in Figures 5.41 and 5.42. For comparison Figure 5.43 profiles the behaviour of the n-butane / acetylene ratio with each °C rise in temperature. The trend observed suggests limited evaporative emissions from n-butane during the period of study.

For isopentane and 1-butene in Figures 5.41 and 5.42 the positive trends with increasing temperature is obvious, with the increase in ratio occurring above 10°C, the temperature above which significant evaporative emissions are observed (Field et al, 1994). This increase in ratio

with temperature is clear indication of a relative rise in iso-pentane and 1-butene concentrations due to evaporative emissions.

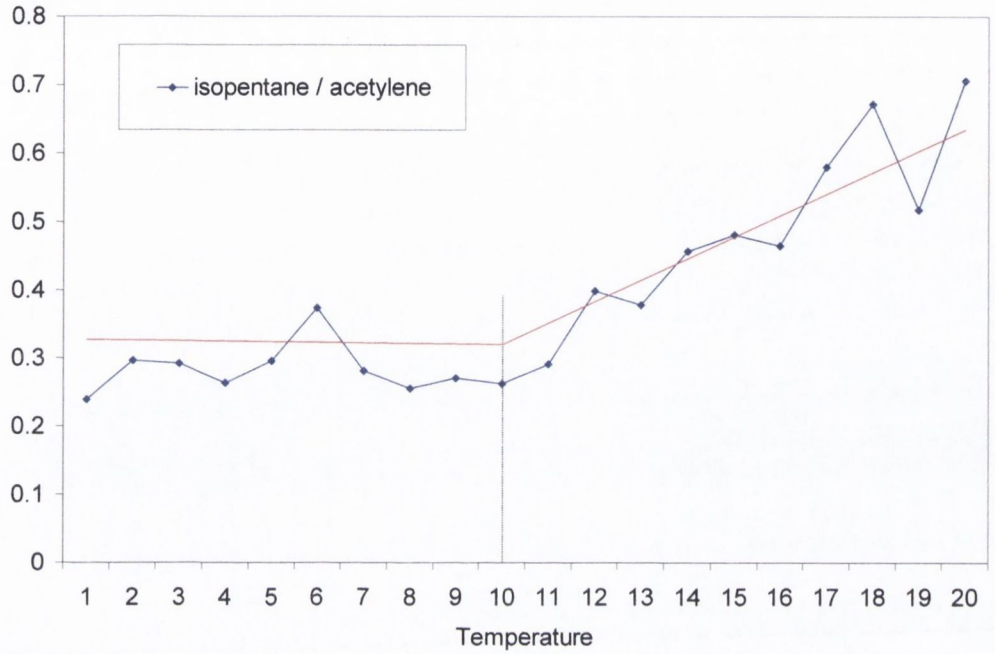


Figure 5.41 Average iso-pentane / acetylene ratio for each °C rise in temperature, using filtered data for wind direction 105-285°

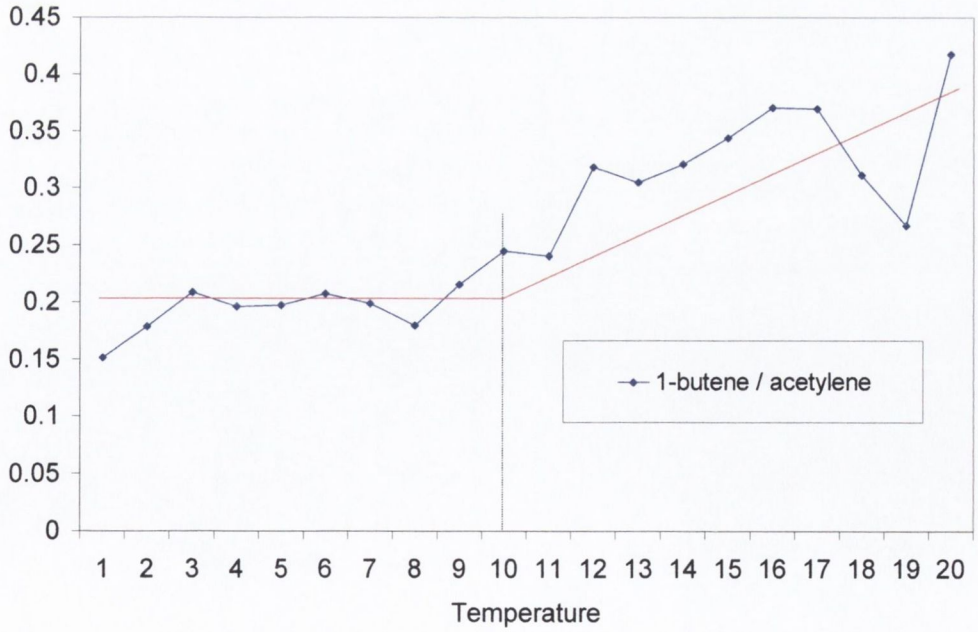


Figure 5.42 Average 1-butene / acetylene ratio for each °C rise in temperature, using filtered data for wind direction 105-285°

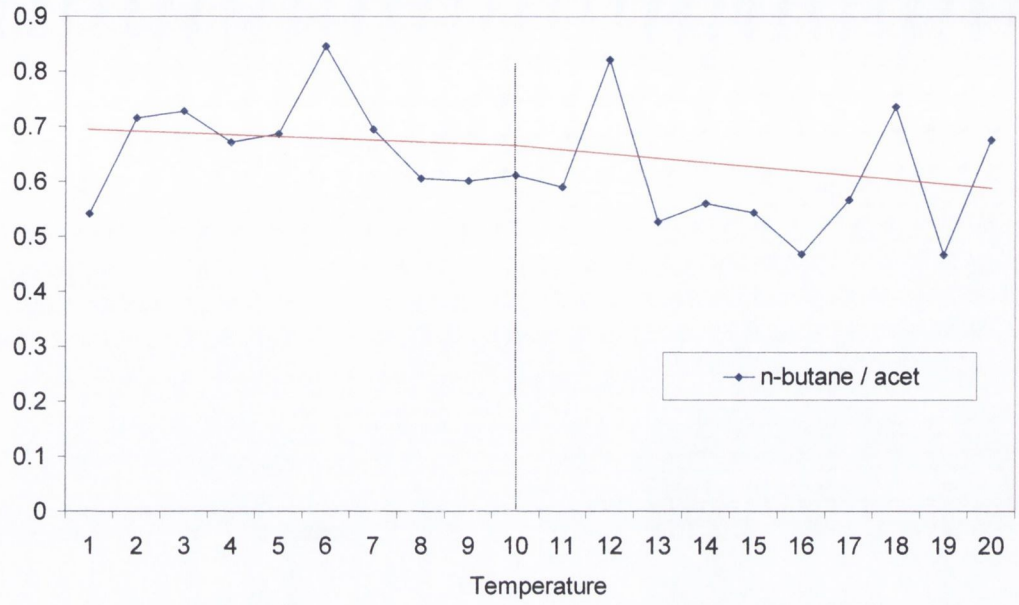


Figure 5.43 Average n-butane / acetylene ratio for each °C rise in temperature, using filtered data for wind direction 105-285°

Correlation's between average HC / acetylene ratios and (°C) rise in temperature can be seen in Table 5.8 below. All compounds which show a positive correlation in Table 5.7, also do in Table 5.8, however, Table 5.8 suggests stronger correlations.

The correlations presented in Table 5.8 are an indication of how the emissions (relative to acetylene) of each HC behave in relation to increased temperature. They are an indicator of how readily each HC evaporates and not a quantitative estimation of their evaporative contribution. As actual amounts of evaporative emissions of a given compound will depend on the quantity of that compound present in fuel, some compounds which yield a relatively high correlation, may contribute very little to overall evaporative emissions.

The most surprising correlations seen are those for n-butane and iso-butane. These are widely reported as being strongly associated with evaporative emissions, but for our analysis they show no such trend.

Hydrocarbon	Correlation between ratio and temperature	Hydrocarbon	Correlation between ratio and temperature
1-butene	0.88	o-xylene	0.46
m+p xylene	0.88	ethylbenzene	0.21
iso-pentane	0.86	trans-2- pent	0.07
toluene	0.83	ethane	-0.01
cis-2-butene	0.70	n-butane	-0.37
trns-2-butene	0.65	iso-butane	-0.45
1,3 butadiene	0.60	benzene	-0.51
cis-2-pentene	0.54	propane	-0.90

Table 5.8 correlation between average HC / acetylene ratio and °C rise for 0-20°C, using filtered data for wind directions 105-285°

A final investigation was carried out to examine how the HC / acetylene ratio behaved over the course of the average day. All compounds which showed a positive correlation between HC / acetylene ratio and temperature were seen to behave in a similar manner. A plot for iso-pentane is shown below (Figure 5.44). Evidence for diurnal evaporative emissions is clearly seen where the diurnal profile of the ratio agrees well with the average temperature profile.

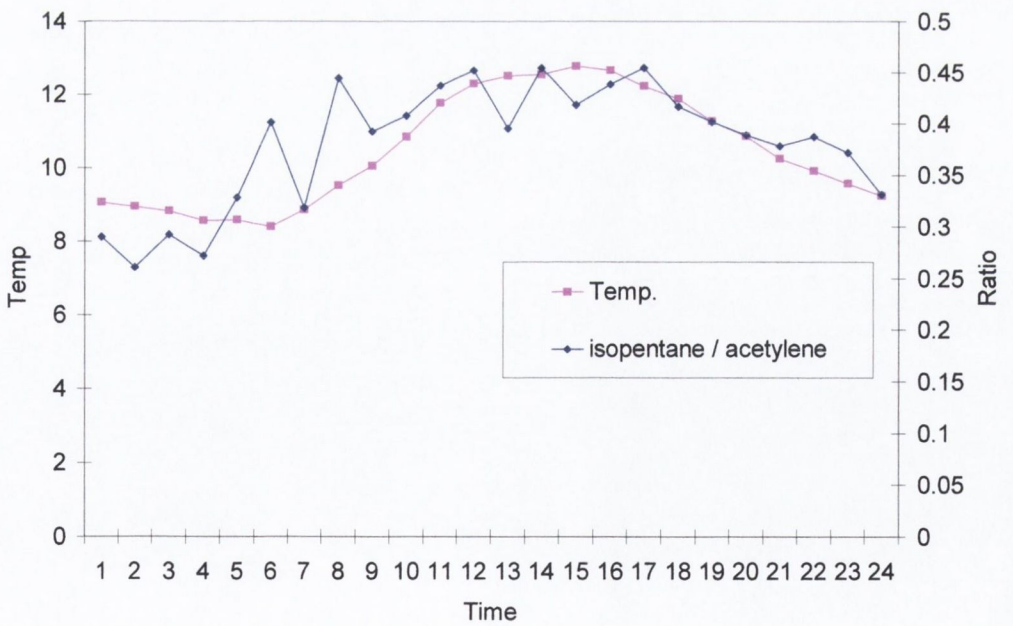


Figure 5.44 24 hour average iso-pentane / acetylene ratio versus average hourly temperature using filtered data for wind directions 105-285°

In addition to the overall trend observed, relating to diurnal evaporative losses, some ancillary peak ratios were observed throughout the day. The first peak seen at 05:00-06:00 is not due to evaporative emissions as the average temperature at this time is the lowest seen over the 24 hour period. From between 07:00-9:00 the ambient temperature is seen to rise to on average 10°C, which is the temperature required to see significant evaporative emissions (Field *et al.*, 1994). A peak ratio is observed at this time, coinciding with peak morning traffic flow, which could relate to running losses from vehicles on the M4. Similar reasoning can explain the peak seen at 17:00. The night-time peak seen at 21:00-23:00 is possibly due to hot-soak evaporative losses emanating from residential areas in this general wind direction.

5.8 COMPARISONS WITH WORLDWIDE STUDIES

The amount of rural / sub-urban monitoring studies are relatively few compared to those investigating ambient hydrocarbon concentrations in urban environments. The majority of the monitoring campaigns focus on the concentrations of the BTEX compounds. A selection of several studies can be seen summarised in Tables 5.9, 5.10 and 5.11.

Table 5.9 shows comparisons between, ambient concentrations obtained at the Leixlip site and several continental European rural monitoring sites, taking part in the EMEP study during 2001 (www.nilu.no/projects/ccc/emepdata.html.). Caution should be exercised when comparing ambient concentrations at different site locations due to differences in meteorological and topographical conditions. However, agreement between compounds where comparisons can be made are generally very good, with the % contribution of each compound to the total HC concentration similar at each site to those observed at Leixlip (percentages in brackets). This again illustrates the minimal effect the M4 has on overall ambient concentrations at the study location.

Table 5.10 illustrates the most comprehensive comparison, where average concentrations for 2001, obtained from the UK Hydrocarbon Monitoring Network, for the Harwell rural monitoring site (Durnitrian (a), 2002), are compared to the average values from the M4 site. Excellent agreement is seen between the two sites for almost all compounds monitored, with the exception of 1,3 butadiene which we previously observed had an unidentified additional local source other than the M4.

The 1,3 butadiene / propene ratio at Harwell was found to be 0.2, the expected ratio according to Ye *et al.* (1997), when the main source for both compounds is road traffic activity. The ethene / acetylene ratio for concentrations obtained at the M4, is higher than at Harwell (1.5 as opposed to 1.0), possibly due to traffic activity on the nearby M4. This ratio decreases significantly when filtered data is used but still remains higher than that observed at Harwell (1.2 as opposed to 1.0).

Column (a) in Table 5.11 also shows concentrations obtained at the Harwell site, these were obtained in 2002 (Durnitrian (b),2002), though the number of hydrocarbons monitored was limited compared to 2001. The results show a slight increase on the 2001 values but this is possibly due to the limited monitoring period reported, 3 months in 2002 as opposed to 12 months in 2001.

Columns (b) and (c) relate to suburban and rural concentrations observed in the greater Munich area by Rappengluck and Fabien (1999) from 1993 to 1997. The concentrations obtained at the M4 site are greater than the rural concentrations in Munich (c) and less than the sub-urban values (c).Columns (d) to (g) relate to a study carried out in the United States by Pankow *et al.* (2003), where semi-rural BTEX concentrations were ascertained at 4 different sites in Ilinois (d) and New Jersey (e to g). The Pearson correlations between the BTEX compounds at each site was similar to the M4 study, with coefficients of 0.8 or greater obtained. The average concentrations at the M4 site, broadly compare well with the values observed in this US study.

Columns (h) to (k) relate to separate studies at various rural locations. Column (h) shows the concentrations of alkanes and acetylene found at a rural monitoring site in Japan, by Sharma *et al.* (2000), (i) shows the concentrations observed by Penkett *et al.* (1993), in low tropospheric altitudes over the North Atlantic. Column (j) shows results obtained at a rural Scandanavian site by Laurilla and Hakola (1996), while (k) shows the average concentrations found in Moerdijk, Holland between 1981 and 1991 when the wind direction was observed from the relatively clean marine direction (Roemer *et al.*, 1999). The comparisons with concentrations obtained at the M4, outline the minimal effect the M4 has on ambient concentrations at the Lexlip site and also the relatively unpolluted nature of the ambient air at the receptor location.

Hydorcarbon	M4 average conc (ppbv)	Switzerland conc (ppbv)	Czech rep. conc (ppbv)	Germany (a) conc (ppbv)	Germany (b) conc (ppbv)	Germany (c) conc (ppbv)	Germany (d) conc (ppbv)
ethane	1.43 (25%)	1.38 (31%)	1.86 (31%)	1.78 (33%)	1.55 (34%)	1.65 (35%)	1.78 (34%)
propane	0.72 (12%)	0.58 (13%)	0.77 (13%)	0.83 (15%)	0.60 (13%)	0.65 (14%)	0.78 (15%)
n-butane	0.46 (8%)	0.29 (6%)	0.33 (5%)	0.37 (7%)	0.26 (6%)	0.31 (7%)	0.34 (6%)
isobutane	0.28 (5%)	0.15 (3%)	0.21 (4%)	0.20 (4%)	0.16 (4%)	0.16 (4%)	0.19 (4%)
isopentane	0.28 (5%)	0.28 (6%)	0.23 (4%)	0.23 (4%)	0.21 (5%)	0.19 (3%)	0.20 (4%)
ethene	0.78 (13%)	0.59 (13%)	0.96 (15%)	0.71 (13%)	0.60 (13%)	0.55 (12%)	0.66 (13%)
propene	0.22 (4%)	0.12 (3%)	0.15 (2%)	0.13 (2%)	0.09 (2%)	0.09 (2%)	0.10 (2%)
1,3 butadiene	0.24 (4%)	0.02 (<1%)	-	0.01 (<1%)	0.01 (<1%)	0.01(<1%)	0.01 (<1%)
toluene	0.31 (5%)	0.28 (6%)	0.18 (3%)	0.19 (4%)	0.17 (4%)	0.18 (4%)	0.16 (3%)
o-xylene	0.11 (2%)	0.04 (1%)	0.03 (<1%)	0.02 (<1%)	0.01 (<1%)	0.02 (<1%)	0.01 (<1%)
m+p xylene	0.21 (4%)	0.09 (2%)	0.07 (1%)	0.06 (1%)	0.05 (1%)	0.07 (1%)	0.05 (1%)
benzene	0.16 (3%)	0.17 (4%)	0.19 (3%)	0.19 (3%)	0.17 (4%)	0.18 (4%)	0.19 (4%)
ethylbenzene	0.09 (2%)	0.04 (1%)	0.03 (1%)	-	-	-	-
acetylene	0.52 (9%)	0.45 (10%)	1.07 (18%)	0.71 (13%)	0.71 (15%)	0.68 (14%)	0.73 (14%)

Table 5.9 Comparisons with worldwide studies

Hydorcarbon	M4 average concentrations (ppbv)	Harwell average concentrations for 2001 (ppbv)	Hydrocarbon	M4 average concentrations (ppbv)	Harwell average concentrations for 2001 (ppbv)
Ethane	1.43	1.75	cis-2 butene	0.05	0.03
Propane	0.72	1.00	trans-2 pent	0.06	0.02
n-butane	0.46	0.63	cis-2 pentene	0.04	0.01
Isobutane	0.28	0.27	toluene	0.31	0.36
Isopentane	0.28	0.37	o-xylene	0.11	0.08
Ethene	0.78	0.60	m+p xylene	0.21	0.18
Propene	0.22	0.26	benzene	0.16	0.19
1-butene	0.12	0.04	ethylbenzene	0.09	0.07
1,3 butadiene	0.24	0.05	acetylene	0.52	0.59
Trans-2-but	0.10	0.04	-	-	-

Table 5.10 comparison of average values obtained at the M4 with those obtained in 2001 at the Harwell rural UK hydrocarbon monitoring network site (Durnitrian (a), 2002)

	M4	(a)2002 Harwell (3 months)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)
ethane	1.43	-	-	-	-	-	-	-	1.9	2.5	2.4	2.1
propane	0.72	-	-	-	-		-	-	0.8	0.9	1.3	0.9
n-butane	0.46	-	-	-	-	-	-	-	0.4	0.5	0.6	0.6
iso-butane	0.28	-	-	-	-	-	-	-	0.2	0.3	0.3	0.3
toluene	0.31	0.38	0.5	0.2	0.23	0.29	0.56	0.85	-	-	-	-
o-xylene	0.11	0.10	0.2	-	0.03	0.05	0.1	0.16	-	-	-	-
m+p xylene	0.21	0.10	0.5	0.1	0.1	0.12	0.29	0.42	-	-	-	-
benzene	0.16	0.10	0.4	0.1	0.17	0.23	0.36	0.43	-	-	-	-
ethylbenzene	0.09	0.05	0.2	-	0.03	0.04	0.09	0.12	-	-	-	-
acetylene	0.52	-	-	-	-	-	-	-	0.6	0.7	0.8	0.6

(a) Durnitrian b (2002), (b)and(c) Rappengluck and Fabien (1998), (d) to (g) Pankow et al (2003), (h) Sharma et al (2000), (i) Plunkett (1993), (j) Larilla and Hakilla (1996), (k) Roemer et al (1999)

Table 5.11Comparison of average concentrations obtained at the M4 to other rural / sub-urban studies carried out worldwide

5.9 SUMMING UP

The monitoring campaign carried out at the M4, Leixlip, represented the longest single monitoring study undertaken in this research project. Approximately eight months of online-sampling was carried out to investigate the road traffic source-effect, emanating from the M4 at the sub-urban / rural location chosen.

Through various analysis techniques, the M4 source effect has been established as quite weak, with associated concentrations most prominent during peak time traffic flow when wind directions emanate from a near parallel, 105° direction. A similar source effect might have been expected from the near parallel wind direction 285°, however, the influence of the river Liffey passing under the M4 and the resultant local wind turbulence could impact on the dispersal of vehicular emissions associated with this wind direction, resulting in a less well defined source effect.

General levels at the sub-urban / rural M4 site compared very favourably with those reported at the rural UK Hydrocarbon Monitoring site at Harwell.

6. SPATIAL VARIATION OF HC LEVELS AT A MOTORWAY SITE

The primary objective of this monitoring campaign was to ascertain the spatial variation of HC compounds in the vicinity of a sub-urban Motorway site, using the mobile sampling method. The results obtained could then be used to validate the CALINE4 dispersion model for the HC compounds of interest using the meteorological conditions observed during monitoring.

6.1 SITE DESCRIPTION AND SAMPLING LOCATIONS

The monitoring site was located at a section of the M50 motorway, bisecting the sub-urban areas of Tallaght and Templeogue, approximately 10km South-West of Dublin city centre. Although the section of Motorway under investigation curves slightly, the general orientation lies approximately 330° to 150°. This sampling location was chosen due to the large expanse of level, green areas either side of the M50 at this point.

Six separate sampling points (receptors), were used at the M50 site, three located on the eastern and western sides, respectively. The three sets of receptors were located at a distance of 25, 120 and 240 metres from the M50. Approximately 100 metres to the west of the most westerly receptor is the nearby Tymon North secondary road. The outermost residential areas of Tallaght, which has a population of 62,799 (CSO, 2003) are situated on the opposite side of this road. On the Eastern side, the outermost residential areas of Templeogue, with a population of 18,383 (CSO, 2003) are situated approximately 250 metres to the east of the most easterly receptor.

A signal controlled roundabout at the intersection of the N81 and the M50 is located approximately 1km to the South-East of the sampling location.

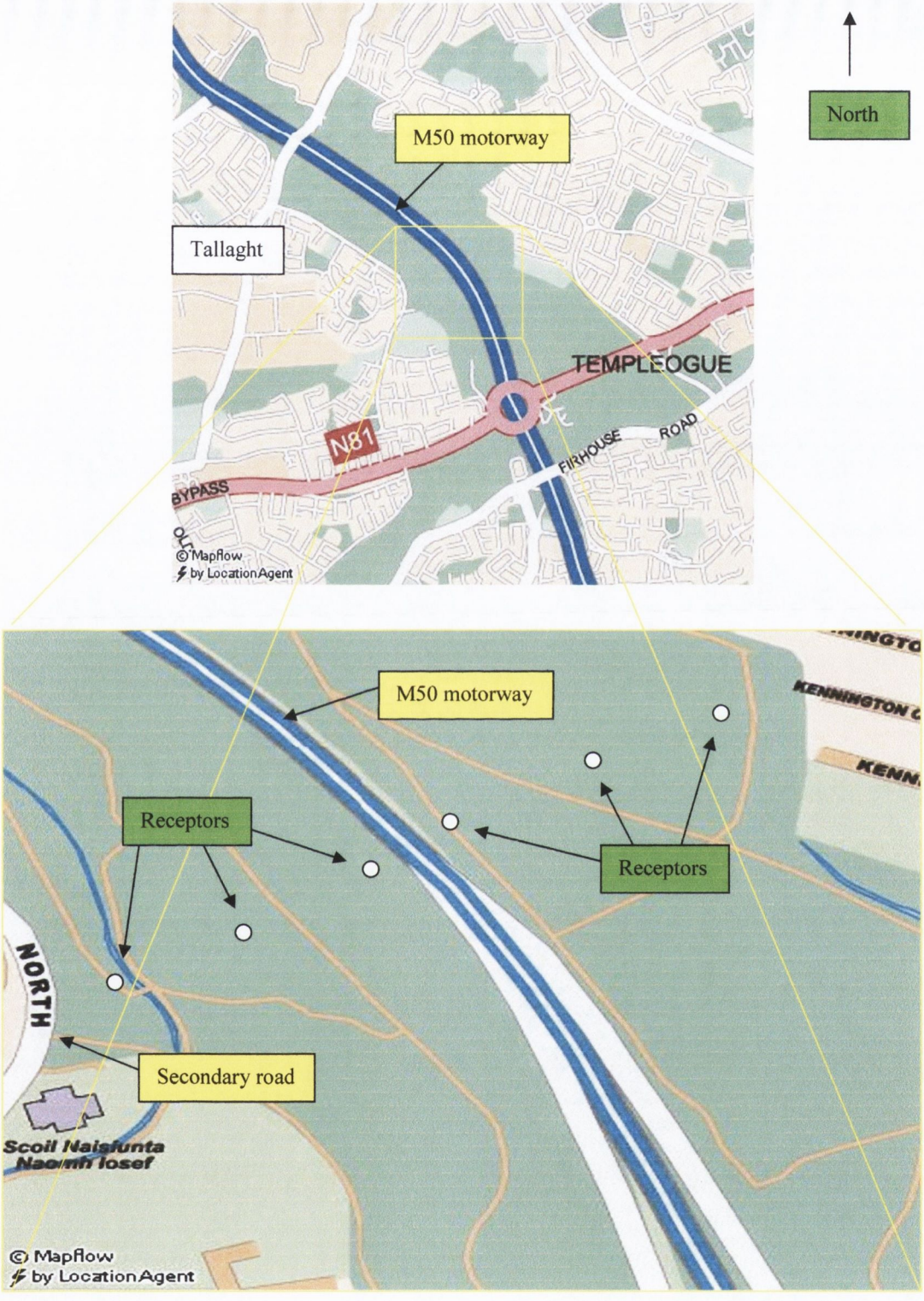


Figure 6.1 Regional and local maps outlining general and specific site location

6.2 MONITORING PERIOD AND DETAILS

The portable sampling method validated in Chapter 4 was used to investigate the spatial variation of 11 hydrocarbons at a motorway site in a sub-urban Dublin location.

The monitoring was carried out during the morning peak traffic period, between the hours of 07:00 and 10:00. The air was sampled for 5 minute periods consecutively at each of the 6 receptor sites. As the procedure in total took approximately 35 minutes, it is assumed that the traffic flow did not change significantly over this relatively short period of time. Twenty two sets of 6 samples were taken over a 6 week period from 16 July 03 to 29 August 03. Due to logistical considerations relating to sample analysis, only weekday sampling was carried out. Table 6.1 summarises the relevant information in regard to each days sampling.

Date	Sample time	No. samples	M50 Traffic volume (total vehicles / hour)	Local wind direction (°)	Local wind speed (m/s)	Local temp. (°C)
16/07/03	8:00-9:00	5	4747	45	0.6	19
17/07/03	07:00-08:00	6	4015	270	0.75	17
18/07/03	07:00-08:00	6	4322	240	1.75	14
22/07/03	07:00-08:00	6	3761	265	2.00	19
23/07/03	07:00-08:00	6	3858	130	0.60	16
24/07/03	07:00-08:00	6	3996	230	0.75	15
25/07/03	07:00-08:00	6	4246	230	0.75	18
28/07/03	07:00-08:00	6	3835	50	1.25	17
29/07/03	07:00-08:00	6	3873	220	1.00	16
05/08/03	09:00-10:00	6	3406	90	0.75	19
06/08/03	09:00-10:00	6	3464	290	1.25	19
08/08/03	8:00-9:00	6	2051	60	0.75	18
11/08/03	09:00-10:00	6	3320	30	0.60	17
12/08/03	8:00-9:00	6	4770	330	0.75	19
13/08/03	8:00-9:00	6	5711	290	1.25	16
15/08/03	09:00-10:00	6	3721	120	0.70	19
19/08/03	09:00-10:00	6	3388	265	1.50	14
21/08/03	8:00-9:00	6	6050	235	1.75	12
25/08/06	09:00-10:00	6	4385	90	0.75	16
26/08/03	8:00-9:00	6	3483	100	1.25	13
27/08/03	8:00-9:00	6	2267	100	1.25	16
29/08/03	8:00-9:00	6	-	320	0.75	16

Table 6.1 Summary of sampling details

6.3 METEOROLOGICAL AND TRAFFIC DATA

6.3.1 Meteorological data

The local meteorological effects monitored were wind speed, wind direction and temperature. A handheld anemometer (Silva windwatch) was used to measure the local wind speed and temperature. A compass and in-house manufactured hand held wind vain were used to estimate the wind direction.

Conditions were relatively calm over the course of the monitoring period. This was influenced by the time of the day at which the monitoring was carried out. Early morning hours (07:00-10:00) are often associated with low wind speeds due to a relative lack of atmospheric convection resulting from lower temperatures and a lower incidence of solar radiation. (Barletta *et al.*, 2002) On only one occasion was the local wind speed seen to rise to 2 m/s. The majority of values were monitored as 1.0-1.5 m/s or less. A very low average wind speed of 1.06 m/s was obtained over the course of the monitoring period, indicative of the calm conditions prevalent at the time.

A higher level of uncertainty is associated with the estimated wind speeds than would be anticipated over a longer period of study, due to the relatively calm conditions monitored and the fact that the hand-held anemometer employed must point directly into the wind to gain an accurate estimate of wind speed.

The hand-held wind vane and compass proved very accurate in ascertaining local wind direction. Each daily local wind direction agreed with regional wind direction observed at Dublin airport. This was checked daily, comparing the wind direction observed at the M50 to that reported for Dublin airport on the Met Eireann web site.

Table 6.1 shows the daily local temperatures from which an average value of 16.6°C was obtained with a relative standard deviation of only 9%, showing the relatively small deviations in temperature over the course of the monitoring. Overall, conditions during the monitoring period were much warmer than would normally be expected, even in mid Summer.

On any particular day, the same wind direction was observed at all 6 sampling locations. Hence, only 22 separate wind directions were obtained, which is too few for detailed sectoral analysis.

As the M50 has an approximately North west-South east orientation or 330° to 150°, at the monitoring location, the observed wind directions were grouped into the two sectors which produce M50 source effects on opposite sides. The two wind sectors range from 345-135°, and 165-315°, and can be considered as easterly and westerly wind direction sectors relative to the M50.

Parallel or near-parallel wind directions were excluded from our analysis due to the difficulty in establishing a background concentration for these conditions and also to exclude any possible emissions associated with the signal controlled round-about to the South-East of the sampling site. This exclusion led to only two days data being omitted from the analysis. Both wind direction sectors were evenly represented over the course of the remaining 20 days, with 10 days of data obtained for each wind direction sector.

When easterly (345-135°) winds were prevalent, a low average wind speed of 0.85 m/s and an average temperature of 16.1°C were obtained. Westerly (165-315°) wind directions were associated with higher average wind speeds of 1.28 m/s and an average temperature of 17.2°C.

The higher average wind speed observed in the 165-315° sector, can be expected to lead to relatively more mixing and relatively lower background concentrations than those obtained for wind direction sector 345-135°.This is examined further in section 6.4.

6.3.2 Traffic data

The National Roads Authority provided data on the average total traffic flow on the M50 between the interchanges of interest (Ballymount, M50 / N81) for the monitoring period of interest. These data were collected using induction loops embedded in both sides of the motorway. Hourly traffic flows on both sides of the motorway (North-South and South-North

directions) were summed to obtain the total flow of vehicles per hour on the M50. Twenty one days of traffic data was obtained for our period of monitoring.

The average hourly traffic flow was seen to be 3936 vehicles / hour, with a relative standard deviation of 23%. This low RSD% shows how the traffic varied to a relatively small degree over the hours of interest. Table 6.2 below illustrates the hourly averages obtained with % relative standard deviations for each hour between 07:00 and 10:00.

Time	Average total vehicles per hour	% relative standard deviation
07:00-08:00	3988	5%
08:00-09:00	4154	41%
09:00-10:00	3614	11%

Table 6.2 Hourly average total traffic flow with associated % relative standard deviations

The highest hourly traffic flow, with the highest deviation was seen between 08:00 and 09:00. The majority of data was collected between 07:00 and 08:00. The lowest average traffic flow was seen between 09:00 and 10:00, during which time interval, the least amount of data was obtained. As the deviation in the hourly averages is relatively small, it is not anticipated that this change in hourly traffic flow will have a major impact on peak daily emission rates. This will be investigated further in the proceeding sections.

6.4 ANALYSIS OF RESULTS

The data was grouped into the two major wind sectors, 345-135° and 165-315°. When determining a suitable background correction it was assumed that there was a limited contribution from the M50 due to mechanical turbulence, to the background concentrations obtained at the upwind site nearest the road (25 metres from the M50) and any contributions would be absorbed in the average background values used. This shall be shown to be a valid assumption in section 6.7.4 where experimental and modelled results are compared

6.4.1 Wind direction sector 165-315°

6.4.1.1 Average values at each receptor

Table 6.3 presents the average concentrations of all 11 compounds observed at each of the 6 receptors when the wind direction was between 165° and 315°. The results distinguish between upwind and downwind concentrations.

	D (m)	ethane	propane	n-but	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
Uwnd	-240	1.33	1.31	2.04	0.69	0.16	0.38	0.69	0.23	0.06	0.73	0.22
Uwnd	-120	1.50	1.01	0.76	0.27	0.12	0.27	0.45	0.14	0.04	0.42	0.15
Uwnd	-25	1.29	0.58	0.58	0.20	0.12	0.25	0.48	0.15	0.05	0.46	0.16
Dwnd	25	1.35	0.51	0.59	0.21	0.24	0.68	1.38	0.50	0.19	0.87	0.31
Dwnd	120	1.22	0.55	0.67	0.21	0.12	0.26	0.62	0.21	0.05	0.47	0.19
Dwnd	240	1.26	0.54	0.59	0.21	0.10	0.20	0.47	0.17	0.06	0.42	0.15

D = distance from motorway. Uwnd = upwind site relative to M50. Dwnd = downwind site. eth = ethene. prop = propene

Table 6.3 Average concentrations (ppbv)for wind directions between 165°and 315°

The strong M50 source effect displayed for compounds n-pentane, iso-pentane, ethene, propene, 1,3 butadiene, acetylene and benzene is apparent. The weak or null impact the M50 has on ethane, propane, n-butane and iso-butane concentrations is also evident, as illustrated in Figure 6.2.

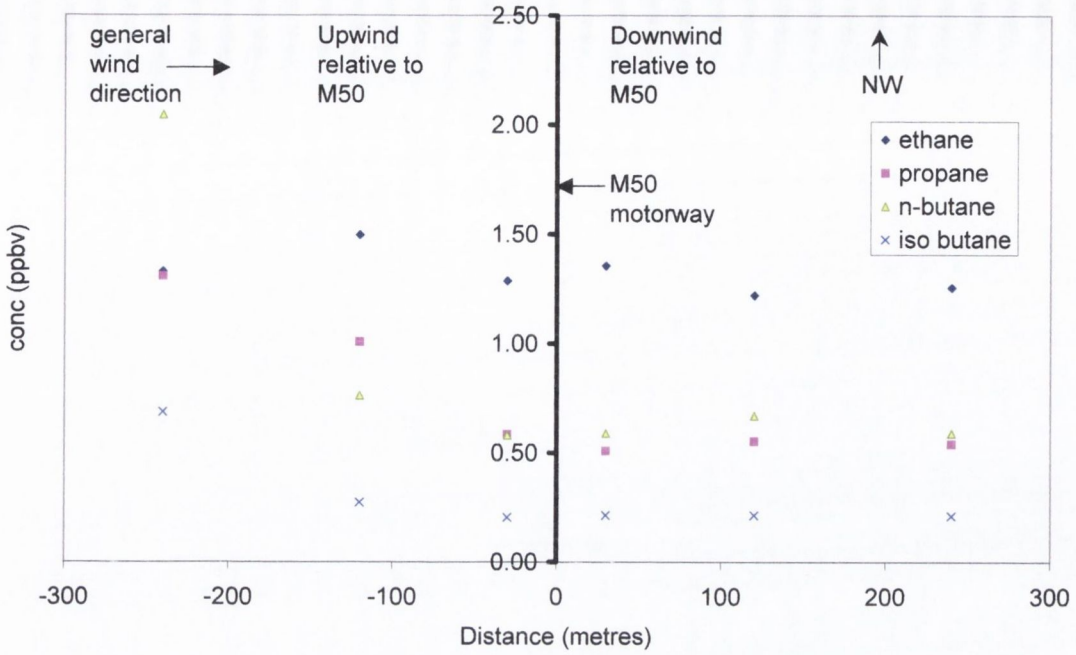


Figure 6.2 Average concentration of four alkanes with wind directions 165-315°

The variation in average concentration over the 6 receptors was relatively small for ethane, which is consistent with the assumption that only general background concentrations of this compound are measured, with no major local source identifiable. The other 3 alkanes all display effects due to the sub-urban area of Tallaght, west of the –240 metres upwind receptor. As no source effect due to the M50 is observed for these compounds, it is very unlikely that the nearby relatively lightly trafficked secondary road has contributed substantially to the higher levels observed at the –240 metres receptor. The most probable cause is fugitive emissions of iso-butane, n-butane and propane from the many industrial estates located in the general Tallaght area.

The local effect does not appear to affect the air quality at the –25 metre receptor where the concentrations are similar to those obtained at the downwind receptors, which showed no M50 source effect. The remaining 7 compounds exhibit spatial trends consistent with an M50 source effect. Example plots for several of these compounds, representative of all 7 are shown below in Figures 6.3(a) (acetylene and ethene) and 6.3(b) (1,3 butadiene and propene). Within 240 metres downwind, the concentrations are seen to reduce significantly.

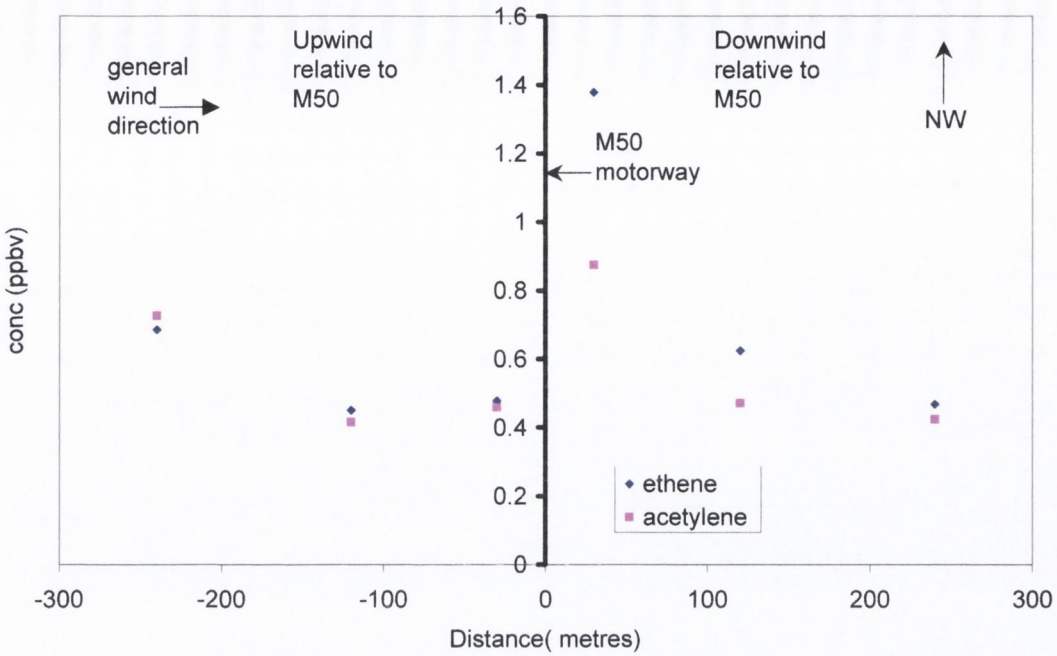


Figure 6.3(a) Strong M50 source effect seen for acetylene and ethene with wind directions 165-315°

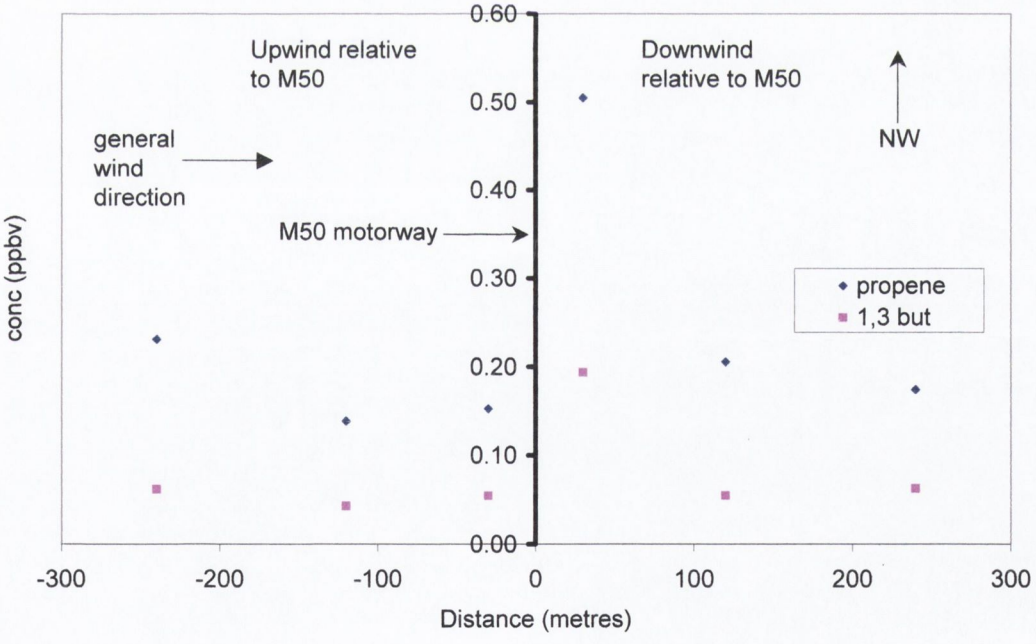


Figure 6.3(b) strong M50 source effect seen for 1,3 butadiene and propene with wind directions 165-315°

The effect from the secondary road approximately 100 metres west of the –240 receptor can be seen in the elevated readings obtained at receptor –240m. However, the relative increase in concentrations is far lower than that observed for the alkanes ; propane, n-butane and iso-butane, confirming that the high levels obtained at this receptor for the aforementioned alkanes were not due to traffic activity from the secondary road. The upwind ethene and acetylene reduce to their background levels over a shorter distance ; 120 metres as opposed to 215 metres for the alkanes.

The downwind spatial profile of concentrations obtained is much more as expected. The highest concentration of both compounds is observed at the downwind +25metres receptor, nearest the M50. The concentrations are seen to decrease with distance from the M50 due to atmospheric dispersion. This process is so successful at reducing concentrations that the levels obtained at receptor +240m display a negligible source effect from the M50. The levels obtained at this receptor are close to the background levels observed at the –25m and –120m receptors on the upwind side.

6.4.1.2 Background corrected concentrations

To quantify the effect of the emissions of each compound from the M50 motorway, the downwind concentrations obtained at the +25m, +120m and +240m receptors are corrected for background values. The average concentrations observed at the –120m and –25m upwind receptors were assumed to represent the background values, and these were subtracted from those obtained at the downwind receptors. The results are presented in Table 6.4.

	D(m)	ethane	propa	n-but.	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
Dwnd	+25	-0.04	-0.29	-0.08	-0.02	0.12	0.42	0.91	0.36	0.14	0.44	0.16
Dwnd	+120	-0.17	-0.24	0.00	-0.02	0.01	-0.1	0.16	0.06	0.01	0.03	0.04
Dwnd	+240	-0.13	-0.26	-0.08	-0.03	-0.01	-0.1	0.00	0.03	0.01	-0.01	0.00

D = distance from motorway. Dwnd = windwrd site propa = propane eth = ethene prop = propene

Table 6.4 Background corrected downwind concentrations relative to the M50 for wind directions 165° to 315°

The absence of an M50 source effect for the alkanes, ethane to iso-butane with these wind directions (165-315°) is quite clear from Table 6.4. The values at each of the downwind sites is actually lower than the average upwind background value calculated. The rate of pollutant dispersal can be seen to be quite extreme for those compounds exhibiting a strong M50 source effect. On average, for this wind direction sector, the M50 concentrations are seen to be reduced by 92% between the 25m and 120m downwind receptors and by 100% between the 25m and 240m receptors.

6.4.1.3 Correlation matrices for upwind and downwind receptors.

Correlation matrices for the upwind (background) and downwind (M50 source effect) receptors are presented in Tables 6.5 and 6.6 respectively. The upwind Pearson's correlation for each compound were calculated by grouping data from the –25 and –120 metre receptors into one data set. The downwind correlations were obtained by grouping the data obtained from the 25m, 120m and 240m downwind receptors and treating this as one data set.

The four alkanes which displayed little or no M50 source effect are seen to correlate very poorly with the other seven compounds, for both upwind and downwind locations, suggesting additional sources other than road traffic.

Within the non-traffic related group, ethane is seen to correlate very poorly with the other three alkanes. Ethane and propane are both associated with natural gas leakage (Derwent *et al.*, 2000), but the poor correlation seen between these two compounds, allied to the relatively good correlations between the butanes and propane suggest an alternative source for these 3 alkanes. The correlations between the 7 traffic related compounds are as expected higher on the downwind side (Table 6.6) than the upwind (Table 6.5), illustrating again the influence the M50 has on downwind concentrations.

These high correlations, in conjunction with the increase in concentrations observed on the downwind side of the M50, verify the importance of the common M50 source effect for these compounds.

	ethane	propane	n-but	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
ethane	1.00	0.35	0.03	0.12	0.30	0.18	0.35	0.34	0.36	0.05	0.35
propane	0.35	1.00	0.61	0.64	0.35	0.24	0.48	0.49	0.08	0.01	0.43
n-butane	0.03	0.61	1.00	0.99	0.32	0.31	0.14	0.23	0.08	0.00	0.26
i-butane	0.12	0.64	0.99	1.00	0.35	0.34	0.19	0.29	0.00	0.04	0.33
n-pentane	0.30	0.35	0.32	0.35	1.00	0.97	0.85	0.86	0.69	0.58	0.79
i-pentane	0.18	0.24	0.31	0.34	0.97	1.00	0.80	0.81	0.73	0.69	0.74
ethene	0.35	0.48	0.14	0.19	0.85	0.80	1.00	0.96	0.61	0.72	0.79
propene	0.34	0.49	0.23	0.29	0.86	0.81	0.96	1.00	0.70	0.66	0.78
1,3 but	0.36	0.08	0.08	0.00	0.69	0.73	0.61	0.70	1.00	0.71	0.63
acetylene	0.05	0.01	0.00	0.04	0.58	0.69	0.72	0.66	0.71	1.00	0.61
benzene	0.35	0.43	0.26	0.33	0.79	0.74	0.79	0.78	0.63	0.61	1.00

eth = ethene prop = propene, acet = acetylene, benz = benzene

Table 6.5 Correlation matrix for upwind receptors (–25m and –120m)

	ethane	propane	n-but.	iso-but	n-pent	iso-pent	Eth	prop	1,3 but	acet	benz
Ethane	1.00	0.61	0.34	0.45	0.59	0.54	0.57	0.57	0.48	0.56	0.57
Propane	0.61	1.00	0.79	0.86	0.30	0.27	0.27	0.30	0.22	0.21	0.38
n-butane	0.34	0.79	1.00	0.95	0.10	0.07	0.07	0.09	0.05	0.06	0.16
i-butane	0.45	0.86	0.95	1.00	0.22	0.21	0.17	0.18	0.17	0.17	0.30
n-pentane	0.59	0.30	0.10	0.22	1.00	0.91	0.86	0.83	0.78	0.90	0.91
i-pentane	0.54	0.27	0.07	0.21	0.91	1.00	0.86	0.85	0.82	0.87	0.87
Ethene	0.57	0.27	0.07	0.17	0.86	0.86	1.00	0.99	0.84	0.91	0.91
Propene	0.57	0.30	0.09	0.18	0.83	0.85	0.99	1.00	0.82	0.88	0.87
1,3 but	0.48	0.22	0.05	0.17	0.78	0.82	0.84	0.82	1.00	0.76	0.76
Acetylene	0.56	0.21	0.06	0.17	0.90	0.87	0.91	0.88	0.76	1.00	0.82
Benzene	0.57	0.38	0.16	0.30	0.91	0.87	0.91	0.87	0.76	0.82	1.00

eth = ethene prop = propene, acet = acetylene, benz = benzene

Table 6.6 Correlation matrix for downwind receptors

6.4.1.4 Effect of traffic flow and wind speed on background-corrected concentrations

As described in Chapter 3, ethene is associated with exhaust emissions. Figure 6.4 presents a scatter plot of daily background-corrected ethene concentrations at the 25m downwind receptor against the hourly traffic flow at the time of sampling. The correlation between the two sets of data in Figure 6.4 is seen to be very poor. This is partly due to the relatively small range of observed traffic flows, but also points to the significance of the meteorological conditions at the time of sampling. Figure 6.5 presents a scatter plot of daily background-corrected ethene concentrations obtained at the 25m receptor against observed wind speed. As expected, concentrations decrease with increased wind speed, and a non-linear relationship yields a better correlation between the two variables, with an R^2 value of 0.59 obtained. The curve shown in Figure 6.5 follows the trend observed in Figure 5.12, which showed the variation in acetylene concentrations with wind speed for the M4 motorway site, where a much greater sample pool was investigated. However, in Figure 6.5, the ethene values have been background-corrected, allowing the influence of wind speed in diluting and dispersing pollutants over a short distance of 25 metres to be clearly observed.

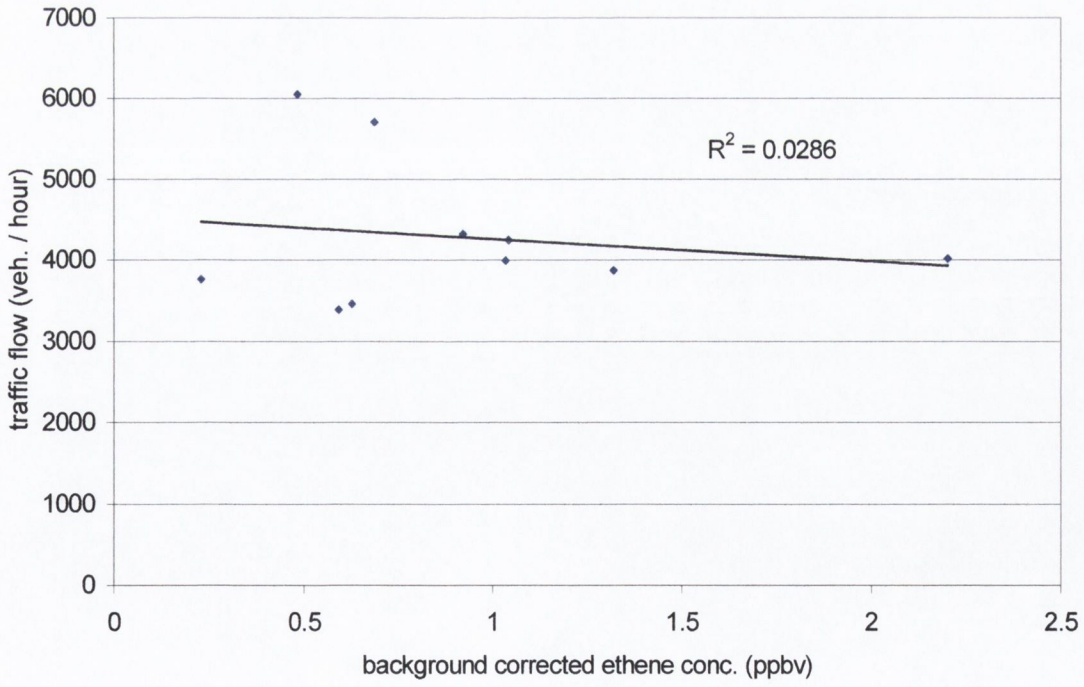


Figure 6.4 Background corrected 25m downwind ethene concentration against traffic flow for wind directions between 165° and 315°

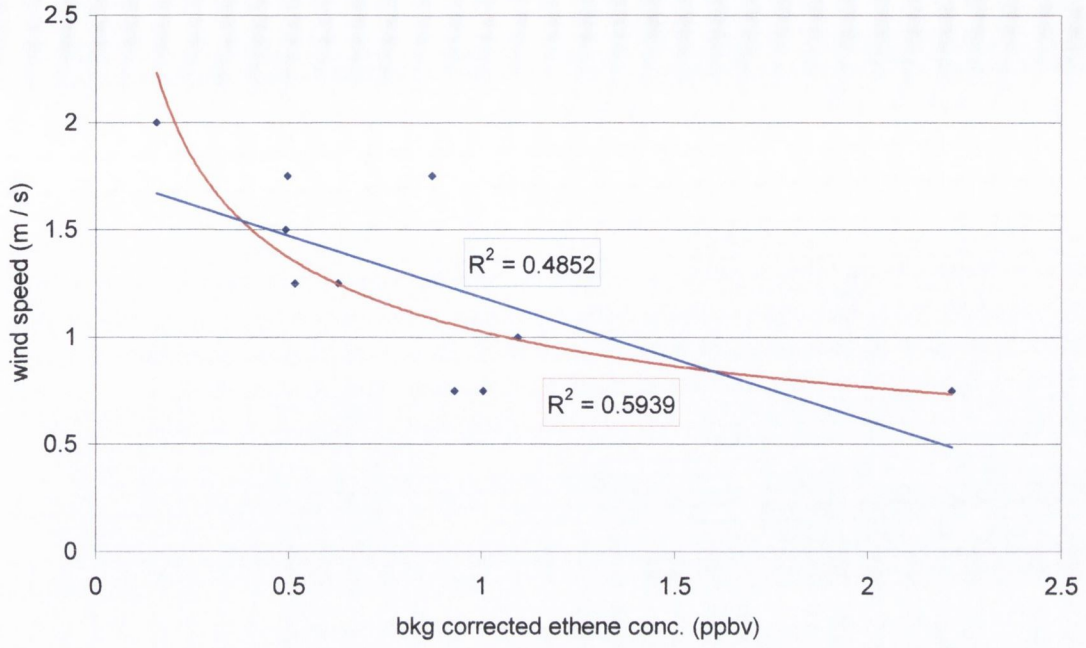


Figure 6.5 Background corrected 25m downwind ethene concentration against daily wind speed for wind directions between 165° and 315°

6.4.2 Wind direction sector 345-135°

6.4.2.1 Average concentrations at each receptor

The average concentrations of each compound at each receptor observed for this wind direction sector are presented in Table 6.7.

	D(m)	ethane	propane	n-but	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
Uwnd	240	1.77	1.07	1.49	0.46	0.23	0.49	0.79	0.25	0.05	0.74	0.27
Uwnd	120	1.83	1.04	0.98	0.40	0.23	0.47	0.78	0.26	0.06	0.70	0.26
Uwnd	25	1.82	1.13	2.09	0.63	0.23	0.51	0.87	0.28	0.06	0.72	0.25
Dwnd	-25	1.98	1.18	1.61	0.59	0.44	1.07	1.58	0.48	0.11	1.17	0.40
Dwnd	-120	1.80	1.03	1.14	0.43	0.31	0.66	1.10	0.33	0.06	0.89	0.31
Dwnd	-240	1.72	0.95	1.58	0.53	0.26	0.57	0.88	0.29	0.06	0.70	0.28

D = distance from motorway. Uwnd = upwind site relative to M50. Dwnd = downwind site. eth = ethene. prop = propene, acet = acetylene

Table 6.7 Average concentrations obtained at each receptor for wind direction 345-135°

A small source effect can be seen for ethane and propane at the –25 m (downwind) receptor. No such effect is seen for n-butane or iso-butane, as illustrated in Figure 6.6. The spatial trend in Figure 6.6 is quite different for ethane and propane than for the butanes. The range of concentration values observed for the butanes is far greater than that for ethane and propane, which are nearly constant except for a slight increase at the downwind –25m receptor. The relatively high deviation in n-butane and iso-butane concentrations may suggest that local source effects other than road traffic contribute to the more scattered spatial profiles.

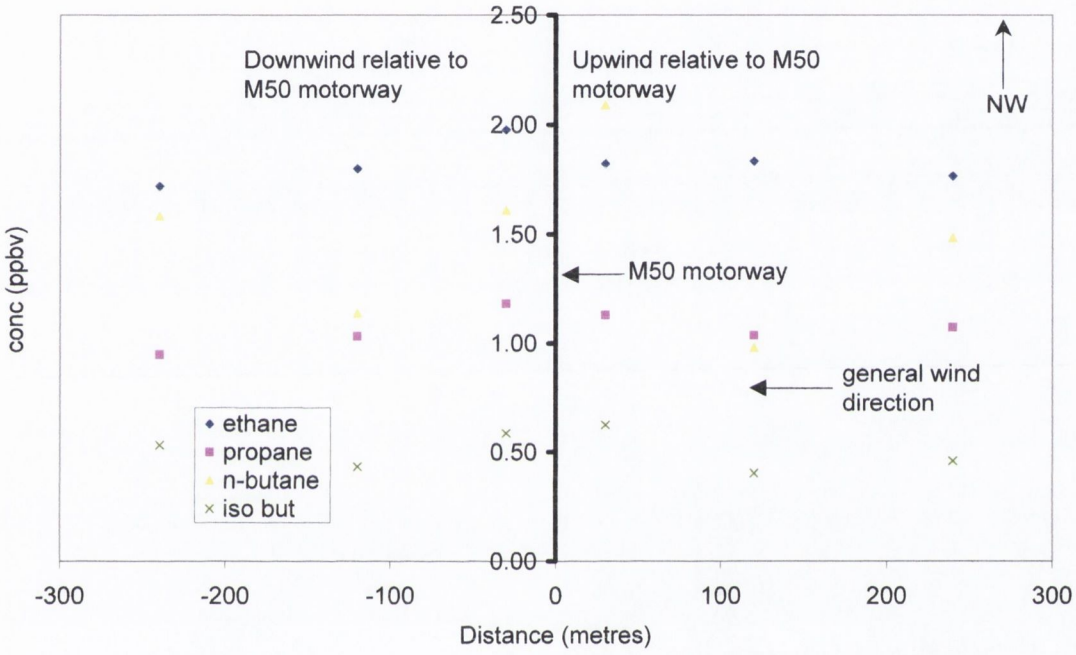


Figure 6.6 Average values at the 6 receptors for 4 alkanes showing slight or no source effects from the M50 from wind directions 345°to 135°

As with wind direction sector 165-315°, the other seven compounds show strong M50 source effects. Four compounds, benzene, acetylene, 1,3 butadiene and propene, representative of all 7 compounds are used in Figures 6.7(a) and 6.7(b) to illustrate the observed spatial variations in concentrations. The spatial trend observed is as expected, with the highest concentrations obtained nearest the M50 on the downwind side. The background concentrations on the upwind side are nearly constant, suggesting that the air is well mixed when it reaches the M50. The slightly higher background levels observed at the upwind receptor nearest the motorway are possibly due to mechanical turbulence, prevalent due to the lower average wind speeds associated with this wind direction sector.

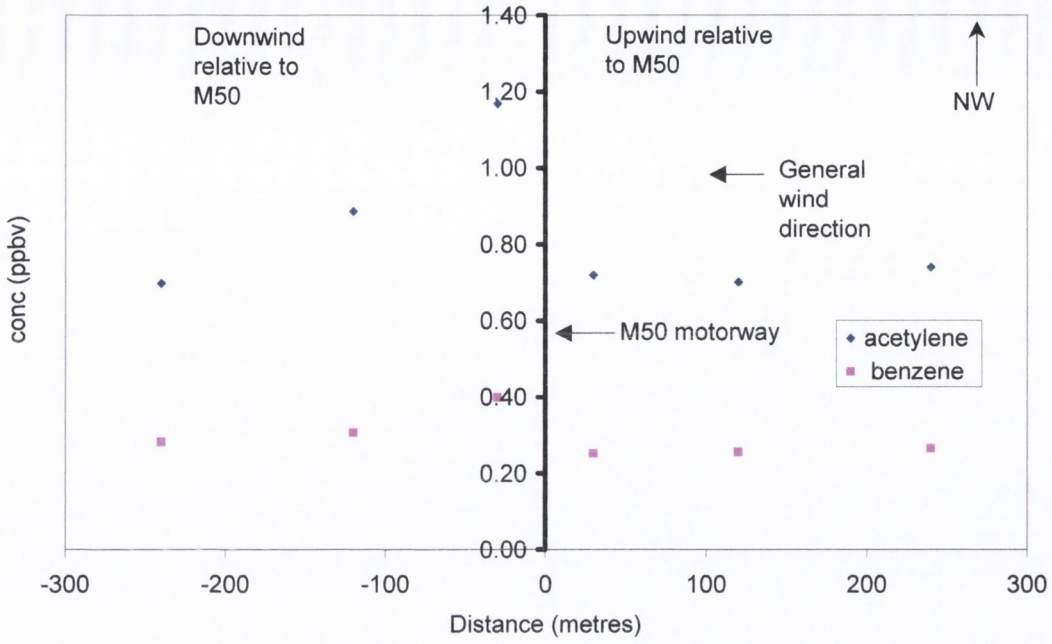


Figure 6.7(a) Average concentrations at the 6 receptors for acetylene and benzene showing source effects from the M50 for wind directions 345-135°

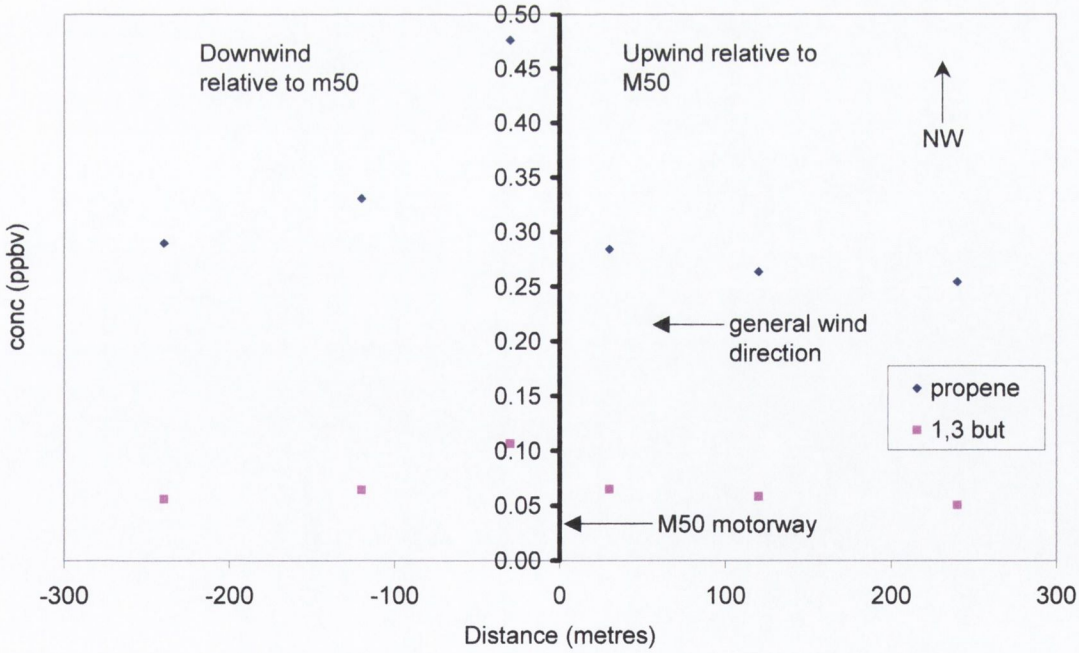


Figure 6.7(b) Average concentrations at the 6 receptors for 1,3 butadiene and propene showing source effects from the M50 for wind directions 345°-135°

6.4.2.2 Background-corrected downwind concentrations.

Downwind concentrations were once background-corrected by subtracting the average upwind background concentrations from the average concentrations obtained at each of the three M50 affected receptors. The results are presented in Table 6.8.

	D(m)	ethane	propane	n-but.	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
Dwnd	-25	0.17	0.10	0.09	0.09	0.22	0.59	0.77	0.21	0.05	0.45	0.15
Dwnd	-120	-0.01	-0.05	-0.38	-0.06	0.08	0.19	0.29	0.06	0.01	0.17	0.05
Dwnd	-240	-0.09	-0.13	0.06	0.04	0.04	0.11	0.13	0.04	0.00	0.11	0.04

D = distance from motorway. Dwnd = downwind site. Eth = ethene Prop = propene

Table 6.8 Background corrected values at downwind receptors for wind directions 345-135°

The –25m background corrected values for iso-butane and n-butane imply a slight source contribution from the M50, but this is contradicted by the spatial variation in concentrations of these compounds observed earlier. In Figure 6.6, the highest average concentrations were obtained at the upwind site nearest the road where there was a negligible M50 source effect, as evidenced by the nearly constant upwind concentrations displayed by the traffic-related compounds in Figures 6.7(a) and 6.7(b). The inconsistent trend in spatial concentrations observed for the butanes is more to blame for this suggested source effect rather than any obvious contribution from M50 road traffic emissions.

In Table 6.8 the seven traffic-related compounds again showed strong M50 source effects, with the background-corrected concentrations obtained at the receptor nearest the M50 being similar to those found for wind direction sector 165-315°. This is examined further in section 6.4.3, which analyses the M50 source effect irrespective of wind direction.

The slower average wind speeds lead to lower dispersion rates compared to that observed for wind direction sector 165-315°. On average concentrations are seen to decrease by 65% between the –25m and the –120m receptors, and by 81%, between the –25m and –240m receptors. These values are shown in Table 6.9, which gives the average background corrected

total HC values obtained at the 120m and 240m downwind receptors as a percentage of that obtained at the 25m downwind receptor. The higher dispersion rate observed for wind direction sector 165-315° can be explained in terms of the difference in average wind speeds observed for both sectors where higher average wind speeds produce greater dilution rates.

Wind direction sector	Average wind speed (m /s)	% reduction at 120m downwind receptor	% reduction at 240m downwind receptor
165-315°	1.28	92%	100%
345-135°	0.8	65%	81%

Table 6.9 Difference in average Total HC dilution rates for each sector compared to difference in average wind speeds for each sector

6.4.2.3 Correlation matrices for upwind and downwind receptors

Tables 6.10 and 6.11 present correlation matrices for upwind and downwind receptors, respectively.

	ethane	propane	n-but	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
ethane	1.00	0.66	0.13	0.26	0.68	0.67	0.61	0.65	0.42	0.28	0.64
propane	0.66	1.00	0.47	0.67	0.85	0.82	0.82	0.89	0.64	0.72	0.86
n-butane	0.13	0.47	1.00	0.94	0.34	0.39	0.45	0.31	0.51	0.16	0.29
i-butane	0.26	0.67	0.94	1.00	0.53	0.57	0.61	0.52	0.64	0.34	0.49
n-pentane	0.68	0.85	0.34	0.53	1.00	0.98	0.80	0.86	0.78	0.69	0.93
i-pentane	0.67	0.82	0.39	0.57	0.98	1.00	0.77	0.84	0.83	0.65	0.92
ethene	0.61	0.82	0.45	0.61	0.80	0.77	1.00	0.92	0.60	0.82	0.85
propene	0.65	0.89	0.31	0.52	0.86	0.84	0.92	1.00	0.73	0.73	0.85
1,3 but.	0.42	0.64	0.51	0.64	0.78	0.83	0.60	0.73	1.00	0.46	0.71
acetylene	0.28	0.72	0.16	0.34	0.69	0.65	0.82	0.73	0.46	1.00	0.82
benzene	0.64	0.86	0.29	0.49	0.93	0.92	0.85	0.85	0.71	0.82	1.00

eth = ethene prop = propene, acet = acetylene, benz = benzene

Table 6.10 Correlation matrix between upwind receptors for wind direction 345-135°

	ethane	propane	n-but	iso-but	n-pent	iso-pent	eth	prop	1,3 but	acet	benz
ethane	1.00	0.88	0.43	0.56	0.88	0.86	0.86	0.87	0.79	0.82	0.84
propane	0.88	1.00	0.52	0.62	0.90	0.91	0.84	0.79	0.79	0.82	0.86
n-butane	0.55	0.64	1.00	0.95	0.41	0.54	0.46	0.36	0.38	0.45	0.53
i-butane	0.72	0.82	0.95	1.00	0.52	0.65	0.62	0.55	0.54	0.61	0.62
n-pentane	0.88	0.90	0.41	0.52	1.00	0.99	0.90	0.88	0.83	0.86	0.94
i-pentane	0.86	0.91	0.54	0.65	0.99	1.00	0.92	0.89	0.85	0.88	0.95
ethene	0.86	0.84	0.46	0.62	0.90	0.92	1.00	0.98	0.92	0.87	0.96
propene	0.87	0.79	0.36	0.55	0.88	0.89	0.98	1.00	0.91	0.81	0.94
1,3 but.	0.79	0.79	0.38	0.54	0.83	0.85	0.92	0.91	1.00	0.80	0.89
acetylene	0.82	0.82	0.45	0.61	0.86	0.88	0.87	0.81	0.80	1.00	0.87
benzene	0.84	0.86	0.53	0.62	0.94	0.95	0.96	0.94	0.89	0.87	1.00

Eth = ethene Prop = propene

Table 6.11 Correlation matrix between downwind receptors for wind directions 345-135°

For the seven HC compounds (n-pentane to benzene) strongly related traffic emissions, the same trend is seen for this wind direction sector, as that observed for westerly winds. The correlations between the different HC compounds are generally good, with as expected, an improvement for downwind conditions.

The exception is the behaviour of 1,3 butadiene on the upwind side of the M50. This compound is seen to correlate very poorly with ethene and acetylene, the two compounds most strongly associated with traffic emissions. This is probably due to the relatively high chemical activity of 1,3 butadiene. It is the most reactive of the HC compounds being monitored and has an atmospheric lifetime of between 20 minutes and 3 hours (Dollard *et al*, 2001). The conditions observed during the monitoring period associated with these wind directions, of relatively high temperatures, allied to relatively little cloud cover (significant cloud cover observed on only 2 occasions) are conducive to increased photochemical activity.

Further credence is added to the above explanation by the correlation of 1,3 butadiene with the other six strongly related traffic compounds for downwind receptors, where correlations are much improved (Table 6.11), relative to upwind values (Table 6.10). The downwind values are much greater due to photochemical activity playing a negligible role in degrading the 1,3

butadiene emissions from the M50 in the time taken for the pollutants to disperse to the furthest downwind receptor.

Additional evidence for increased photochemical activity associated with this wind direction is obtained by comparing the upwind (background) concentrations of 1,3 butadiene for both wind direction sectors. Table 6.12, presents these values.

	Ethane	Propane	n-but	i-but	n-pent	i-pent	Ethene	Prop	**1,3 but**	Acetylene	Benzene	Total average (ppbv)
Upwind conc. 345-135°	1.81	1.08	1.52	0.50	0.23	0.49	0.81	0.27	**0.06**	0.72	0.26	0.70
Upwind conc. 165-315°	1.39	0.79	0.67	0.24	0.12	0.26	0.46	0.15	**0.05**	0.44	0.16	0.43
Ratio	1.30	1.36	2.27	2.09	1.94	1.88	1.75	1.84	**1.19**	1.65	1.66	1.64

Table 6.12 Background concentrations (ppbv) relative to the M50 for both wind direction sectors, for 7 HC compounds strongly related to traffic emissions

Although the average wind speed for the wind direction sector 345-135° (0.8m/s) is much lower than that obtained for 165-315° (1.28 m/s), a corresponding increase in the average background 1,3 butadiene concentration is not observed, presumably because increased photochemical activity counterbalances the effect of low wind speeds. This ultimately leads to the 1,3 butadiene upwind (background) concentration for the wind direction sector 345-135°, being only 19% greater than that observed for the 165-315° sector, whereas an average increase of 64% is observed when all compounds are considered.

The remaining 4 alkane compounds are seen to behave slightly different for this wind direction sector. The correlations between ethane, the butanes and the seven more traffic-related compounds are again seen to be very poor for the upwind receptors, but ethane improves for the downwind receptors, verifying the small M50 source effect source effect displayed in Figure 6.6. The butanes correlate poorly with all compounds on both upwind and downwind sides of the M50, again suggesting contributions from a source other than road traffic emissions.

6.4.2.4 Effect of traffic flow and wind speed on background-corrected concentrations

As with wind direction sector 165-315°, a poor correlation was seen between traffic flow and background corrected ethene concentrations obtained at the receptor nearest the M50 on the downwind side (Figure 6.8). This is most likely due to the small deviation in traffic flow observed during the monitoring period. The negative concentration observed on the 11th August is due to inaccurate estimation of the background concentration, due to the highly variable, near parallel wind direction observed on this day.

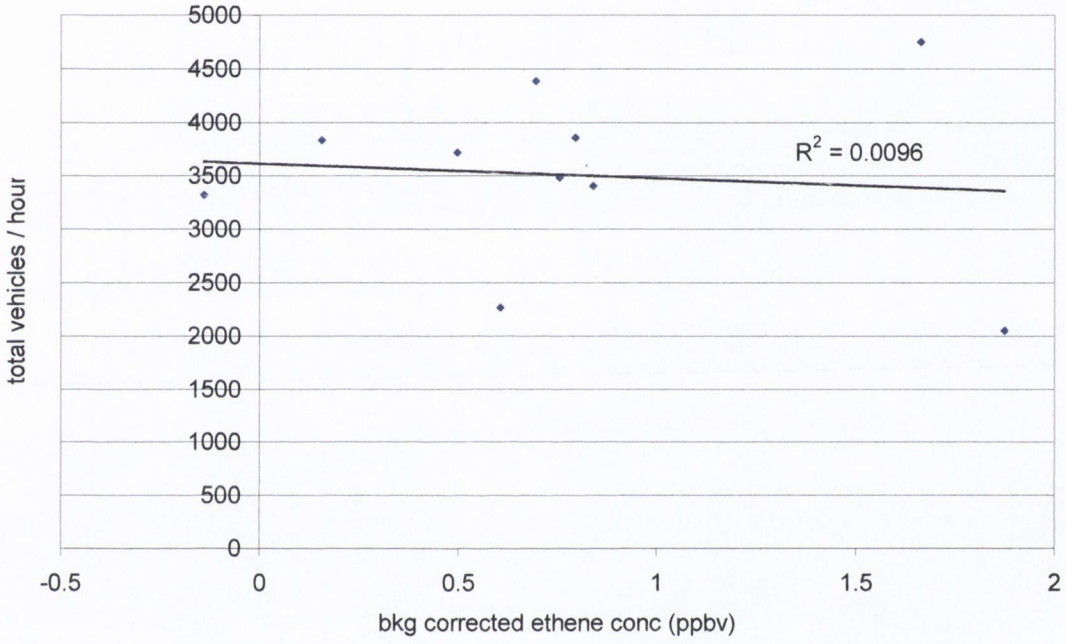


Figure 6.8 Scatter plot of background corrected 25m ethene concentration against total vehicles per hour for wind directions 345-135°

Figure 6.9 shows how the background corrected ethene concentrations were influenced by wind speed. The negative background-corrected values obtained on August 11th were omitted due to the uncertainty associated with the background estimation. The trend is not as pronounced as for wind sector 165-315° due to the lower wind speeds observed. Given the very limited sampling pool, the trend is as expected, with highest concentrations associated with lower wind speeds.

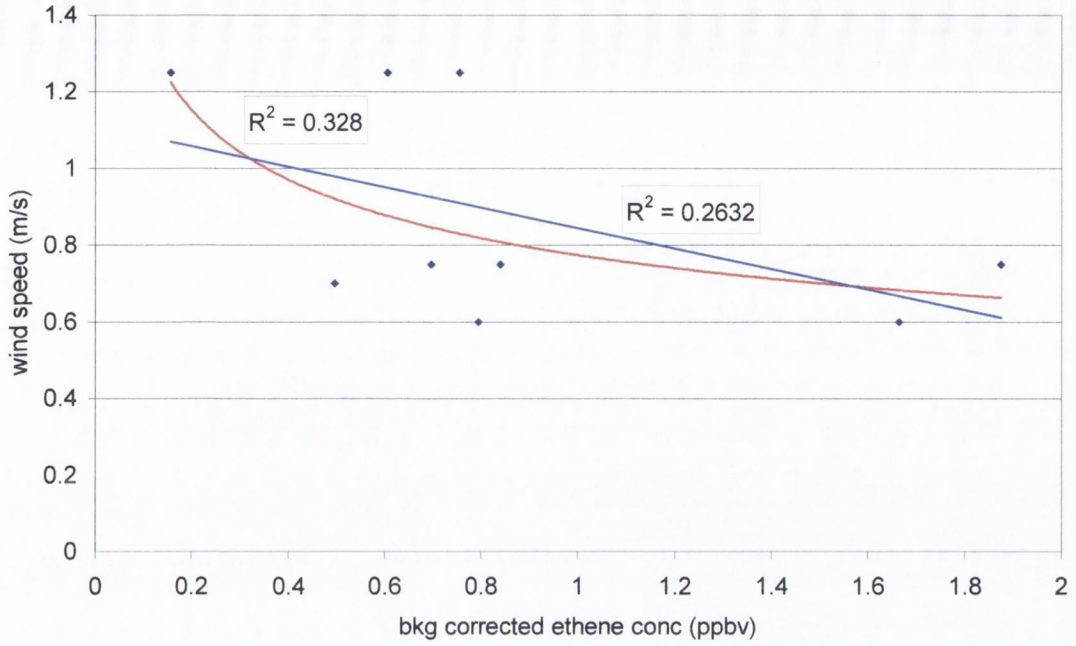


Figure 6.9 Scatter plot of background corrected ethene 25m concentrations against wind speed, showing linear and non-linear trend

6.4.3 M50 source effect regardless of wind direction

Table 6.13 compares and combines the background corrected values at the 25m downwind receptor for both wind sectors

	etha	propa	n-but	i-but	n-pent	i-pent	eth	prop	1,3 but	acet	benz
bkg corrected 25m(345-135°)	0.17	0.10	0.09	0.09	0.22	0.59	0.77	0.21	0.05	0.45	0.15
bkg corrected 25m(165-315°)	-0.04	-0.29	-0.08	-0.02	0.12	0.42	0.91	0.35	0.14	0.44	0.15
Average of both wind sectors[1]	0.07	-0.09	0.00	0.03	0.17	0.51	0.84	0.28	0.10	0.45	0.15

Bkg = background, dwnd = downwind, conc = concentration Etha = ethane, Propa = propane, eth = ethene, prop = propene, acet = acetylene
1 M50 effect regardless of wind direction

Table 6.13 Average background corrected concentrations (ppbv) at the downwind 25m receptor for both wind sectors

It could be expected that similar average background corrected downwind concentrations would be obtained close to the motorway for both wind direction sectors. This is seen to be the case for most compounds strongly related to traffic emissions for which average background

corrected values were very similar for both wind direction sectors. The exception being 1,3 butadiene, possibly due to the very low concentrations measured.

The average values for both wind sectors seen in Table 6.13 represent the M50 source effect observed at the 25m downwind receptor regardless of general wind direction, for the average traffic and meteorological conditions observed during the monitoring period. Ethene, acetylene and benzene show exceptional consistency regardless of general wind direction. The 4 alkanes constantly linked with minimal or no M50 traffic emissions (ethane to iso-butane) show relatively large differences with general wind direction, suggesting the M50 has a very limited impact on the concentrations obtained for these compounds.

The results obtained emphasise the need for an accurate estimation of background concentration if a local source effect is to be accurately quantified. Table 6.14 presents the upwind (background) concentrations of the traffic-related compounds, for both wind sectors, and compares these to the average source effect values given in Table 6.13. In most cases, the difference between the background values is of the same order as the source effect. Hence, assuming a constant background concentration which does not change with wind direction, will lead to large, over or underestimations of the source effect, on average ±49%.

	n-pent	i-pent	eth	prop	1,3 but	acet	benz	Averages
Avg 345-135° bkg	0.23	0.49	0.81	0.27	0.06	0.72	0.26	
Avg 165-315° bkg	0.12	0.26	0.46	0.15	0.05	0.44	0.16	
Diff. in bkg values	**0.11**	**0.23**	**0.35**	**0.12**	**0.01**	**0.28**	**0.10**	**0.17**
M50 source effect	**0.17**	**0.51**	**0.84**	**0.28**	**0.10**	**0.45**	**0.15**	**0.35**
% error (±)								**49%**

eth = ethene, prop = propene, acet = acetylene, benz = benzene

Table 6.14 Potential error in estimating M50 source effect by using incorrect background value

A very limited amount of studies have been carried out into the spatial variation of hydrocarbon concentrations in the vicinity of motorways, and where these studies have been carried out, the focus is primarily on the behaviour of benzene. To our knowledge, no other

study has investigated the short term (hourly), spatial behaviour of such a wide variety of traffic related hydrocarbons over a relatively long period of time, in particular ethene and acetylene, due to the inability to detect these compounds using sorbent tubes. Jannsen *et al.* (2001), reported how benzene concentrations decreased significantly with distance from traffic related sources, while Roorda-knape *et al.* (1998), found no such trend, where elevated benzene concentrations were only reported within 15 metres of the Motorway. A likely reason for the limited gradient observed in 1998 is, downwind concentrations observed at various distances from the motorway were not background corrected. Hence, a relatively large background could possibly absorb the downwind motorway source contribution within a relatively short distance.

6.5 ETHENE / ACETYLENE RATIO

At the M4 motorway in Leixlip (Chapter 5), relatively low ethene / acetylene (E:A) ratios were observed, suggesting a low % of active catalytic converters in the car fleet, or a high proportion of emissions emanating from vehicles without catalytic converter technology installed.

However, estimated percentage's of Irish petrol vehicles with catalytic converters installed (95%), suggests that a higher value for this ratio should have been expected. To investigate possible reasons for the low E:A ratio obtained at the M4, its spatial variation in this ratio at the M50 motorway site is considered, to elucidate if distance travelled from the source impacted on the ratio obtained. The trends observed for both wind direction sectors were similar. Figures 6.10(a), 6.10(b) show the spatial variation in the E:A ratio for wind directions 165-315° and 345-135° respectively, while Figure 6.10(c) illustrates the overall spatial trend regardless of wind direction. As discussed in the preceding chapter a ratio close to three indicates a high percentage of active catalytic converters in the sampled fleet, whereas a value nearer 1 suggests limited catalytic converter activity. The ratio observed at the 25m downwind receptor in Figure 6.10(a), is a significant improvement on the average values observed at Leixlip, but is still someway short of the ideal value of 3. Apart from the higher ratio observed at the receptor nearest the M50, Figure 6.10(a) displays a rapid decrease in E:A ratio with increasing distance from the M50 source. Within 240m downwind, the compounds are seen to disperse down to background concentrations, and an E:A ratio of just 1.1 is obtained.

Although ethene is emitted from road traffic at a higher rate extent than acetylene (see composite emissions factors estimated with the aid of COPERT in section 6.7.4), the background concentrations of both compounds are very similar. This is due to their different atmospheric lifetimes, only two days for ethene (Atkinson, 1995) as opposed to approximately 2 months for acetylene (Kanakidou *et al.*, 1988). Due to these similar background values, the E:A ratio decreases from its originally emitted value down to approximately 1 within 240m, for the average wind speed of 1.28m/s associated with this wind sector. Figure 6.10(b) illustrates the similar trend observed for wind direction sector 345-135°, though the peak ratio obtained at the downwind receptor nearest the M50 was 1.35, slightly lower than that observed for the wind direction sector 165-315. The rate at which the ratio decreased was also lower due to the lower dispersion rates associated with the lower wind speeds observed for this wind sector (0.8m/s). As suggested in section 6.4.2.1, the effect of mechanical turbulence is verified by the increased E:A ratio observed at the upwind 25m receptor.

In an attempt to more accurately ascertain the E:A ratio due to emissions from the M50 traffic exclusively, the ratio was calculated for the background-corrected values obtained at the downwind receptor nearest the road. This more closely replicates conditions in tunnel or dynamometer studies. This yielded a much improved value of 2.1 for wind sector 165-315°, and 1.7 for 345-135°. The overall average value of 1.9 is much nearer the ideal value of three and gives better indicator as to the extent of active catalytic converters in the Irish car fleet. These results indicate how background concentrations affect the catalytic converter efficiency ratio, and suggests that background corrected ratios obtained as near to the source as possible will yield the most accurate indicators of catalytic converter activity. In contrast a background ratio of approximately 1 will be obtained when air is sampled far enough away from any major traffic source, the required distance depending on source strength and meteorological conditions. Hence, the validity of using the E:A ratio as an indicator of catalytic activity is questionable when widespread monitoring data is employed. In conjunction with distance from the source, atmospheric turbulence also affects the E:A ratio. The more turbulent the atmosphere the shorter the downwind distance required to dilute the ratio to its background level, as evidenced by Figure 6.10(b). Figure 6.10(c) shows the behaviour of the overall E:A ratio regardless of wind direction, obtained by calculating the average ratios for upwind and downwind receptors. This illustrates that for our study, the E:A ratio almost reached its

background level within 240m of downwind distance for an overall average wind speed of 1.1 m/s.

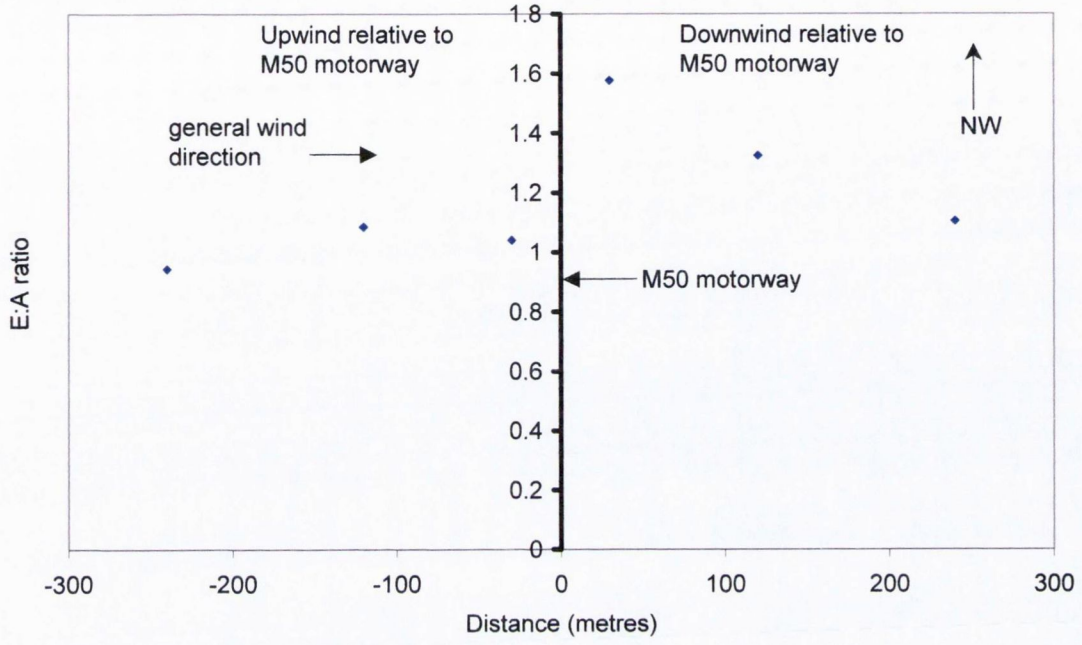


Figure 6.10(a) Spatial variation of E:A ratio for wind direction sector 165°-315°

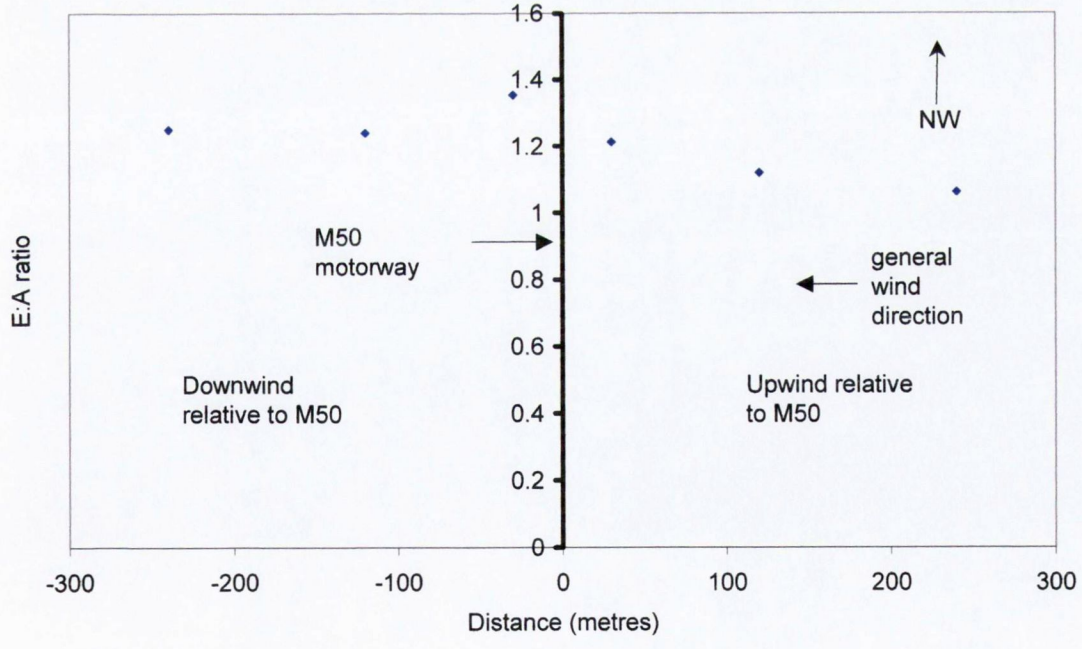


Figure 6.10(b) Spatial variation of E:A ratio for wind direction sector 345°-135°

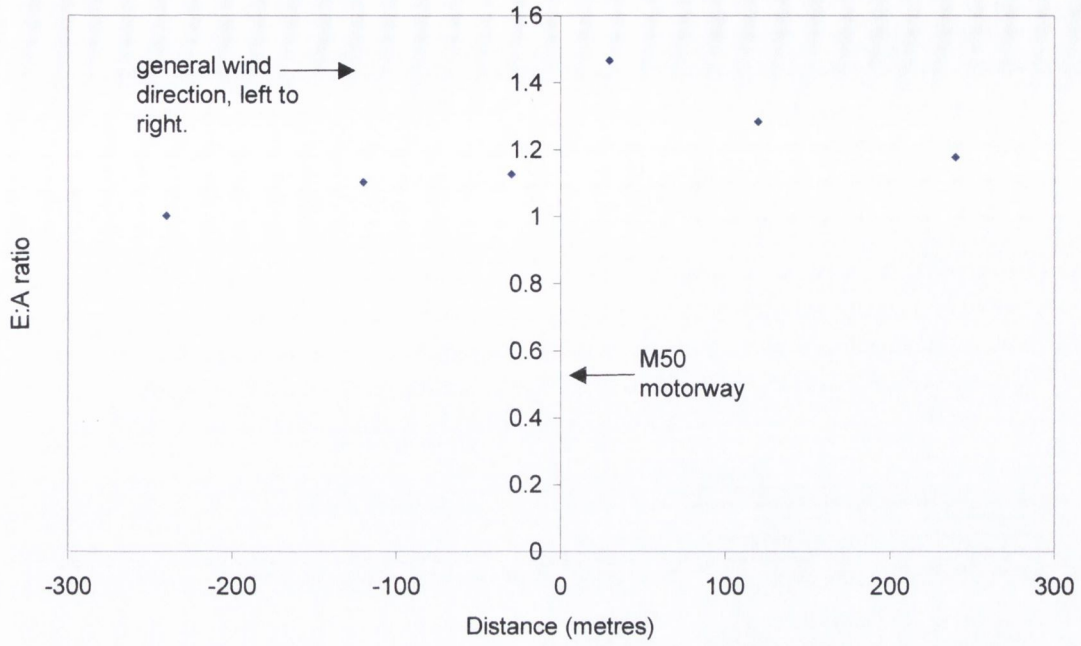


Figure 6.10(c) Overall spatial variation of E:A ratio regardless of wind direction

However, the E:A ratio can still be used as a relative indicator of catalytic converter activity at different locations. By sampling concurrently at different sites where receptors are similar distance from source and where meteorological effects are also similar (same regional conditions), the ratios obtained can be compared and used as indicators of relative catalytic converter activity at the different sites. Alternatively, the E:A ratio obtained at a single site can be used to indicate the relative importance of local traffic emissions at different times. Once the background ratio is known, the E:A ratio can be used to exclude occasions when the observed concentrations are not traffic related, allowing the analyst to focus on data associated with local traffic emissions.

Without the validated portable sampling method applied to this study, it would have been very difficult to establish the spatial variation of the E:A ratio, the main obstacles being the absence of diffusion tubes capable of sampling these very low molecular weight compounds (Wang *et al.*, 2004), and the expense associated with canister sampling.

6.6 EVAPORATIVE EMISSIONS

The amount of useful information which can be extracted from data relating to evaporative emissions is very limited for the M50 monitoring period due to the relatively constant temperature observed. Temperatures varied between 12.0°C and 19°C, with an average of 16.6°C.

In related sections on evaporative emissions in Dublin city (Chapter 7) and the M4 motorway site (Chapter 5), the HC / acetylene ratio was used to investigate the contribution of each compound to total evaporative emissions. The correlation between changes in the HC / acetylene ratio and temperature was indicative of each hydrocarbon's evaporative emission rate. Such correlation analysis was not possible with data from the M50 site due to the aforementioned limited range of temperature. However, in additional analysis in Chapters 5 and 7, iso-pentane was observed to be most strongly associated with evaporative emissions, hence this compound was investigated here also. Table 6.15 presents the average upwind and three downwind iso-pentane / acetylene ratios for both main wind directions.

	iso-pentane / acet (345-135°)	iso-pentane / acet (165-315°)
Avg Upwind ratio	0.72	0.62
Avg 25 metre downwind ratio	0.85	0.76
Avg 120 metre downwind ratio	0.76	0.56
Avg 240 metre downwind ratio	0.79	0.48

Table 6.15 Average iso-pentane / acetylene ratio at each receptor for both wind directions 345-135° and 165-315°

The higher ratios noticed at the 25 metre receptors are likely due to running evaporative losses from traffic on the M50. However, these higher values are a result of one days elevated ratio for each wind direction. If these two days of extremely high ratios are excluded from analysis (one for each wind sector), the 25 metre ratios drop to levels below the average upwind ratio. The higher ratios seen on these two days are probably related to evaporative emissions from poorly maintained pre-euro1 vehicles, with limited evaporative control technology installed.

The higher ratios for wind direction sector 345-135° are most likely due to evaporative emissions emanating from Dublin City and surrounding suburbs, which are associated with this general wind direction. The overall ratios obtained at all six receptors for either wind direction sectors, can be compared with those obtained for similar wind directions and temperatures obtained in Dublin City centre (chapter 7).To this end, data obtained at the M50 for wind sector 165-315° was compared with data obtained from the city centre, for sector 160-270°. Figure 6.11 shows the variation with temperature of the iso-pentane / acetylene ratio at the city centre. For the average temperature of 16.1°C pertaining at the M50 site, a ratio of 0.59 would be expected at the city centre, which is very close to the average value of 0.60 obtained at the M50.

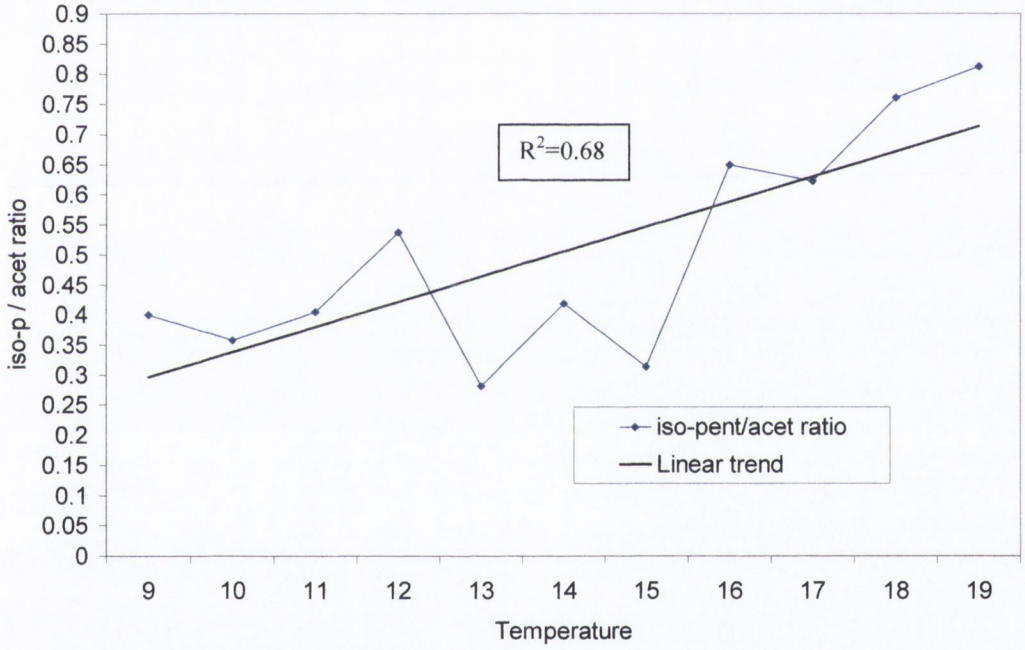


Figure 6.11 iso-pentane / acetylene ratios for wind directions 160°-270° for Dublin city data

The ratio observed for wind direction sector 345-135° at the M50 can be compared to that obtained for the 40-90° wind sector in Dublin city. For the corresponding average temperature of 17°C, the M50 ratio of 0.76 again compares well with that of 0.82 obtained in Dublin City. Although by no means conclusive, due to the limited amount of data obtained and the relatively limited temperature range observed, these comparisons suggest similar iso-pentane evaporation rates at both sites. Furthermore, the good agreement serves to verify the accuracy

of the ratios obtained at the M50. In order to ascertain to a greater extent, the evaporative emissions emanating from the M50, changes in HC / acetylene ratio would need to be evaluated over a much wider temperature range, with a far greater sampling pool than that available in this study. Each receptor would need to be evaluated on an individual basis, and the rate of increase in ratio with temperature determined for each receptor. This was not possible with the limited data set available here.

6.7 DISPERSION MODELLING

Due to the impracticality of continuous air pollution measurements on a wide scale, a large proportion of air pollution assessments utilise simulations of the dispersion of pollutants from a given source or sources to estimate concentrations at a receptor site. A vast array of mathematical models have been developed for this purpose and their applications include stack design, site selection and environmental impact assessments. In addition, as part of the EU quality framework directive, dispersion modelling has been specified as a key component in urban air quality assessment (European Commission, 1998). These models quantitatively simulate factors affecting the fate of pollutants in the atmosphere, namely (Zanetti, 1990): pollutant advection (transport), diffusion (migration of pollutant due to concentration gradient), deposition, chemical reactions (transformation) and emission. Plume rise and the aerodynamic effects of terrain are also modelled. The models vary in complexity from a simple line source gaussian approach to numerical solutions of fluid dynamic equations (Sharma and Khare, 2001). Many of the popular models for estimating pollutant concentrations from road traffic are based on the relatively straight-forward gaussian dispersion approach. This is not to condemn more sophisticated methods, but for most practical applications, the quality of the available emission and meteorological data does not justify the increased resources required to set up and run more complex models (Harrison, 2001). Accordingly, it is always important to evaluate the accuracy of dispersion models as applied to different pollutants, in different regions, and in different traffic situations. The spatial distribution of HC concentrations presented in the previous sections represent an ideal database for one such assessment, namely the ability of CALINE4 dispersion model to calculate the elevated concentrations of hydrocarbons that occur adjacent to a busy motorway during a relatively hot and calm period. The validation of this model for HC behaviour

contributed to a broader study analysing the models performance for NO_X, CO and particulate matter.

6.7.1 Composition of 2003 traffic fleet

Short term dispersion modelling usually requires information on the emissions of pollutants from the target source. To calculate representative composite emissions factors, up to date vehicle fleet statistics are required. This is especially important for hydrocarbon modelling, as the emissions of these compounds from new (Euro1, 2 and 3) cars are much lower than those from older vehicles. The most recent information which could be obtained on the total Irish car fleet related to both 2001 and 2002 (DELG, 2002; DELG, 2003). However, by analysing trends from these vehicle fleet publications, allied to a Central Statistics Office report (CSO, 2004) which outlines the number of vehicles registered for the first time in 2003, the total 2003 vehicle fleet was estimated. From the 2002 vehicle fleet report (DELG, 2003), the number of vehicles registered for the first time was compared with the overall increase in the fleet size for each year back to 1993. The difference between the two figures represented the amount of primarily older vehicles, replaced by new ones in that year. This was done for passenger cars (petrol and diesel) and goods vehicles (petrol and diesel LDVs and HGVs). Table 6.16 shows the trends observed for goods vehicles and passenger cars since 1993.

Year	No. pass. cars registered for the first time	Pass. car fleet increase	% of vehicles registered for the first time which replaced older vehicles	No. Goods vehicles registered for the first time	No. Goods vehicles fleet increase	% of Goods veh. registered for the first time which replaced older vehicles
2002	150485	63204	58%	28412	13559	52%
2001	160908	35454	78%	30622	14000	54%
2000	225269	50005	78%	33606	17000	49%
1999	170322	73000	57%	30066	18000	40%
1998	138538	62000	55%	23811	12000	50%
1997	125818	77000	39%	18895	12000	36%
1996	109333	67000	39%	16445	5000	70%
1995	82730	51000	38%	13790	6000	56%
1994	77773	48000	38%	12845	700	95%
1993	60792	33000	46%	9887	-9000	N/a

Table 6.16 Percent of passenger cars and goods vehicles registered for the first time, which replaced older vehicles

For passenger cars, the lower percentage of vehicles replacing older ones observed in the mid-nineties relates to the high level of economic growth observed during this period.

The number of cars registered for the first time has remained very high over the past 3 years, but a much higher percentage of these vehicles are replacing older ones. To estimate what percentage of passenger cars registered for the first time in 2003 replaced older vehicles, the average percentage obtained for 2000 to 2002 was applied (70%). The number of passenger cars registered in 2003 was 142,992 (CSO, 2004), therefore approximately 100,094 (70%) older passenger cars can be assumed to have been replaced.

For goods vehicles the trend was similar for each year back as far as 1993 and 1994. In 1993 more vehicles were taken out of the fleet than were registered for the first time, while in 1994 the two values were similar. Since then, average replacement rate over the eight years prior to 2002 was 50% and it was anticipated that the 2003 figures would not deviate greatly from this. Hence, given that 30532 goods vehicles were registered for the first time in 2003 (CSO, 2004), 15266 (50%) can be assumed to be replacing older goods vehicles.

To determine the age profile of the vehicles to be removed from the 2002 vehicle fleet to make up the 2003 vehicle fleet, the change in the age profile of the fleet between 2001 and 2002 was examined for both passenger cars and goods vehicles. For passenger cars, the number of cars of eight years old and older decreased according to the distribution shown in Figure 6.12. Table 6.17 illustrates how this distribution was used to allocate the spread of 100,094 passenger cars removed from the 2002 car fleet. The number of passenger cars registered for the first time in 2003 was then added to this modified 2002 fleet to obtain the 2003 car fleet, shown in Table 6.17.

The same methodology was applied for goods vehicles, where the distribution in Figure 6.13 was applied to allocate the spread of 15266 goods vehicles to be removed from the 2002 fleet. The number of goods vehicles registered for the first time in 2003 was then added to this modified 2002 fleet to obtain the 2003 goods vehicle fleet, shown in Table 6.18.

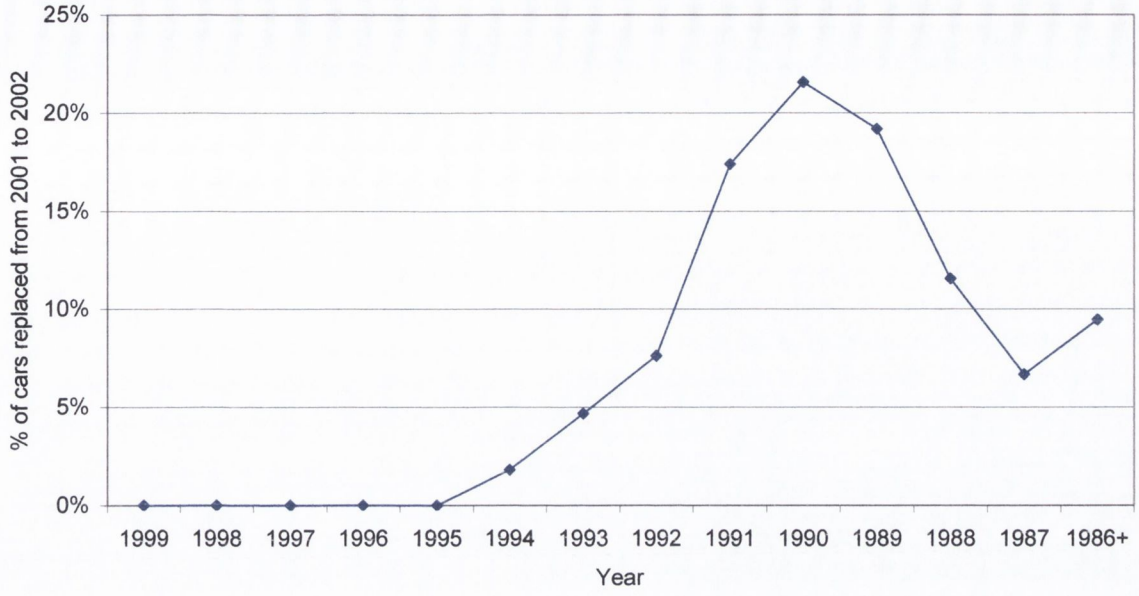


Figure 6.12 Percentage distribution of passenger cars replaced between 2001 and 2002

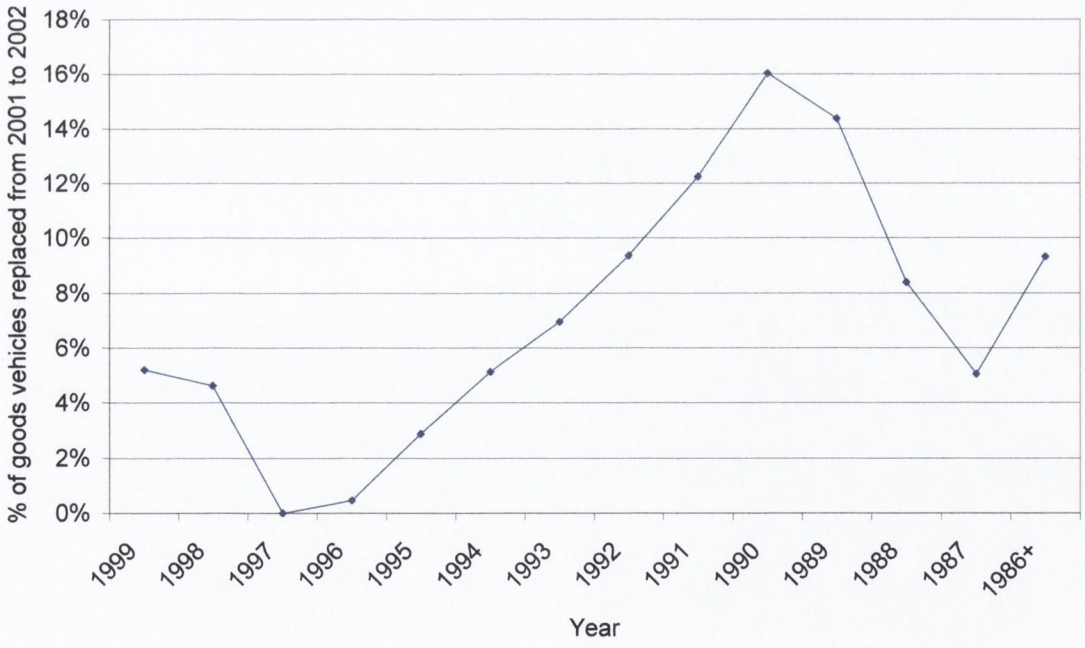


Figure 6.13 Percent distribution of goods vehicles replaced between 2001 and 2002

Year	2002 passenger car fleet	Percentage of cars removed from 2002 fleet	Number of cars removed from 2002 fleet	2003 passenger car fleet
2003	-	-	-	142992
2002	139000	0%	0	139000
2001	149000	0%	0	149000
2000	212000	0%	0	212000
1999	156000	0%	0	156000
1998	131000	0%	0	131000
1997	125000	0%	0	125000
1996	108000	0%	0	108000
1995 (8 year old)	85000	2%	2002	82998
1994	79794	5%	5005	74789
1993	63654	8%	8008	55646
1992	58529	17%	17016	41513
1991	45008	22%	22021	22987
1990	39416	19%	19018	20398
1989	23000	12%	12011	10989
1988	12654	7%	7007	5647
1987+	17300	9%	9008	8292
total	1444355		100094	1486252

Table 6.17 Changes to 2002 passenger car fleet, to estimate 2003 fleet

Year	2002 Goods vehicle fleet	Percentage of Goods vehicles removed from 2002 fleet	Number of Goods vehicles removed from 2002 fleet	2003 Goods vehicle fleet
2003	-	-	-	30532
2002	26019	0%	0	26019
2001	27382	0%	0	27382
2000 (3 year old)	30996	5%	793	30203
1999	26251	5%	706	25545
1998	21823	0%	0	21823
1997	17497	<1%	69	17428
1996	15515	3%	441	15074
1995	13370	5%	783	12587
1994	11427	7%	1061	10366
1993	8878	9%	1428	7450
1992	7790	12%	1870	5920
1991	7294	16%	2448	4846
1990	7275	14%	2192	5083
1989	4985	8%	1279	3706
1988	2650	5%	772	1878
1987+	3921	9%	1423	2498
total	233073		15266	248339

Table 6.18 Changes to 2002 goods vehicle fleet, to estimate 2003 fleet

In conjunction with passenger vehicle age, the 2002 fleet information (DELG, 2003) also covers passenger car engine size distributions for vehicles of all ages in the 2002 fleet. Although the number of passenger cars of a certain age differs between 2002 and 2003 (Table 6.17), the percentage distribution of cars of specific engine size was assumed to remain the same. The percentage of passenger cars with engine sizes less than 1.4 litre, between 1.4 and 2.0 litre and greater than 2.0 litre, for each year, obtained from the 2002 fleet, were applied to the 2003 fleet figures in Table 6.17. The engine size distributions of vehicles registered for the

first time in 2003 were assumed to be the same as those given in 2002. This engine size categorisation included both diesel and petrol engines. To segregate the different fuel types, the average percent diesel cars in the passenger fleet registered for the first time over the previous 6 years (1996-2002) was calculated, and this 12% value was removed from each years total passenger cars at a split of 90:10 from cars between 1.4L –2.0L and greater than 2.0L respectively (the number of diesel vehicles of engine size less than 1.4 litre was assumed to be negligible). Table 6.19 shows the distribution of petrol and diesel cars in the 2003 fleet.

For goods vehicles the number and age of petrol LDVs (<3.5T), diesel LDVs (<2.5T and 2.5-3.5T) and HGVs (3.5-7.5T, 7.5-16T and >16T) were required.

All petrol goods vehicles were assumed to be petrol LDVs, and using the percentages in the 2001 and 2002 goods vehicle fleets, and continuing the trend of decreasing their percentage in proportion with that observed from 2001 (1.9%) and 2002 (1.5%), an LDV percentage of 1.2% was estimated for the 2003 goods fleet. This corresponds to 2975 petrol LDVs in the 2003 fleet. As both the number and percentage of these vehicles is seen to be decreasing, it was assumed that a higher proportion of these vehicles are older, hence the age profile of the 2975 vehicles was assumed to be evenly distributed from 2003 to pre-1987, with 175 petrol LDVs assumed for each year. This value of 2975 was subtracted from the total number of goods vehicles in 2003 to obtain the number of diesel goods vehicles.

For the remaining goods vehicles, the total number of vehicles of a particular age in the 2002 fleet was presented separately from the total unladen weight distributions in the 2002 fleet. Unlike the passenger car information, the age profile of goods vehicles in the 2002 fleet was not subdivided into separate unladen weight categories (equivalent to engine sizes for passenger cars). The percentage of each goods vehicle category to be applied to the age profile of the 2003 fleet (Table 6.20), was therefore obtained from the percentage of each category in the total 2001 and 2002 fleet, by assuming that the relative proportions in each category are the same for each individual year as in the total fleet. From this, 83% were estimated to be diesel LDVs less than 2.5 Tonne, 2.6% LDVs between 2.5 and 3.5 Tonne, 4.4% HGVs between 3.5 and 7.5 Tonne, 9.3% HGVs between 7.5 and 16 Tonne and 0.3% HGVs of greater

unladen weight than 16 Tonne. Table 6.20 shows the resulting estimated goods vehicle fleet for 2003.

Year	Number of diesel passenger cars (12% of each years total)	Number of petrol passenger cars <1.4L	Number of petrol passenger cars 1.4 - 2.0L	Number of petrol passenger cars >2.0L
2003	17159	82935	36034	6864
2002	16680	69500	47538	5282
2001	17880	77480	46488	7152
2000	25440	137800	47064	1696
1999	18720	99840	25272	12168
1998	15720	74670	35632	4978
1997	15000	80000	27750	2250
1996	12960	66960	25056	3024
1995	9960	45649	25065	2324
1994	8975	38890	24830	2094
1993	6678	29493	18475	1002
1992	4982	22417	12952	1162
1991	2758	13333	6712	184
1990	2448	10199	5140	2611
1989	1319	6923	2549	198
1988	678	3671	1197	102
1987+	995	5307	1758	232
Total	178350	865066	389513	53322

Table 6.19 estimated 2003 passenger car fleet

Year	Petrol LDVs <3.5T	Diesel LDVs, <2.5T (83% of each year)	Diesel LDVs, 2.5-3.5T (2.6% of each year)	Diesel HGVs, 3.5-7.5T (4.4% of each year)	Diesel HGVs, 7.5-16T (9.3% of each year)	Diesel HGVs >16T 0.3% of each year
2003	175	25196	789	1336	2823	91
2002	175	21451	672	1137	2403	78
2001	175	22582	707	1197	2530	82
2000	175	24923	781	1321	2793	90
1999	175	21057	660	1116	2359	76
1998	175	17968	563	953	2013	65
1997	175	14320	449	759	1604	52
1996	175	12366	387	656	1386	45
1995	175	10302	323	546	1154	37
1994	175	8459	265	448	948	31
1993	175	6038	189	320	677	22
1992	175	4768	149	253	534	17
1991	175	3877	121	206	434	14
1990	175	4073	128	216	456	15
1989	175	2930	92	155	328	11
1988	175	1414	44	75	158	5
1987+	175	1928	60	102	216	7
Total	2975	203652	6379	10796	22819	736

Table 6.20 estimated 2003 Goods vehicle fleet

6.7.2 Calculation of composite emissions factors

COPERT3 (Computer Programme to calculate Emissions from Road Traffic), is an emission model developed by the European Environment Agency (Ntzaichristos and Samaras, 2000; Kouridis *et al.*, 2000), to estimate emissions of a wide range of pollutants from road transport.

The emission equations and methodology of this programme can be applied to estimate the composite emission factors for the hydrocarbons of interest. The methodology covers a wide range of vehicles, divided into five primary categories, and sub-divided by model year, emission-reduction technology, engine volume, weight, fuel type etc. Methods to calculate hot (exhaust), cold start and evaporative emissions are outlined, each of which is considered below.

Composite emission factors were only estimated for compounds which showed a strong M50 source effect, as modelling was only carried out for compounds which were strongly traffic related. This excluded ethane, propane, n-butane and iso-butane.

Hot (exhaust) emissions

Tables 6.21 and 6.22 summarise the equations used to estimate hot (exhaust) emissions for uncontrolled (pre-Euro 1) and controlled (Euro 1 and later) passenger cars and goods vehicles. Also included is the emission reduction percentages to be applied to post-Euro1 passenger cars and post-conventional HGVs. As the number of 1987 or older passenger cars in the 2003 fleet is so small, it was assumed that the amount older than 1985 was insignificant and hence no passenger cars older than ECE-04 (1985-1991) were anticipated to contribute to the average emissions rate.

	Petrol passenger cars			Diesel cars
Engine size	<1.4L	1.4-2.0L	>2.0L	N/A
ECE-04	$2.608 - 0.037V + 0.000179V^2$ (1985-1991)			$4.61V^{-0.937}$ (1985-1991)
Euro 1	$0.628 - 0.01377V + 8.52E\text{-}05V^2$ (1992-1996)	$0.4494 - 0.00888V + 5.21E\text{-}05V^2$ (1992-1996)	$0.5086 - 0.00723V + 3.3E\text{-}05V^2$ (1992-1996)	$0.1978 - 0.003925V + 2.24E\text{-}05V^2$ (1992-1995)
Euro 2 (reduction)	79% (1997-2000)	79% (1997-2000)	76% (1997-2000)	0% (1996-1999)
Euro 3 (reduction)	85% (2001-2004)	86% (2001-2004)	84% (2001-2004)	15% (2000-2004)

Table 6.21 Emission functions for passenger vehicles, where V is speed and results are in g/km of total VOCs

	Petrol LDVs	Diesel LDVs (<2.5T)	Diesel LDVs (2.5-3.5T)	HGVs (3.5-7.5T)	HGVs (7.5-16T)	HGVs (>16T)
Conv.	$6.77E\text{-}05V^2 - 0.117V + 5.4734$ (1985-1991)	Same as diesel pass. cars	$1.75E\text{-}05V^2 - 0.00284V + 0.2162$ (1985-1991)	$40.12V^{-0.8774}$ (1985-1991)		
Euro1	$5.77E\text{-}05V^2 - 0.01047V + 0.5462$ (1992-1995)	Same as diesel pass. cars	$1.75E\text{-}05V^2 - 0.00284V + 0.2162$ (1992-1995)	25% (1992-1995)	25% (1992-1995)	25% (1992-1995)
Euro2	76% (1996-1999)	Same as diesel pass.	0% (1996-1999)	30% (1996-1999)	30% (1996-1999)	35% (1996-1999)
Euro3	86% (2000-2004)	Same as diesel pass.	38% (2000-2004)	51% (2000-2004)	51% (2000-2004)	54.5% (2000-2004)

Conv. = conventional vehicles (uncontrolled)

Table 6.22 Emission functions for goods vehicles, where V is speed and results are in g/km of total VOCs

	Petrol engine (pre-euro1) %	Petrol engine (Euro 1) %	Diesel pass. and LDVs %	HGVs %
n-pentane	1.78	2.15	0.04	0.06
iso-pentane	4.86	6.81	0.52	-
ethene	8.71	7.3	10.97	7.01
propene	4.87	3.82	3.6	1.32
1,3 butadiene	1.42	0.91	0.97	3.3
acetylene	5.5	2.81	2.34	1.05
benzene	6.83	5.61	1.98	0.07

Table 6.23 contributions of hydrocarbons of interest to total hot emissions for each vehicle type

For each particular vehicle category, the total VOC hot exhaust emissions were calculated using the equations in Tables 6.21 and 6.22, and an average speed (V) of 100km/hr. The g/km of the hydrocarbons of interest were then calculated from the contribution of each compound to the total VOC mix, outlined in COPERT3 and summarised for each vehicle type in Table 6.23. From Tables 6.21, 6.22 and 6.23, the 2003 traffic fleet and the estimated annual kilometres travelled for each vehicle type (obtained from Department of the Environment statistics ; Reynolds, 2000), the weighted emissions factors for each vehicle type were estimated, from which the overall emission factors for hot exhaust emissions were calculated as per the methodology outlined in COPERT3 (Ntzaichristos and Samaras, 2000) and presented in Table 6.24.

The accuracy of these composite exhaust emission factors were estimated by comparing them with those calculated using data from the UK National Atmospheric Emissions Inventory (NAEI) (www.Naei.org.uk/other/vehicle_emissionsv7.xls). The composite emissions factors could only be compared for benzene and 1,3 butadiene (Table 6.24).

Agreement between the COPERT3 and NAEI estimations using the 2003 vehicle fleet are very good, the difference due to the method of calculating Euro2 and Euro3 emission factors. The NAEI emissions factors for these vehicles are based on test results, whereas the COPERT3 values are based on legislative reduction requirements for post-Euro1 vehicles.

Cold start emissions

Heeb *et al.* (2001), outlines that 90% of cold start emissions from Euro1 and 2 cars are emitted within the initial 1.6km travelled, and within 0.5km for Euro3 cars. These three vehicle types make up the vast majority of the 2003 fleet, and as the minimum travel distance to reach the motorway sampling point is 1.8km (Glenview estate, Tallaght), cold start emissions can be assumed to be negligible. Heeb *et al.* (2001), also cites that cold start emissions are not significant from Motorway driving and Ntzaichristos and Samaras (2000), outline in the COPERT3 methodology that cold start emissions are in the main confined to urban driving conditions. As a result, the equations in COPERT3 do not cater for cold start emissions, given that the average motorway driving speed is 100km/hr and, the highest speed for which cold start emissions can be estimated is 45km/hr. Finally, the ambient temperatures experienced during the study were unseasonably high, limiting further the possibility of significant cold start emissions. For these reasons cold start emissions were assumed to be minimal and not considered during this study.

Evaporative emissions

Evaporative emission factors were estimated with the aid of COPERT3. Of the hydrocarbons of interest only iso-pentane, n-pentane and benzene are assumed by COPERT3 to contribute to evaporative emissions. Of total evaporative emissions, 25% are estimated to be from iso-pentane, 15% n-pentane and 1% benzene. As per the COPERT methodology, only petrol vehicles are assumed to contribute significant evaporative emissions.

Running evaporative losses were the only form of evaporative emissions considered to be significant at the M50 site. Hot soak emissions are by definition related to periods when the engine is turned off and diurnal emissions relate to the change in ambient temperature over the course of the day, anticipated to be at their highest at midday and therefore minimal during the early morning sampling time implemented in this study.

According to COPERT3, the evaporative emissions are not dependant on engine size but are divided according to the technology used to control evaporative emissions (Euro1 and pre-Euro1). As evaporative emissions are mainly dependant on ambient temperature, evaporative running losses were estimated on a daily basis.

The overall COPERT equation used to estimate the running loss evaporative emissions is:

$$R = M_j [p(e^{HOT}) + w(e^{WARM})] \quad (6.1)$$

Where,

R = hot and warm running evaporative losses,

p = fraction of trips finished with hot engine,

w = fraction of trips finished with cold or warm engines, or with catalyst below light off temperature. (engines are defined as cold or warm if the water temperature is below 70°C).

Mj = total annual kilometres travelled by petrol powered vehicles of category j,

e^{HOT} = emission factor of HC for hot running losses for vehicles of category j,

e^{WARM} = emission factor of HC for warm running losses for vehicles of category j.

As 100% of trips were assumed to finish with hot engines, giving maximum estimates for evaporative losses, the equation simplifies to :

$$R = Mj (e^{HOT}), \quad (6.2)$$

where e^{HOT} for uncontrolled vehicles (pre-euro 1) is estimated from :

$$e^{HOT} = 0.136 (\exp^{[-5.967 + 0.4259 (RVP) + 0.1173 (t)]}), \quad (6.3)$$

and,

RVP = Reid Vapour Pressure (Kpa), where a value of 60 Kpa was used (Summertime EU fuel quality standard limit value).

t = ambient temperature (°C).

e^{HOT} for controlled vehicles (euro1 and later) = 0.1 [e^{HOT} (uncontrolled)]

As the ambient temperature varied slightly throughout the monitoring period, separate running loss emissions (R) were calculated for each day of monitoring. The resulting value for R was weighted in proportion to each vehicle category's contribution to the total annual kilometres travelled by petrol vehicles in the 2003 fleet. The summation of these individual contributions gave the running loss evaporative emission factor for total VOCs for the 2003 fleet, 25%, 15% and 1% of which were attributed to iso-pentane, n-pentane and benzene respectively.

As only petrol vehicles are considered, the daily evaporative emissions were multiplied by 0.76, corresponding to the contribution of petrol vehicles (76%) to the overall fleet kilometres travelled.

Composite emissions factors

The daily estimates of evaporative losses (Table 6.25) for the three evaporative compounds were added to the exhaust emission factors to compute daily composite emission factors. Evaporative emissions have a strong influence on composite emission factors for iso-pentane and n-pentane but not on that for benzene. For the remaining compounds, the composite emission factors were simply the hot exhaust emission factors (Table 6.24).

Hydrocarbon	COPERT3 exhaust emission factors (g/km)	NAEI exhaust emission factors (g/km)
n-pentane	0.00096	-
iso-pentane	0.00287	-
ethene	0.00552	-
propene	0.00245	-
1,3 butadiene	0.00110	0.00151
benzene	0.00303	0.00332
acetylene	0.00202	-

Table 6.24 Hot (exhaust) emission factors using COPERT3 and NAEI data, composite emissions factors for ethene, propene, 1,3 butadiene and acetylene (no fuel evaporation)

Date	n-pentane		iso-pentane		benzene	
	Daily evap. running losses (g/km)	Daily composite emission factor (g/km)	Daily evap. running losses (g/km)	Daily composite emission factor (g/km)	Daily evap. running losses (g/km)	Daily composite emission factor (g/km)
16/07/03	0.00199	0.00295	0.00332	0.00619	0.00013	0.00316
17/07/03	0.00140	0.00236	0.00233	0.00520	0.00009	0.00312
18/07/03	0.00082	0.00178	0.00137	0.00424	0.00005	0.00308
22/07/03	0.00199	0.00295	0.00332	0.00619	0.00013	0.00316
23/07/03	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311
24/07/03	0.00091	0.00187	0.00152	0.00439	0.00006	0.00309
25/07/03	0.00167	0.00263	0.00278	0.00565	0.00011	0.00314
28/07/03	0.00140	0.00236	0.00233	0.00520	0.00009	0.00312
29/07/03	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311
05/08/03	0.00199	0.00295	0.00332	0.00619	0.00013	0.00316
06/08/03	0.00199	0.00295	0.00332	0.00619	0.00013	0.00316
08/08/03	0.00167	0.00263	0.00278	0.00565	0.00011	0.00314
11/08/03	0.00140	0.00236	0.00233	0.00520	0.00009	0.00312
12/08/03*	0.00186	0.00282	0.00310	0.00597	0.00012	0.00315
13/08/03	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311
15/08/03	0.00199	0.00295	0.00332	0.00619	0.00013	0.00316
19/08/03	0.00082	0.00178	0.00137	0.00424	0.00005	0.00308
21/08/03	0.00058	0.00154	0.00096	0.00383	0.00004	0.00307
25/08/06	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311
26/08/03	0.00069	0.00165	0.00114	0.00401	0.00005	0.00308
27/08/03	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311
29/08/03*	0.00117	0.00213	0.00195	0.00482	0.00008	0.00311

* = day not modelled due to parallel wind directions, evap = evaporative.

Table 6.25 Daily evaporative running losses and daily composite emission factors (exhaust emissions factors + evaporative emission factors) for n-pentane, iso-pentane and benzene

To estimate the accuracy of these composite emission factors, the values given in Tables 6.24 and 6.25, normalised for differences in molecular weight (CEF / HC molecular weight) were compared to the average background corrected concentrations obtained nearest the M50 (Table 6.14).

These normalised values facilitate a graphical examination relationship between the CEFs and the average HC concentrations obtained at the downwind receptor nearest the M50. An ideal scatter plot would reveal a straight line with an R^2 value of 1. For the three compounds associated with evaporative emissions and hence daily varying composite emission factors, the average composite emission factors were employed. Figure 6.14 illustrates the results.

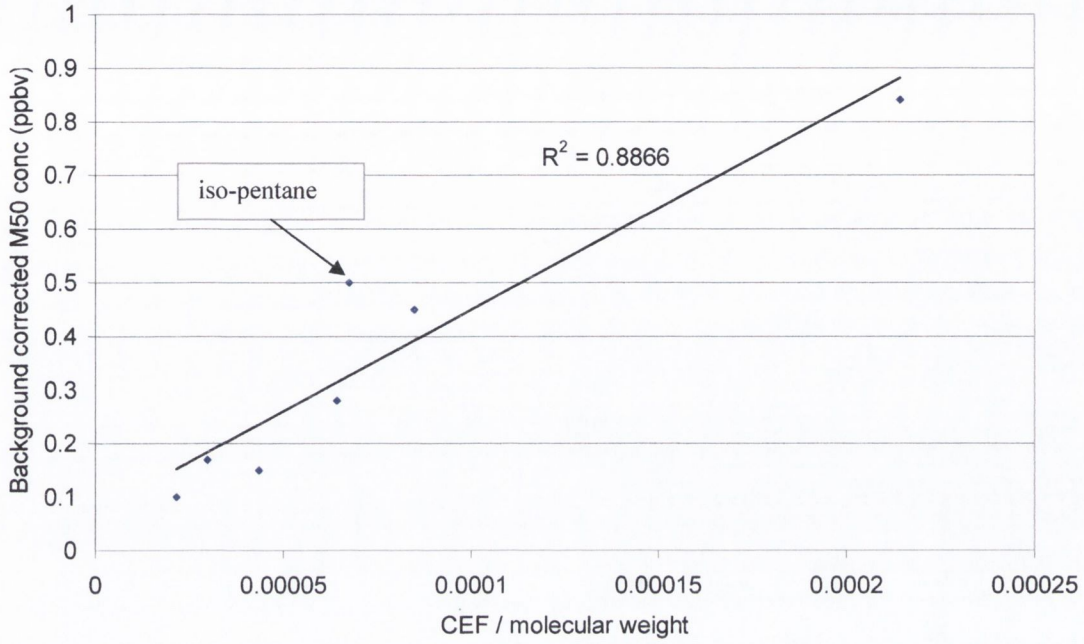


Figure 6.14 Average M50 background corrected concentrations against normalised composite emission factors (cef / molecular weight) for seven HC compounds strongly related to road traffic emissions on the M50

In Figure 6.14, iso-pentane deviates from the linear trend by the greatest amount, most likely due to an underestimation of the evaporative emissions in COPERT3, even-though no warm emissions were assumed and a maximum value for fuel RVP of 60kPa was assumed. The high probability of underestimating evaporative emissions was cited by Ntzaichristos and Samaras (2000) when using COPERT3. As a result this compound is excluded from the second scatter plot shown in Figure 6.15.

An improved R^2 value of 0.97 is obtained when iso-pentane is removed. The equation of the best fit line in Figure 6.15 was used to estimate the extent to which the CEF for iso-pentane has been underestimated. For a measured iso-pentane concentration of 0.5ppbv, a composite emission factor of approximately 0.0087 is estimated from the equation, equating to an underestimation of 44%. These findings lead to the observation that modelled concentrations for iso-pentane are also likely to be underestimated.

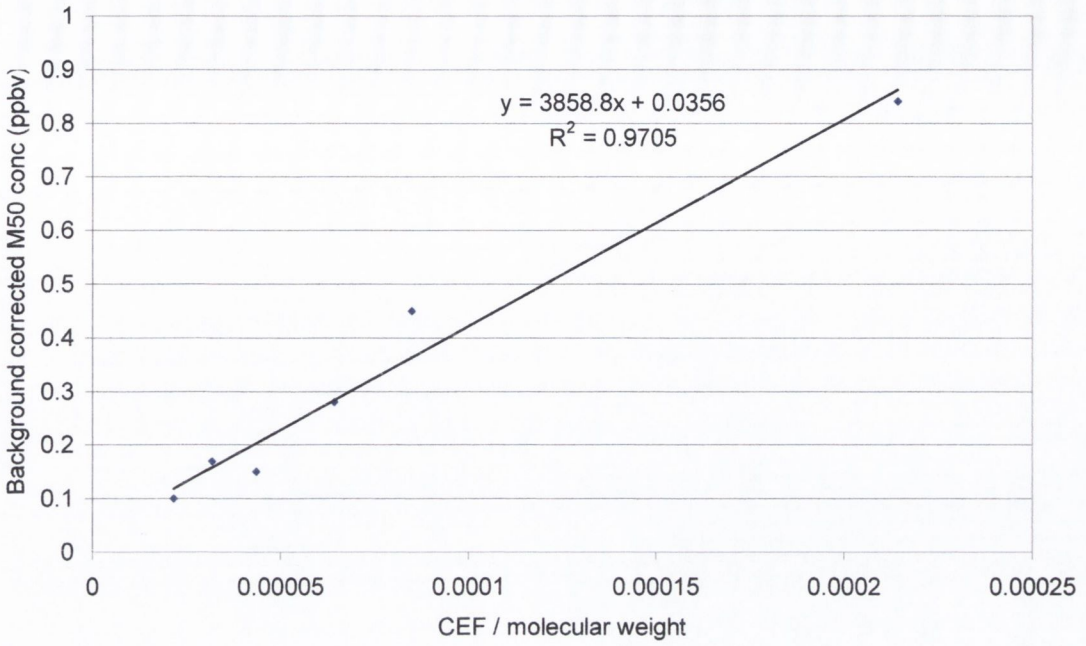


Figure 6.15 Scatter plot of average M50 background corrected concentrations against normalised composite emission factors (cef / molecular weight) for n-pentane ethene, propene, 1,3 butadiene, acetylene and benzene emissions from the M50

6.7.3 The gaussian dispersion equation

In the gaussian plume approach the expanding plume has a gaussian, or normal, distribution of concentration in the vertical (z) and lateral (y) directions, as shown in Figure 6.16 for the case of an elevated point source.

The concentration (C) at any point (x,y,z) assuming a perfectly reflecting surface, is given by (Harisson, 2001) :

$$C(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z u}\exp\left[\frac{-y^2}{2\sigma_y^2}\right]\left[\exp\left(-\frac{(z-H_e)^2}{2\sigma_z^2}\right)+\exp\left(-\frac{(z+H_e)^2}{2\sigma_x^2}\right)\right] \qquad (6.4)$$

where,

Q is the pollutant mass emission rate (in units of g / s for example),

u is the wind speed (m / s),

x, y, z are the along wind, cross wind and vertical distances,

H_e is the effective "stack" height, given by the "stack" height plus the plume rise due to buoyancy effects, σ_y and σ_z are a measure of the extent of plume growth and in the gaussian formalism are the standard deviations of the horizontal and vertical concentrations respectively in the plume.

The dispersion equation includes many assumptions which can result in significant inaccuracies in the resulting predictions. As a result, long term average concentrations can be predicted with a greater degree of accuracy than short term, hour by hour concentrations. The assumptions generally implied in the basic Gaussian model include (Arya, 1999) :

- continuous emissions at a constant rate,
- steady state flow and constant meteorological conditions,
- conservation of mass in the plume, even after reflection,
- 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,
- no wind shear in the vertical direction,
- windspeeds in the downwind direction which are strong enough to make turbulent diffusion in this direction negligible.

The most popular method for estimating the plume dispersion characteristics (σ_y and σ_z), 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 1 kilometre.

The limited data, collected in these experiments, on which the curves for calculating the diffusion parameters are based, also imply inherent inaccuracies (Arya, 1999). However, the ease with which stability classes can be calculated from standard meteorological data has resulted in the continued popularity of this method (Marnane, 2000).

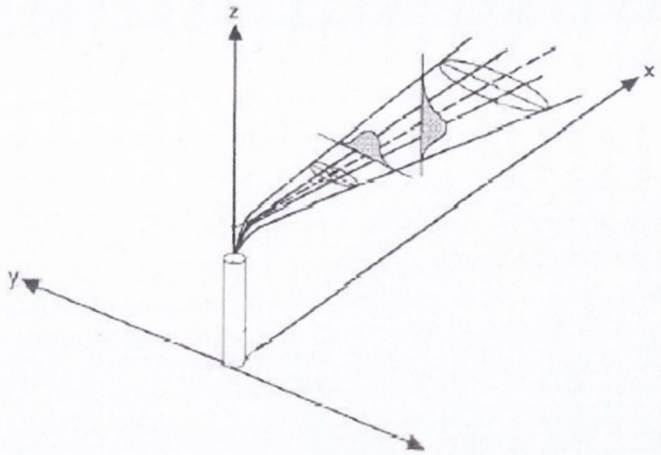


Figure 6.16 Gaussian plume distribution (Harisson, 2001)

6.7.4 CALINE4

One of the most well developed packages for the analysis of busy road pollution is CALINE4 (Benson, 1992) that has been designed by the California Department of Transportation, for the analysis of carbon monoxide pollution on the basis of knowledge of gaseous emission factors from stationary and moving vehicles (Gramotnev *et al.*, 2003). Along with CALINE3, it is one of the most widely applied models for highway dispersion problems.

CALINE4 is a computer based line-source gaussian dispersion model which uses semi-empirical solutions to the gaussian dispersion equation (Sharma and Khare, 2001). In addition to its applicability to carbon monoxide, it can be used to predict the concentrations of various other pollutants (NO_X, inert gases and particulates) in various road conditions including intersections, bridges and depressions (Marmur and Mamane, 2003).

The inputs for the package include: roadway geometry, meteorological parameters (wind speed, wind direction and its standard deviation and temperature), background concentration (concentration of the pollutant in the absence of the traffic on the considered road) in ppm, traffic volume (in vehicles per hour), and receptor positions. The program also requires

emission factors for vehicles on the road in grams per vehicle per mile (Gramotnev *et al.*, 2003).

The CALINE4 model represents roadway links as a series of elements with corresponding finite line sources (FLS). The pollutant concentration at a receptor location is estimated by summing the concentration contribution from each FLS. The CALINE4 model uses a parameterization scheme quite similar to CALINE3 for pollutant dispersion, and in general, CALINE3 and CALINE4 pollutant estimates are statistically similar (Held *et al.*, 2003). A comprehensive review of these models can be found elsewhere (Benson, 1979; Benson, 1984 and Benson, 1992).

At the heart of both CALINE models is the concept of a "mixing zone" that exists above the roadway where the intense mechanical turbulence, augmented by buoyancy, results in enhanced mixing of pollutants (Held *et al.*, 2003). The primary use of the mixing zone is to establish initial gaussian dispersion parameters at a reference distance near the edge of a roadway. The CALINE dispersion parameterizations are based in part on roadway geometry and wind direction. Downwind of the roadway edge, the CALINE model determines the gaussian dispersion parameters with modified Pasquill–Turner curves.

A CALINE roadway link is assigned an equivalent line source strength based on the product of a fleet-averaged vehicle emission factor (grams of pollutant per vehicle per mile travelled) and vehicle flow rate (vehicles per hour). The roadway link emissions are distributed to each element's FLS, which is centred on the midpoint of each element and oriented perpendicular to the mean wind direction. The length of each FLS is based on the wind direction, link width, and element length. Incremental downwind concentrations are calculated according to the cross-wind gaussian formulation for a line source of finite length (Marmur and Mamane, 2003):

$$C(x,y,0;H) = \frac{Q}{\pi\delta_Z u}\int_{Y_1=Y}^{Y_2-Y} \exp\left(\frac{-Y^2}{2\delta_Y^2}\right)dy \qquad (6.5)$$

where Q is lineal source strength; u is wind speed; σ_y and σ_z are horizontal and vertical gaussian dispersion parameters; and y_1, y_2 are finite line source endpoints y-co-ordinates ($y_1<y_2$). σ_y is estimated directly from the wind direction standard deviation and σ_z, using a method developed by Draxler (1976).

In this study, the CL4 interface was employed, which facilitates user input of the CALINE4 data required to calculate a single hours concentrations. The model was run using the traffic and meteorological data observed in each hour for which sampling took place. Although the CALINE4 model was developed to calculate the concentration of carbon monoxide, it can be employed to calculate the concentration of any inert pollutant by allowing for different molecular weights.

6.7.5 CALINE 4 Model results

When comparing measured concentrations to those estimated by the CL4 model emphasis was placed on those HC compounds which exhibited a strong M50 source effect, i.e. n-pentane, iso-pentane, ethene, propene, 1,3 butadiene, acetylene and benzene. To directly compare the actual M50 source effect to that predicted by the model, background corrected measurement results were compared to modelled results (in which background concentrations were assumed to be zero). When using this model the number of possible variables which can be changed are in the main limited to meteorological conditions, emission factors and traffic flow.

For this comparison, any negative background corrected measured value was assumed to be 0 (ie no contribution from the M50, as opposed to a negative one). This mainly affected measured results at the downwind 120m and 240m receptors, as on only one occasion were the 25m downwind concentrations below the background for that day. As a result slight differences can be seen between the background corrected measured values presented in section 6.4 and those in Appendix K.

Appendix K, Tables K.1 to K.7, present the daily modelled and background corrected results at each receptor for each day studied. The traffic flow, wind direction and wind speed data from Table 6.1 was used to model each days concentrations.

The results from CL4 are expressed as ppm CO. The emission factors given in Tables 6.24 and 6.25 for each HC were multiplied by 1000 in order to obtain an output concentration within the CL4 data format limit of 1 decimal place. Consequently, the result given by CL4 represents parts per billion.

To correct for the differences in molecular weight between the HC compounds and CO, a scaling factor was applied to the CO results to obtain the desired HC concentration. This was simply the ratio of CO molecular weight to the HC molecular weight for the compound of interest. Table 6.26 presents the scaling factors used.

Compound	Molecular weight (g)	Scaling factor
carbon monoxide	28	-
n-pentane	72.5	0.39
iso-pentane	72.5	0.39
ethene	28	0.99
propene	42	0.66
1,3 butadiene	54.1	0.52
benzene	78	0.36
acetylene	26	1.08

Table 6.26 Scaling factors to be applied to CL4 output results (as CO) for each HC of interest

The average results for the monitoring period are presented in Table 6.27. On no occasion did the model predict a source effect from the M50 due to mechanical turbulence at the 25 metre upwind receptor, hence only downwind average concentrations are shown.

HC	Dwnd receptor (metres)	Avg measured conc. $(\overline{C_O})$	Avg modelled conc. (bkg = 0) $(\overline{C_P})$	$\frac{\overline{C_O}}{\overline{C_P}}$	Fraction. bias (FB)	Pearsons R value	NMSE	% hours $0.5 \leq C_O/C_P \leq 2$
n-pentane	25	0.170	0.150	1.1	-0.13	0.27	1.3	50%
	120	0.054	0.046	1.2	-0.16	0.38	3.1	30%
	240	0.028	0.027	1.0	-0.04	-0.01	3.0	25%
Iso-pentane	25	0.514	0.330	1.6	-0.44	0.12	3.2	45%
	120	0.125	0.102	1.2	-0.21	0.35	3.8	25%
	240	0.061	0.060	1.0	-0.02	-0.02	2.2	15%
Ethene	25	0.896	0.913	1.0	0.02	0.19	0.4	75%
	120	0.256	0.282	0.9	0.10	0.24	1.6	45%
	240	0.109	0.165	0.7	0.41	-0.15	1.5	40%
Propene	25	0.289	0.270	1.1	-0.07	0.05	0.6	70%
	120	0.075	0.083	0.9	0.11	0.07	1.0	50%
	240	0.041	0.049	0.8	0.16	-0.31	2.1	25%
1,3 but	25	0.099	0.096	1.0	-0.03	0.12	0.8	55%
	120	0.015	0.030	0.5	0.66	0.26	1.5	35%
	240	0.015	0.017	0.9	0.11	0.00	1.8	25%
Acetylene	25	0.451	0.362	1.3	-0.22	0.11	0.6	55%
	120	0.144	0.112	1.3	-0.25	0.33	3.2	25%
	240	0.085	0.065	1.3	-0.26	-0.03	1.7	35%
Benzene	25	0.151	0.188	0.8	0.22	0.30	0.3	70%
	120	0.052	0.058	0.9	0.10	0.26	1.5	40%
	240	0.032	0.034	0.9	0.07	0.05	1.6	25%

Table 6.27 Statistical comparison of measured and modelled concentrations

In addition to the averages shown in Table 6.27 and discussed later, microstatistical tools which analyse the concentrations at each receptor on a datum-by-datum basis are presented. The R-value (Pearson's correlation co-efficient) is a measure of how well fluctuations in predicted concentrations follow fluctuations in observed concentrations. It does not however, measure correlation in actual numerical values between predictions and observations (Marmur and Mamane, 2003). For this the normalised mean square error is presented, which measures the correlation between numerical values of predicted and observed concentrations. The normalised mean square error is defined as:

$$NMSE = \frac{\overline{(C_P - C_O)^2}}{\overline{C_P C_O}} \qquad (6.6)$$

Where, C_p and C_o are predicted and observed concentrations respectively and the bar represents average values. A result of 0 means perfect agreement between predicted and observed values. A value of NMSE=0.5 means a factor of two, between predicted and observed values.

The low R values in Table 6.27 allied to the relatively high NMSE indicate the difference between modelled and measured values on a daily basis. NMSE values of less than 0.5 were only obtained for ethene and benzene at the 25metre receptor. All daily values differed on average by more than a factor of 2 (NMSE>0.5) at the 120 and 240 metre receptors. The lowest NMSE values were obtained nearest the M50 for hydrocarbons most strongly related to exhaust emissions, where all values were less than 0.8. In contrast, the NMSE values of compounds associated with evaporative emissions, were still relatively high at the nearest M50 receptor.

The ability of the model to predict short term concentrations was further explored by calculating the percent frequency of the daily ratio for modelled to measured concentrations between 0.5 and 2.0, a criteria sometimes used to assess the effectiveness of the model (Marmur and Mamame, 2003). The lower percentages observed at the 120m and 240m receptors were in the main due to the higher frequency of background corrected measured concentrations of 0 at these locations. The highest percentages were observed nearest the M50 source, where concentrations were also highest. Here, on at least 55% of occasions, for the compounds strongly related to exhaust emissions, the model predicted the measured concentrations within a factor of 2. Figures 6.17 and 6.18 illustrate daily modelled and measured concentrations for ethene and benzene at the 25m receptor

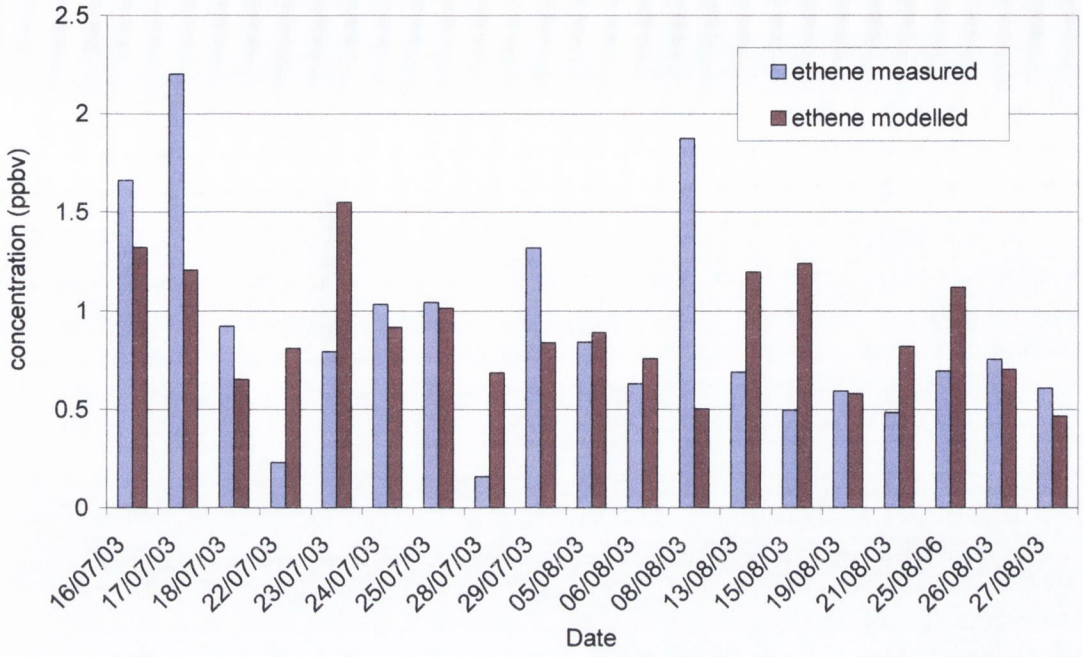


Figure 6.17 Daily measured and modelled concentrations for ethene at the 25metre receptor

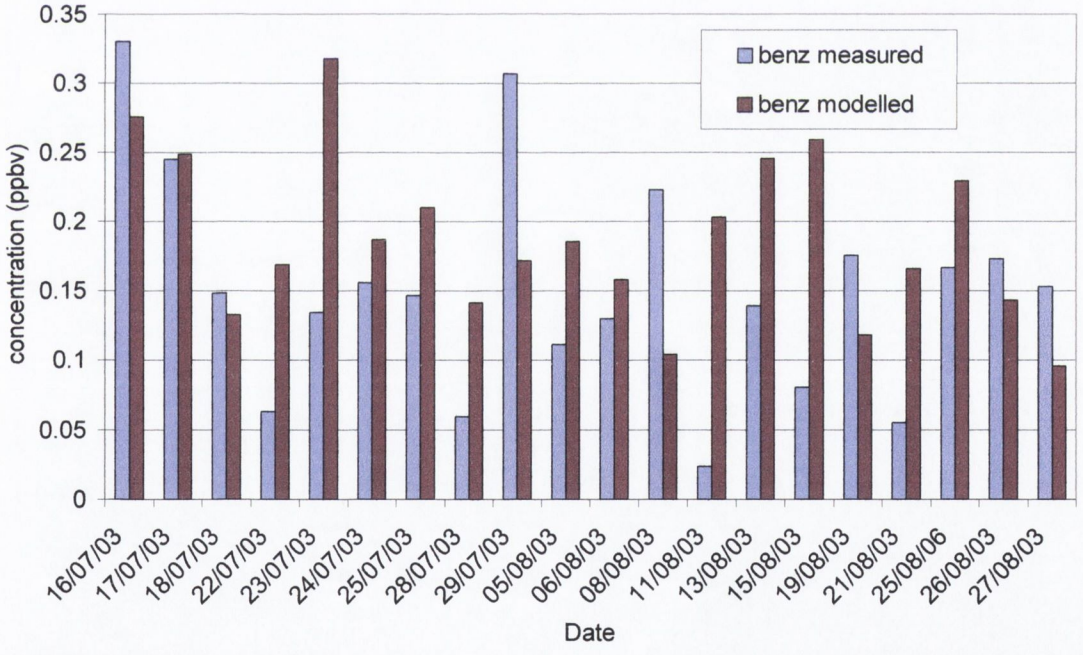


Figure 6.18 Daily measured and modelled concentrations for benzene at the 25metre receptor

From Figures 6.17 and 6.18 it is evident that the model both under-predicts and over-predicts observed concentrations. To ascertain if wind direction had an effect on this behaviour, the daily ratios of measured to modelled ethene concentrations at the 25 metre receptor were examined against daily wind direction. The daily wind directions were grouped into 6 separate wind sectors, corresponding to two cross-wind sectors relative to the M50 (40-80° and 220-260°) and 2 nearer parallel wind sectors (80-135° and 260-315°). Only on one occasion were wind directions observed from the sectors 345-40° or 165-220°. On the 11/08/03, a wind direction from 30° was observed, however, as a negative background corrected measured value was obtained, a comparison against the modelled value is not useful. As a result these wind sectors were excluded from analysis. The ratios obtained for the four sectors are shown in Table 6.28 (relative standard deviations in brackets).

	Cross winds		Nearer parallel winds	
Wind sector	40-80°	220-260°	80-135°	260-315°
Average measured / modelled ratio for ethene at the 25m receptor	1.74 (63%)	1.14 (31%)	0.81 (42%)	0.90 (65%)
Mean wind speed (m/s)	0.85	1.20	0.80	1.35

Table 6.28 Average modelled / measured ratios for ethene at the 25metre receptor with wind direction

From Table 6.28, the model on average under-predicts concentrations for cross wind directions and overestimates the concentrations for nearer parallel wind directions, with the trend exacerbated by lower wind speeds. Irrespective of wind direction (whether cross or near-parallel winds), the modelled and measured values agree better at higher average wind speeds. On a daily basis, 66% of modelled concentrations associated with cross winds were underestimated, and 75% of concentrations associated with nearer parallel winds over-estimated. This behaviour confirms results reported by Sharma and Khare (2001), where a review of previous studies showed the CALINE model overestimated concentrations for near-parallel winds and under predicted concentrations for oblique and crosswinds.

On a short-term daily basis, the model is seen to behave reasonably well, however, over the entire monitoring period where average values at each receptor are considered, the model performance improves substantially.

The data in Table 6.27 indicate that background corrected measured values and modelled values with background set to 0 ppb, deviate with distance from the M50 source ($\overline{C_O}$ / $\overline{C_P}$). The model is seen to predict both the average concentrations and the average rate of dispersion very well. As predicted in section 6.7.2, the concentrations of iso-pentane were underestimated by CL4: the measured concentration at the 25metre receptor is underestimated by approximately 35% which agrees with the estimate made in section 6.7.2 based on the normalised CEF for iso-pentane. Figure 6.19 shows the agreement between average measured and modelled concentrations at each receptor. The low intercept allied to the slope near 1 and the high R^2 value highlight the trend. With the over-predicted iso-pentane concentration at the 25m downwind receptor removed from the graph, an improved equation of $y = 0.98x + 0.0016$ is obtained, along with an R^2 value of 0.98.

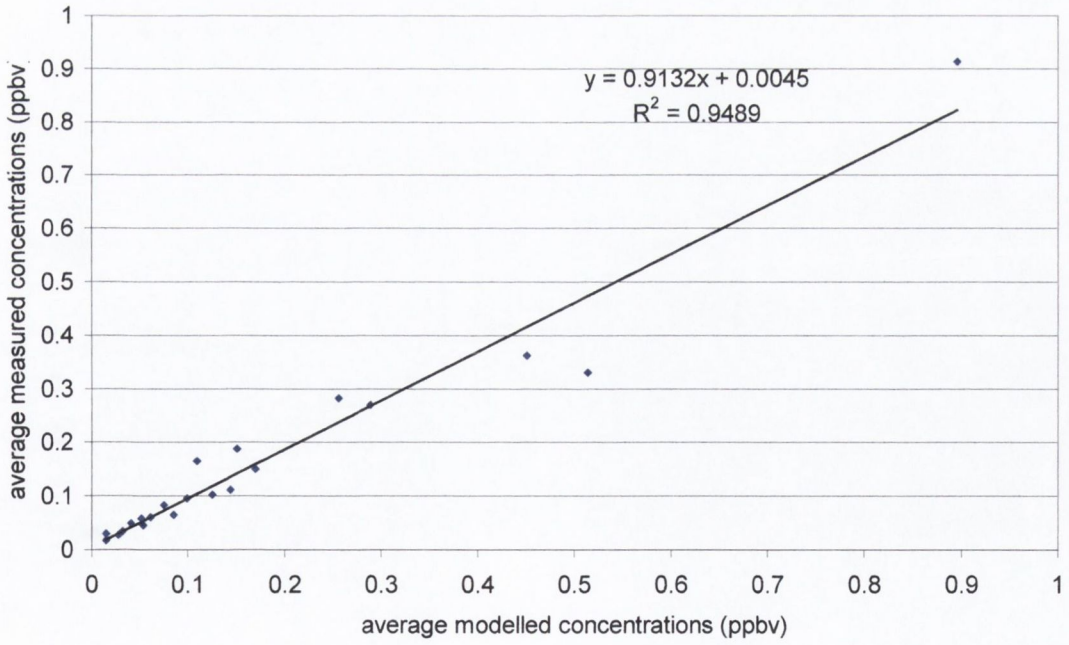


Figure 6.19 Average modelled versus measured concentrations at each receptor

Table 6.29 shows the overall ratio of total HC modelled to measured concentrations at each receptor. The values obtained indicate how accurately CL4 estimates the rate of dispersion of pollutants from the M50. Excellent agreement is observed at all three receptors, with the lower ratio at the 25metre receptor mainly due to the underestimation of the iso-pentane CEF.

Downwind receptor distance	Avg modelled conc. / Avg measured conc.
25m	0.90
120m	1.01
250m	1.05

Table 6.29 Ratios of average modelled to average measured concentrations

In addition to the average concentrations and the average measured to modelled ratios at each receptor, an additional macro statistical tool was used to investigate model performance. The Fractional Bias (FB) is defined as (Marmur and Mamame, 2003):

$$FB = 2\frac{\overline{C}_P - \overline{C}_O}{\overline{C}_P + \overline{C}_O} \tag{6.7}$$

It is a measure of the agreement between the average predicted and observed values, and has a range of between –2 and +2. A value of 0 indicates perfect agreement between average predicted and observed values, while a result of ±0.67 indicates that model and measured average concentrations differ by a factor of 2.Table 6.29 shows the calculated FB values for each compound at each receptor. . Most of these values are close to zero. The only value approaching 0.67 is observed at the 120metre receptor for 1,3 butadiene, where lower than anticipated measured concentrations were observed. At the 25m receptor, all values except iso-pentane are less than 0.25.The statistics presented outline the difference in model behaviour for short and long term predictions The model is seen to predict concentrations to a reasonable degree of accuracy on a day to day basis, with concentrations under or over-predicted depending on wind direction and speed. However, over a longer term basis, the measured and modelled values agree to a high level of accuracy. Average predicted to observed ratios are mush less than a factor of two for all three receptors, where an overall ratio of 1.01 is obtained.

6.8 SUMMING UP

The initial objectives were completed, as spatial variations in HC concentrations in the vicinity of a sub-urban Motorway site were ascertained. Each of the two main wind direction sectors, gave very different overall spatial concentrations. However, when these values were background corrected, the M50 source effect was seen to be very similar for compounds strongly related to road traffic emissions , regardless of wind direction sector. A number of other factors which influenced the observed concentrations were also investigated, such as traffic flow, local wind speed and evaporative emissions. The spatial variation in the E:A was also examined, and was shown conclusively to deviate with distance from the road traffic source. Mechanical turbulence was postulated to effect results in both sections 6.4.2.1 and 6.5. Section 6.4.2.1 showed an increase in concentrations (above those observed for the 120m and 250m background receptors) at the nearest upwind receptor for wind directions 165° to 315°, when the average wind speed was relatively low (0.8 m/s) .Under such relatively calm conditions, the effect of mechanical dispersion was seen to impact on concentrations 25m upwind of the M50, an effect the CALINE4 dispersion model did not predict. In addition, section 6.5 showed an increase in the ethene / acetylene ratio at the upwind receptor nearest the M50 relative to the 120m and 250m background receptors, for the same wind direction sector and low average wind speeds. This serves to both validate the fact that the ethene / acetylene ratio can be used to ascertain road traffic emissions and also that road traffic emissions were observed via the dispersion mechanism of mechanical turbulence. The measured data set offered an excellent basis on which to evaluate dispersion model performance. The concentrations of Hydrocarbon compounds with no significant evaporative emissions were most accurately predicted by CALINE4. Closest agreement between measured and modelled concentrations was observed for all compounds during periods of higher wind speed regardless of wind direction. The model was found to predict concentrations more accurately for longer term averages than day to day concentrations. Excellent agreement was observed in the average values over the entire 5 week monitoring period, mainly due to the similar frequencies of cross winds and near parallel winds, thereby cancelling out the under and over predicting nature of the model. The limitations of the model are highlighted by the wide range in daily predicted to measured ratios observed, as illustrated graphically in Figures 6.17 and 6.18, highlighting the limited success of CALINE4 in predicting short term HC concentrations, especially during periods of associated low wind speeds.

7. ONLINE HC MONITORING IN DUBLIN CITY CENTRE

The aim of this monitoring campaign was to establish the ambient concentrations of various Hydrocarbons at a heavily trafficked Dublin City centre junction. The results obtained were compared to those reported for a similar study in 1998 at the same location.

7.1 MONITORING LOCATION AND PROGRAMME

Figure 7.1 Map of Dublin City centre and general receptor location

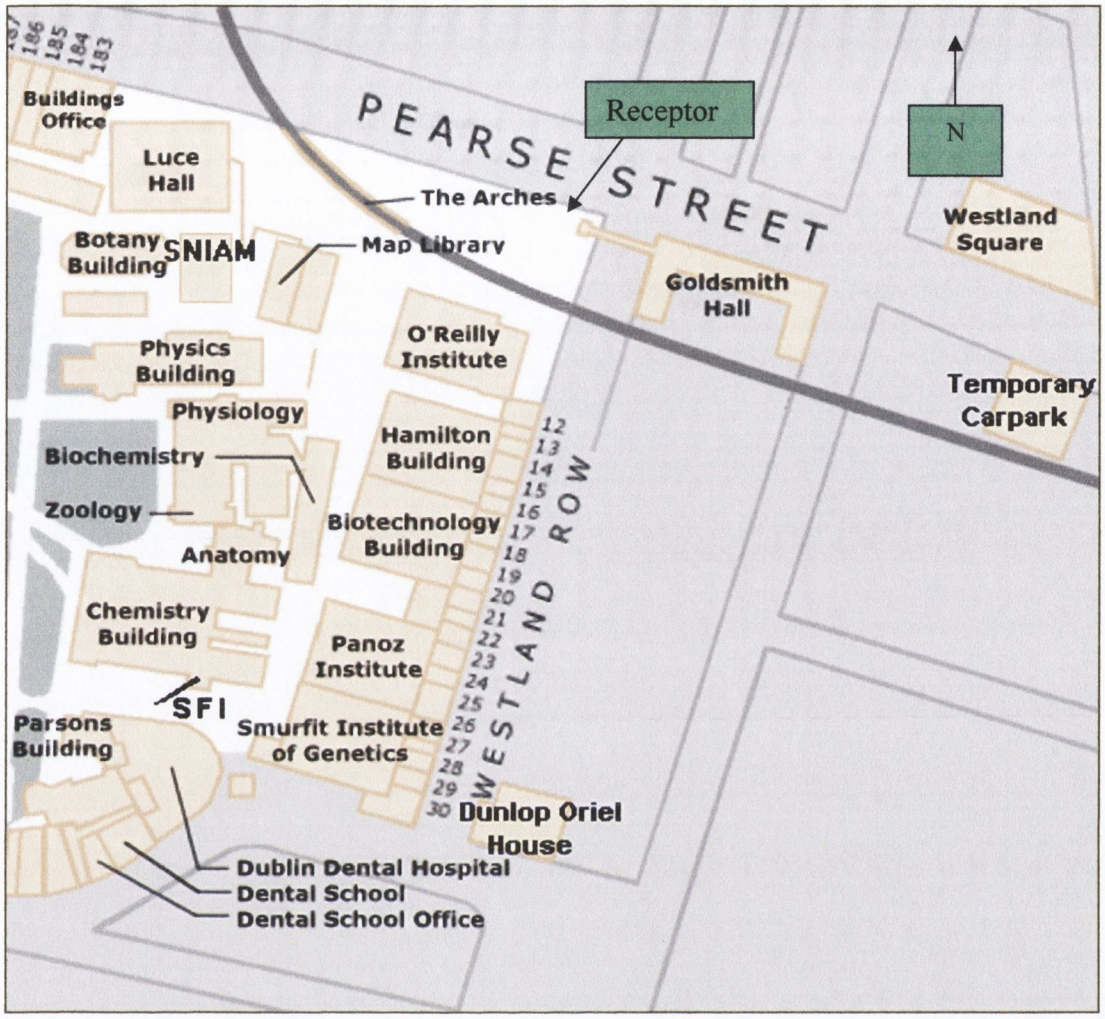


Figure 7.2 Map of specific receptor location

The monitoring site was situated in Dublin city centre on the grounds of Trinity College. Dublin county is the most populated of Ireland`s 26 counties. Of the 3.9 million inhabitants of the Rep.of Ireland, 29 percent live in Dublin and surrounding boroughs (CSO, 2003). The receptor was situated on a busy cross city route. The receptor location was identical to that of a previous study, on ambient hydrocarbon concentrations in 1998 (Marnane, 2000). Maps indicating the general and specific receptor locations are shown in Figures 7.1 and 7.2. The distance from the monitoring unit to the road was 4.5 metres, with a sampling height of 3 m. These values imply that it can be categorised as a roadside monitoring site, as defined by the UK Department of the Environment note on monitoring for air quality (DETR, 1998a). The

monitoring site was located behind a 1.5 metre high wall (for security reasons) which was not expected to interfere with measured hydrocarbon concentrations. Data obtained from the Dublin Transportation Office revealed that the average morning peak traffic flow through the junction is approximately 3500 vehicles between 08:00 and 09:00.

Online HC monitoring was carried out at the site on weekdays, over a six month period, between 28/01/03 and 16/07/03. Of the 4064 potential hours of sampling, 30% were analysed equating to 1206 hours. This percentage was obtained due to instrument downtime as a consequence of similar analytical problems encountered to those referred to in Chapter 5. In addition, the validation of the mobile sampling method described in Chapter 4 was carried out concurrently to the Dublin City online measurement campaign, reducing the potential number of online measurements.

7.2 METEOROLOGICAL DATA

Local meteorological data was obtained from a meteorological station housed in the mobile trailer. The reference regional receptor is the same as that used for a similar study in 1998, namely Dublin Airport. As in the preceding chapters, only hourly meteorological data in which hydrocarbon data were obtained are considered

7.2.1 Wind direction

The frequency of regional winds for each 10° sector was first examined. As portrayed by the wind rose in Figure 7.3, the vast majority of regional winds emanated from south-easterly and south-westerly directions. Wind directions from other sectors were relatively rare. The wind rose portraying local wind directions shown in Figure 7.4 is very different due to local obstructions affecting wind directions at the receptor.

The local frequencies are seen to be concentrated in two principal sectors, 40-60° and 190-250°. With regard to source effects, the 40-60° sector relates to the heavily trafficked junction between Pearse Street and Lombard Street / Westland Row, while the 190-250° sector is associated with the Trinity College campus and Dublin City beyond.

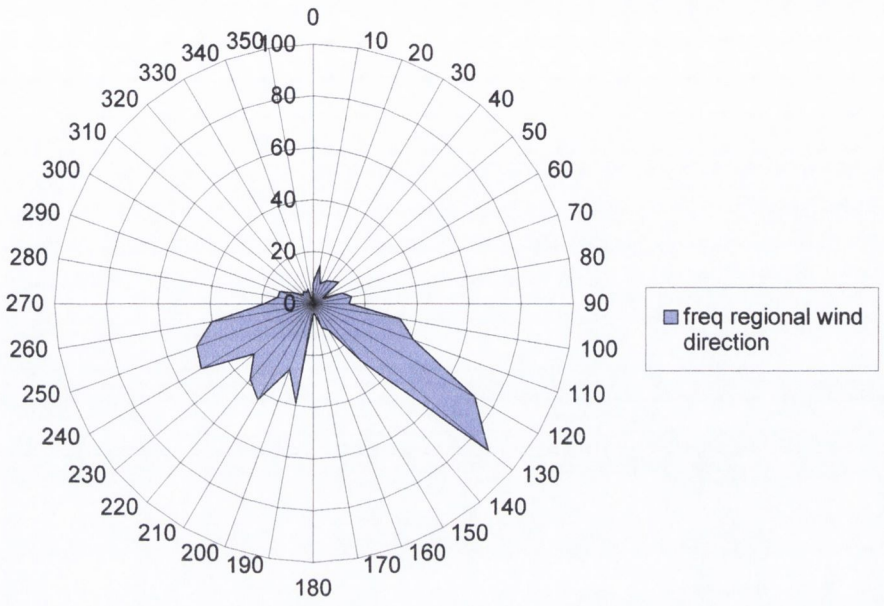


Figure 7.3 Frequency of regional wind direction for each 10° wind sector

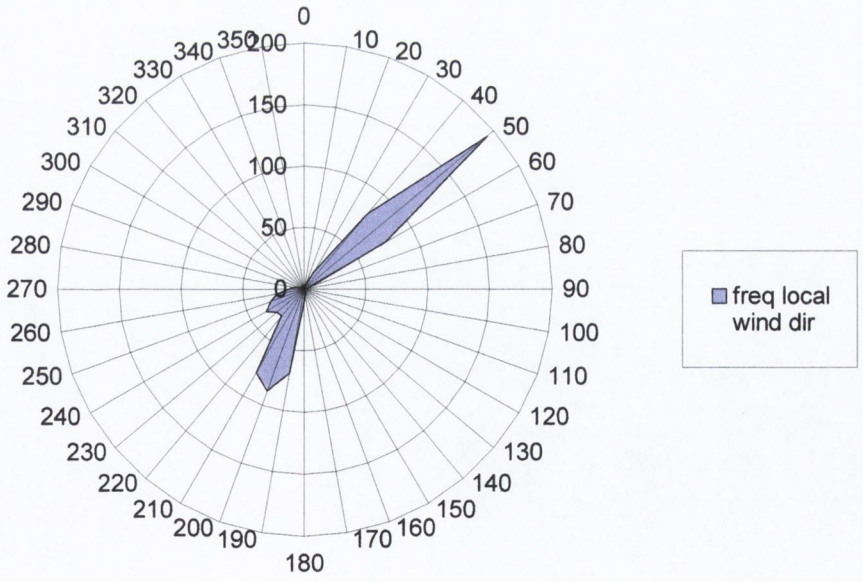


Figure 7.4 Frequency of local wind directions for each 10° wind sector

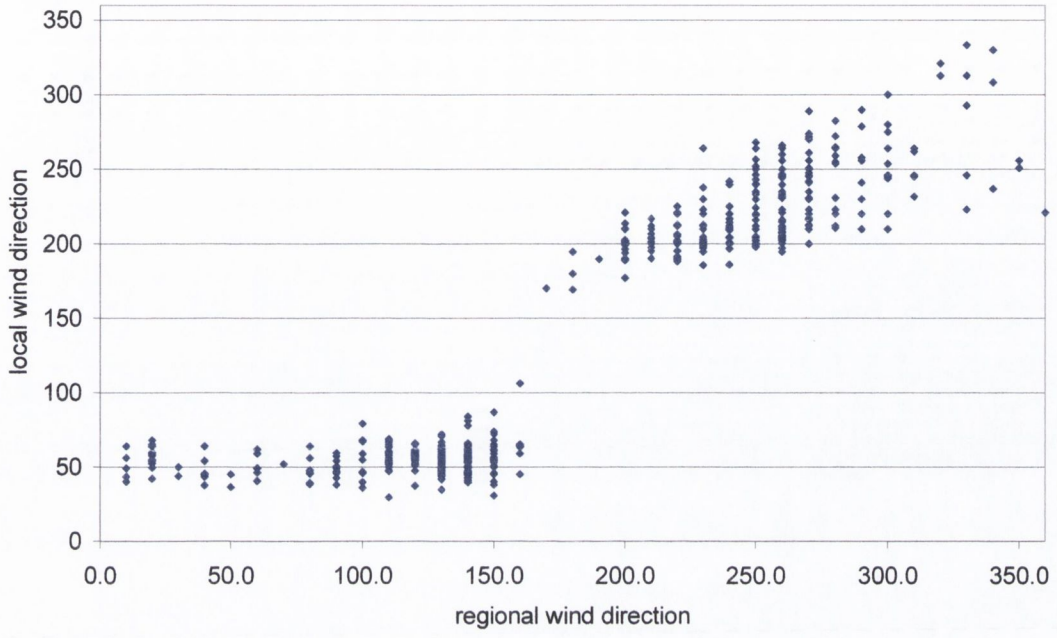


Figure 7.5 Scatter plot of regional against local wind direction

The scatter plot shown in Figure 7.5 compares the regional and local wind direction data sets. When the regional wind is between 0 and 160°, local wind directions within the relatively narrow band of 40-90° were obtained. This is probably due to local obstructions in the Pearse Street area funnelling regional winds into this local wind direction band. In contrast regional directions of 170-360° yield local wind directions in the same sector with a much stronger correlation. Combining the information in Figure 7.5 with that obtained in Figure 7.4, it can be seen that when a local wind direction of between 40-60° is observed on a regional scale the wind could emanate from anywhere between 0 and 160°. This poor correlation implies that only local source effects can be ascertained with local wind data in this sector. In contrast, when a local wind direction of between 190-260° is obtained, a regional wind direction in the same sector can be assumed. Hence, the local wind directions in this direction sector are applicable to source apportionment on a regional scale. The two main local wind direction sectors of 40-60° and 190-260°, conveniently give very contrasting source effects. The 40-60° sector relates to the heavily trafficked junction, while the 190-260° sector gives an indication

of background city centre concentrations, as the air from this direction is likely to have travelled over the TCD campus which has limited traffic emissions.

7.2.2 Wind speed

Local and regional wind speed compare quite well considering the city centre terrain associated with local receptor readings (Figure 7.6). As expected the local wind speeds are generally lower than those observed at Dublin airport due to local obstructions at the city centre site and the height difference between anemometers at both sites (10metres at Dublin airport, 4metres at local receptor). For the two principal wind direction sectors analysed in greater detail in section 7.3.3, the average wind speeds are outlined in Table 7.1, where filtered data relates to periods of unstable atmospheric conditions or wind speeds greater than 1 m/s.

	Wind speed (m / s)	
Wind direction sector	Unfiltered data	Filtered data
40-90°	1.5	1.7
170-260°	1.7	1.8

Table 7.1 Average wind speed for the two principal wind direction sectors

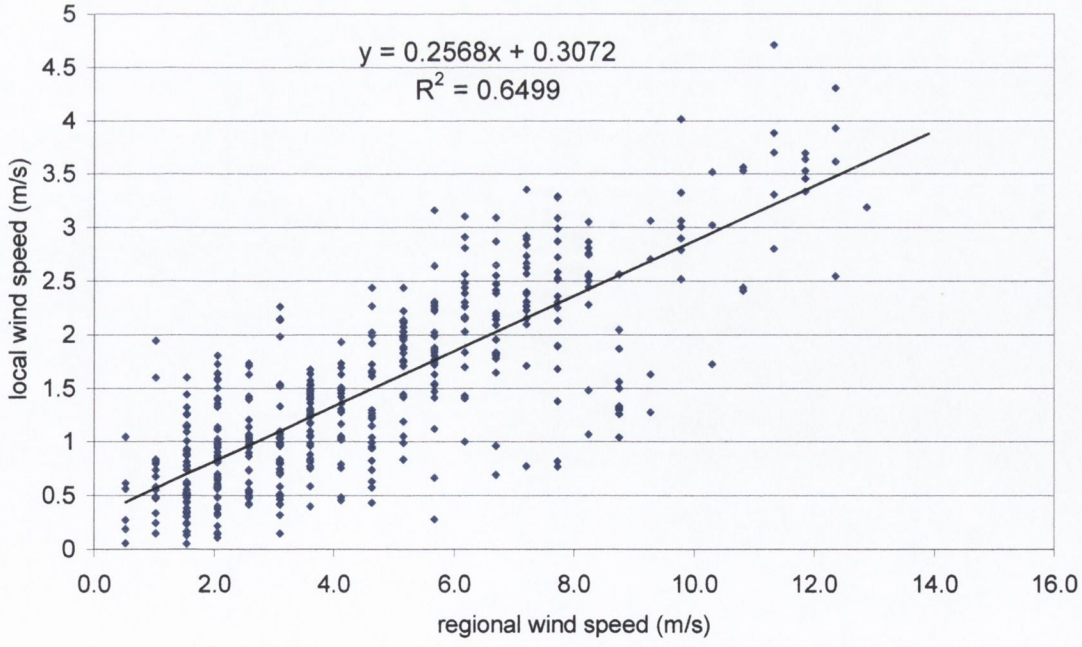


Figure 7.6 Scatter plot of regional against local wind speeds

7.2.3 Temperature

Local ambient temperature readings were not available due to a fault in the local meteorological station. Regional data however was available and average hourly temperatures over the monitoring period are shown in Figure 7.7. As expected, the regional ambient temperature shows a general increase from January to July.

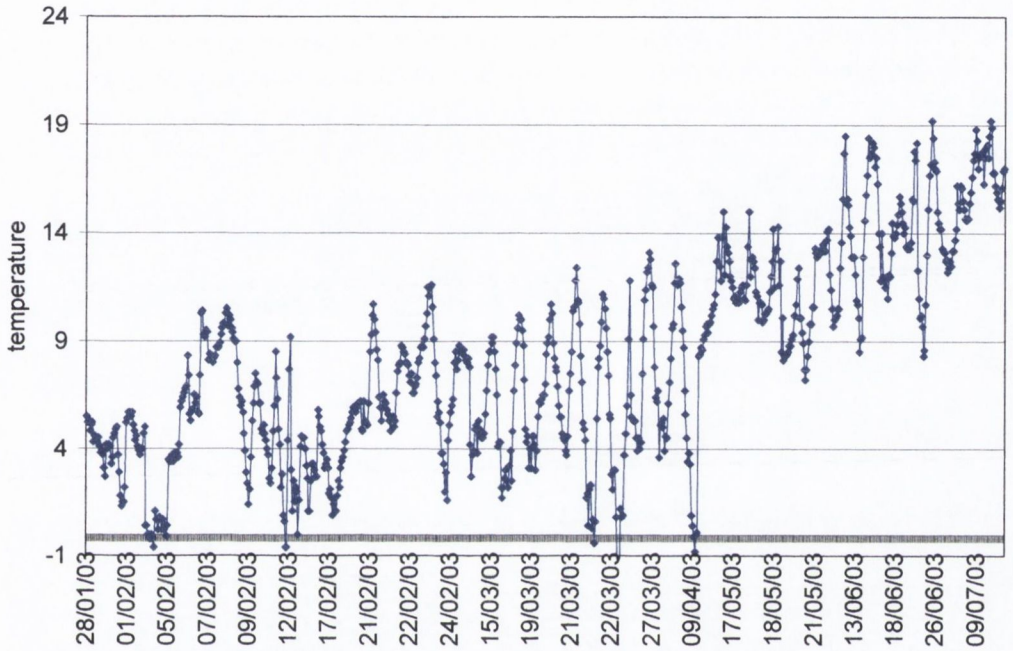


Figure 7.7 Average hourly regional temperature for monitoring period

Local temperature was not predicted to be much different to that obtained for regional data. This assumption was verified by analysing data obtained for a similar study carried out at the same location in 1998 (Marnane, 2000), in which agreement between local and regional temperature was very good. In the study carried out in 1998, local temperature was seen to be on average 2°C higher.

7.2.4 Stability class

Atmospheric stability class is related to the degree of upward motion of air due to thermal buoyancy and is dependant upon the temperature gradient of the atmosphere. During an atmospheric inversion, the mixing layer height can reduce from 800 to100 metres in Ireland (Caruthers *et al.*, 1996). During summer this height can expand to 1500 metres, improving

atmospheric mixing and lowering ambient hydrocarbon levels. Inversions are most likely to occur during periods of night-time stable atmospheric conditions, when elevated concentrations of hydrocarbons can be experienced.

Stability classes are grouped from A to G, with A being associated with a very unstable atmosphere and G with very stable conditions. The predominant stability class in Ireland is D, which represents conditions close to neutral stability. Occurrences of stability classes E, F and G are usually confined to night-time hours where cooler air and lower mixing heights are more common.

Figures 7.8 and 7.9 show the frequency of stable conditions (class E, F or G) with different regional and local wind direction, respectively. These identify the wind directions for which stable atmospheric conditions most frequently give rise to elevated hydrocarbon concentrations. In the plot of regional wind the most frequent occurrences of stable air are associated with wind directions 70-140°, which relates well to the high frequency observed with local wind directions between 40-60°. The relative frequencies of stable air within 190-260° on regional and local levels also agree well.

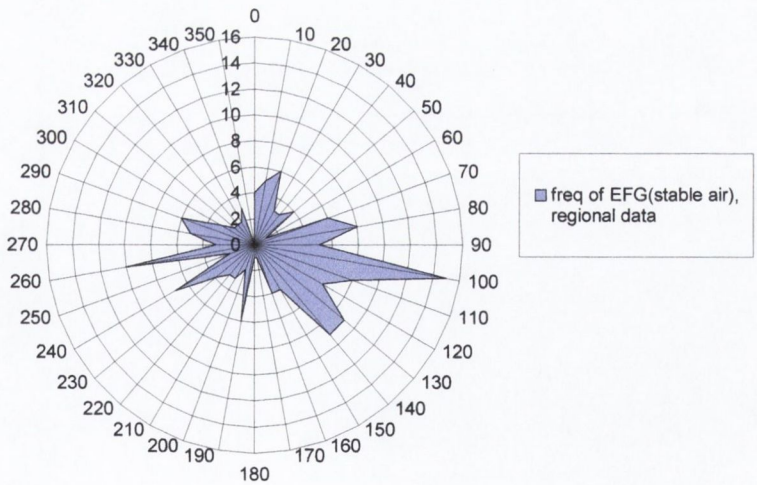


Figure 7.8 Frequency of stability classes E,F and G (stable air) with regional wind directions

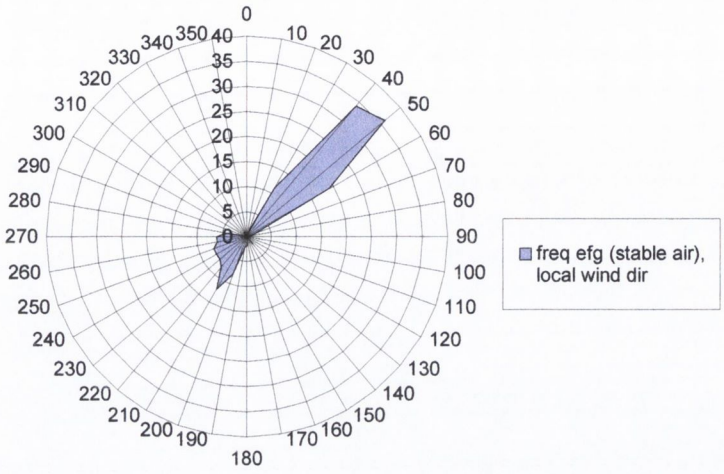


Figure 7.9 Frequency of stability of stable air with local wind directions

The much higher regional frequency of 70-140° relative to 190-260° relates well to the higher frequency on a local scale seen for 40-60° relative to 190-260°, this also explains the greater increase in average wind speed for filtered data (stability classes E, F and G removed) associated with wind direction sector 40-90° in Table 7.1.

7.3 ANALYSIS OF MEASURED CONCENTRATIONS

7.3.1 All data

In addition to all the compounds monitored at the M4 Leixlip motorway site (Chapter 5), n-pentane was also examined at the Dublin city site. Basic statistics and overall average values for the monitoring period, are presented towards the end of this chapter (section 7.7), when the overall levels obtained are compared to those observed in the 1998 study.

Preliminary investigations were initially carried out on data with no filters applied, in an attempt to ascertain overall general trends at the receptor.

7.3.1.1 Diurnal trends

To elucidate the hourly trend over the average day, the average hourly concentrations for all HC compounds of interest were plotted over a 24 hour period. The results are discussed below.

All compounds bar ethane showed a diurnal profile strongly associated with peak time traffic flow. Differences between compounds related the extent to which each followed the expected trend. The 24 hour ethane concentration profile, shown in Figure 7.10, exhibits a very weak relationship with known peak traffic flows. A relatively small peak is observed between 08:00 and 09:00, suggesting minimal influence from traffic emissions. The midnight peak value is consistent with other city findings (Derwent et al, 2000), where natural gas plays a major role.

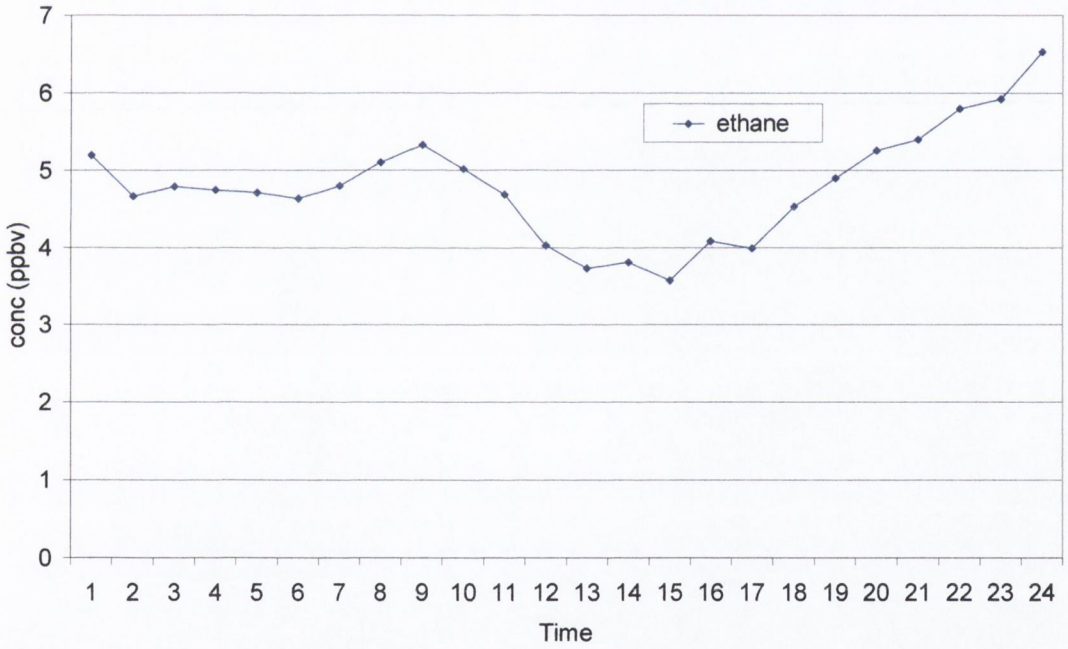


Figure 7.10 Weak diurnal profile obtained for ethane

In Figure 7.10, concentrations remain relatively constant over the average day, with maximum atmospheric mixing around midday yielding the lowest 24 hour average concentration. Limited atmospheric dilution will occur at midnight due to boundary layer shrinkage resulting in the 24 hour maximum value observed.

All other compounds monitored exhibited similar diurnal trends, as illustrated in Figure 7.11. An alkane, an alkene and an aromatic are graphed, each representative of the common profile observed.

The observed trend in concentrations correlates very well with expected traffic flow. Concentration peaks are observed between 07:00-10:00 and 17:00-20:00, leaving little doubt that vehicle emissions are the dominant emission source at the receptor for the HC compounds of interest.

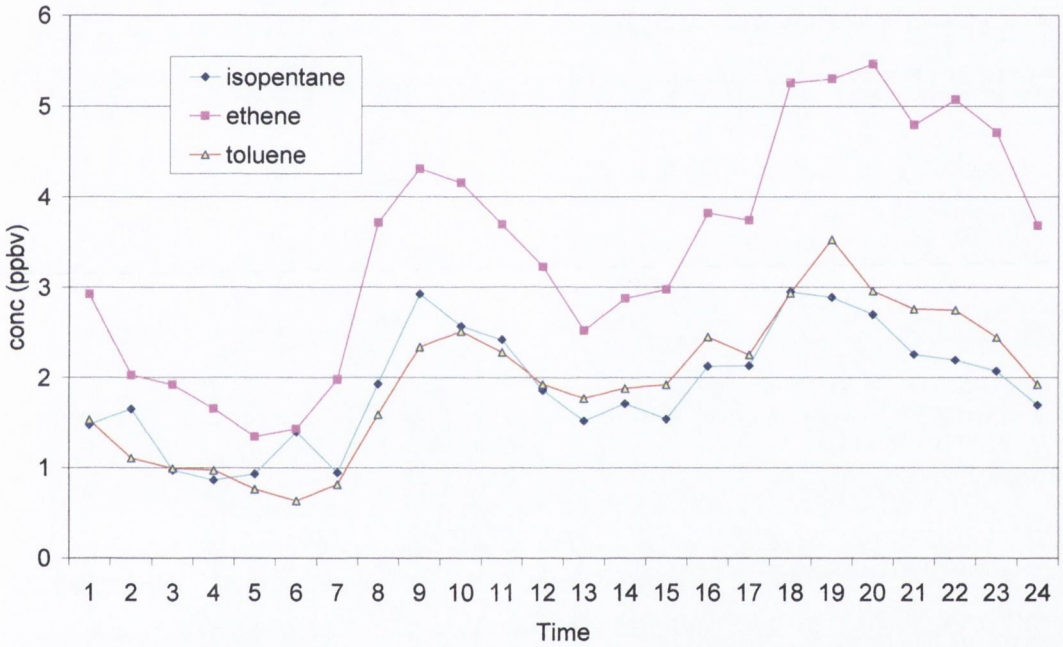


Figure 7.11 Diurnal profiles for iso-pentane, ethene and toluene, representative of all compounds monitored except ethane

The evening peak is seen to be higher than that in the morning, probably due to the higher "baseline" level concentrations seen around mid-day as opposed to early morning.

The more protracted evening peak is due to the extended evening peak traffic flow allied to a gradually shrinking boundary layer. In addition, an increase in traffic flow from Westland Row onto Pearse Street during this evening period, leads to traffic emissions from vehicle sources closer to the receptor, leaving less time for dispersion, relative to morning traffic flow.

7.3.1.2 Concentration roses

Figure 7.12 shows the average ethane and ethene concentrations obtained for each 10° local wind sector. In each case the largest peak occurs at 340°. This peak is attributable to elevated concentrations occurring during a relatively small number of atmospheric inversions and / or lower wind speed episodes.

The plot shown in Figure 7.12 for ethane and ethene is representative of all compounds monitored, but is of little use in establishing local source effects due to the inclusion of data pertaining to stable atmospheric conditions and low wind speeds. When all data is considered, as in Figure 7.12, the local traffic effect is not dominant, as both profiles are similar for ethane (not strongly traffic related) and ethene (strongly traffic related).

The effect wind speed has on ambient concentrations is shown in Figure 7.13 for ethene plotted against regional wind speed. As expected, a higher R^2 value is obtained for the non-linear trend.

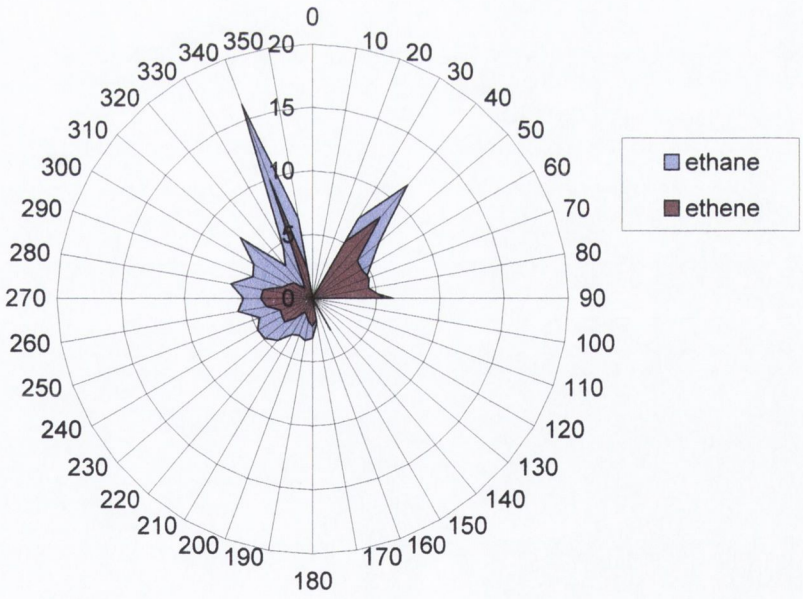


Figure 7.12 Average concentrations for ethane and ethene for each 10° wind direction sector

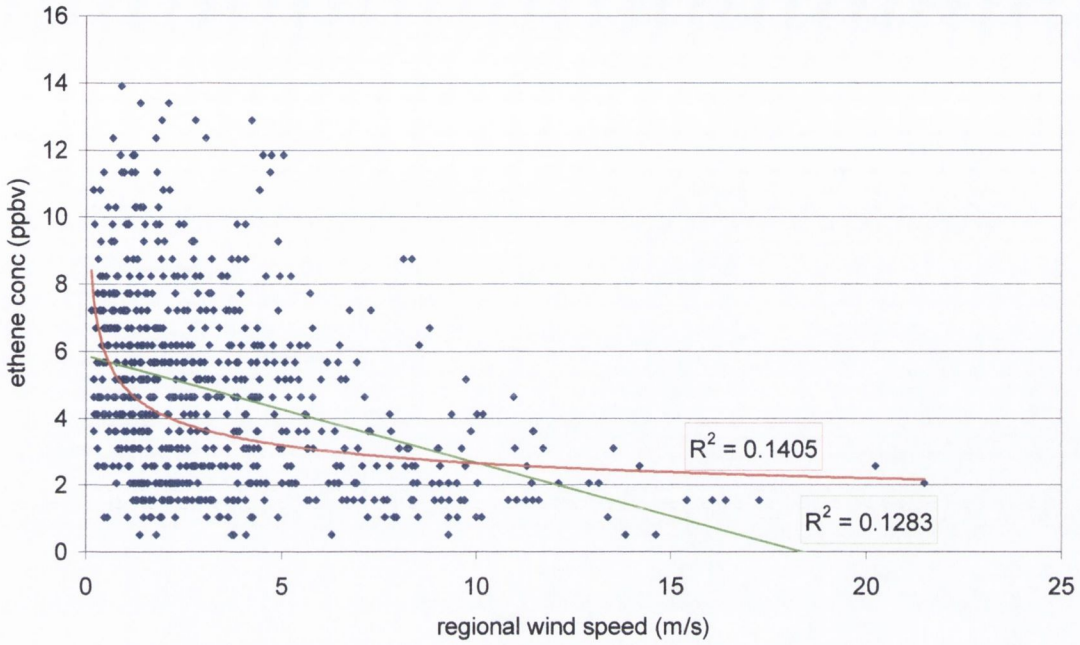


Figure 7.13 Scatter plot of wind speed (m / s) against ethene concentration (ppbv) for all data

7.3.2 Filtered data

To eliminate the problems associated with source apportionment in regard to stable atmospheric conditions a filtering process similar to that described in Chapter 5 was carried out, in which HC data associated with stability classes E, F and G and wind speeds lower than 1 m/s, were excluded from analysis. Concentration roses and diurnal trends were then investigated using this reduced data set, in the expectation that local sources would become more pronounced.

7.3.2.1 Diurnal trends

Figure 7.14 shows that with the reduced data set, a more pronounced diurnal profile is obtained for all compounds monitored. The average night-time values have decreased to levels below the mid-day concentration and the evening peak is sharper and less exaggerated with the night-time decrease in concentrations occurring earlier than in the plots with stable air included (Figure 7.11). With the removal of these elevated, mainly night-time concentrations, ethane is also seen to show a pronounced diurnal characteristic suggesting a contribution from

vehicle emissions to concentrations obtained. However, the profile observed is still markedly weaker than for any other compound monitored (Figure 7.15).

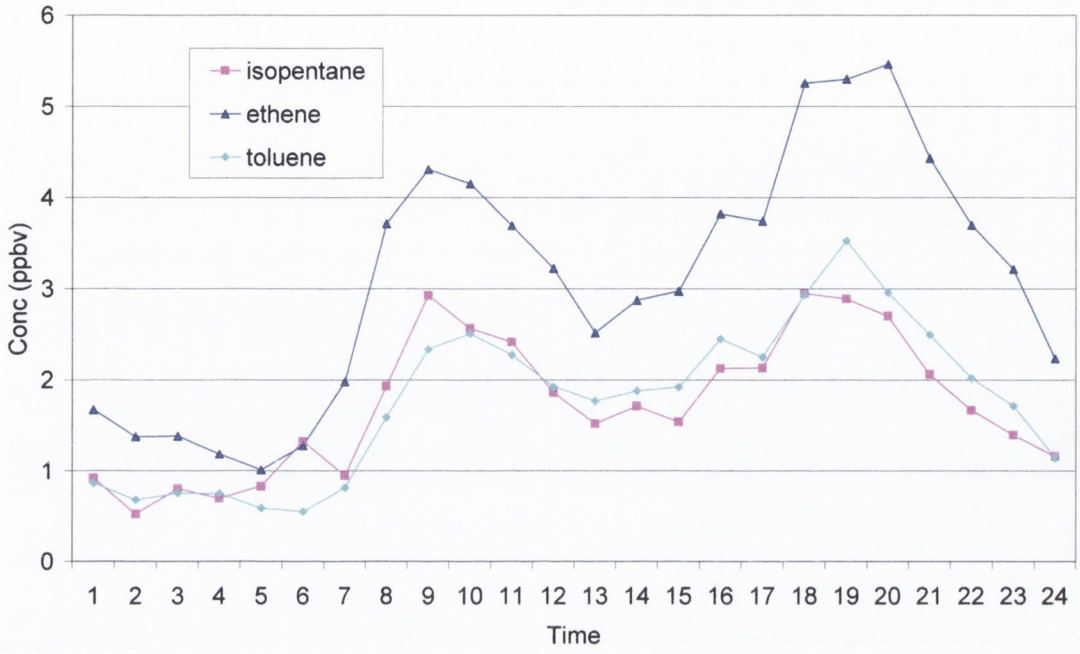


Figure 7.14 Diurnal profile for iso-pentane, ethene and toluene for unstable atmospheric conditions and wind speeds greater than 1 m/s

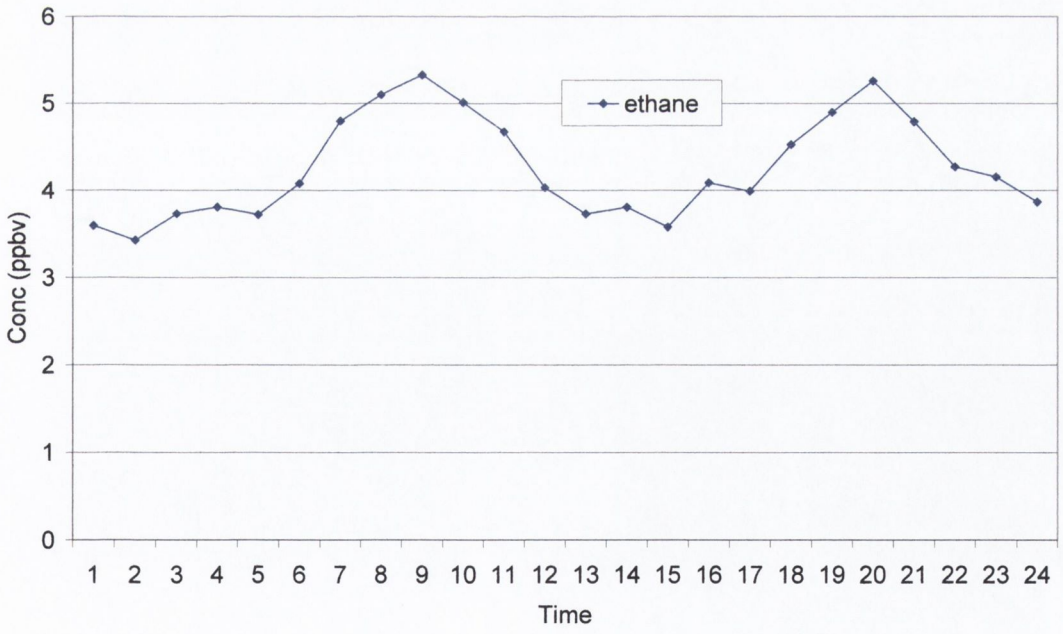


Figure 7.15 Improved diurnal plot seen for ethane with data associated with unstable atmospheric conditions and wind speeds greater than 1 m/s

7.3.2.2 Concentration roses

To extract more useful information on local source effects, concentration roses were plotted using the reduced data set. An example plot for the road traffic emission markers ethene and acetylene is shown in Figure 7.16, this plot being representative of all compounds except ethane. The highest concentrations are obtained with winds from the 40-90° sector, the wind direction associated with the Pearse Street / Lombard Street junction. The second most dominant peaks are seen from 270-290°, wind directions almost parallel to Pearse Street. Both the 40-90° and 270-290° suggest strong source effects from local road transport sources. The lowest concentrations were obtained from the 200-260° local wind direction sector. These winds would have travelled over the TCD campus, which includes open spaces in the form of sports playing pitches. The values obtained for the 270-290° sector is however based on only 10 hourly observations of winds in this direction. Figures 7.4 and 7.5 show that the vast majority of data is associated with wind direction sectors 40-90° and 170-260° and combining these with local source effects seen in Figure 7.16, we can obtain a large amount of data for two very different local source effects. Higher average values associated with the junction (40-90°) and lower general Dublin city background concentrations emanating from TCD campus (170-260°) were observed. Data associated with both of these sectors are examined separately in the following section.

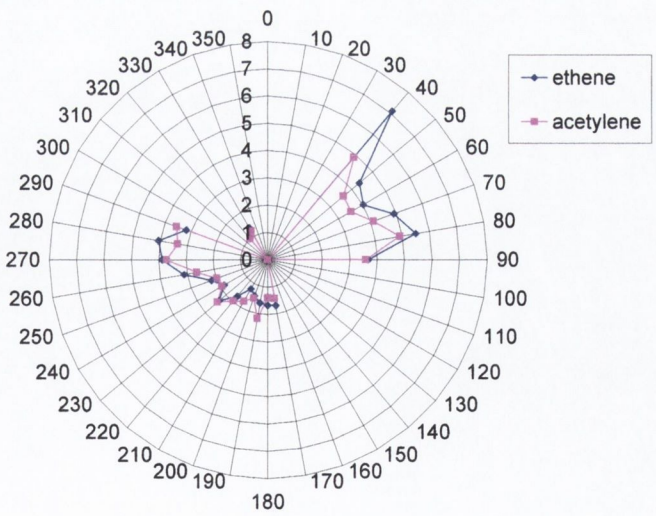


Figure 7.16, Average ethene and acetylene concentrations for each 10° local wind direction sector

7.3.3 Sectoral analysis of two main wind directions, 40-90° and 170-260°

To investigate the differences between these two main wind direction sectors, the HC diurnal profile was examined for each sector separately. All compounds monitored showed a strong diurnal profile for 40-90°. The alkanes differed somewhat in that the morning peak was much greater than the evening peak as seen in Figure 7.18 for n-butane. Ethane is also seen in Figure 7.17 to show a morning peak associated with traffic flow through the junction, however the profile obtained is much less pronounced than for any other alkane.

For wind direction sector 170-260°, the alkanes all exhibit behaviour associated with back ground measurements, where the day-time concentrations are not seen to vary to any great extent, and no strong diurnal trend relating to road traffic emissions is displayed. The ethene and toluene diurnal plots are shown in Figures 7.19 and 7.20. These are representative of all remaining compounds, namely the alkenes, the aromatics and acetylene.

As expected, the local source junction effect seen in both graphs is very clearly related to traffic flow in this area with clearly defined morning and evening peaks obtained. The profiles seen in both graphs for wind directions 170-260° are very similar, with morning peaks occurring later than for sector 40-90° and evening peaks occurring earlier. As with the alkanes, the deviation over the course of the day is relatively small.

From Figures 7.17 to 7.20 we can conclude that wind direction sector 40-90° gives a source effect strongly related to vehicle emissions for all compounds monitored. Very limited diurnal profiles are seen from wind directions 170-260°, which are more associated with Dublin City background concentrations. The average hourly wind speed profiles are seen to be very similar for both wind direction sectors (Figure 7.21), ruling out the possibility of a difference in average wind speeds affecting the concentrations observed.

Figure 7.17 Ethane diurnal plot for 2 main wind direction sectors

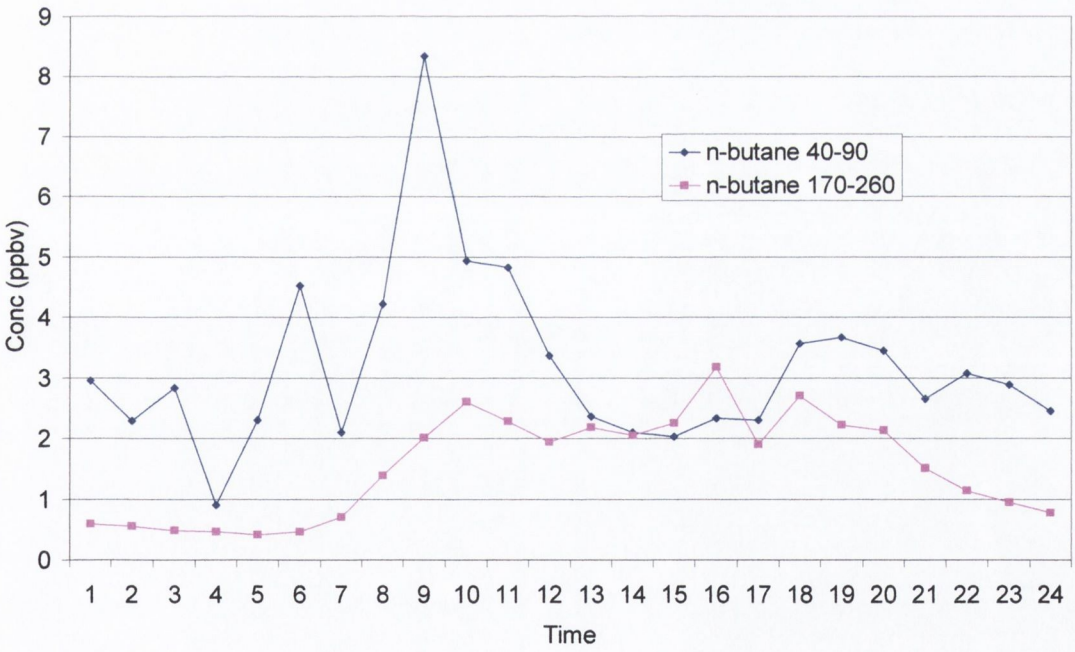


Figure 7.18 n-Butane diurnal plot for 2 main wind direction sectors

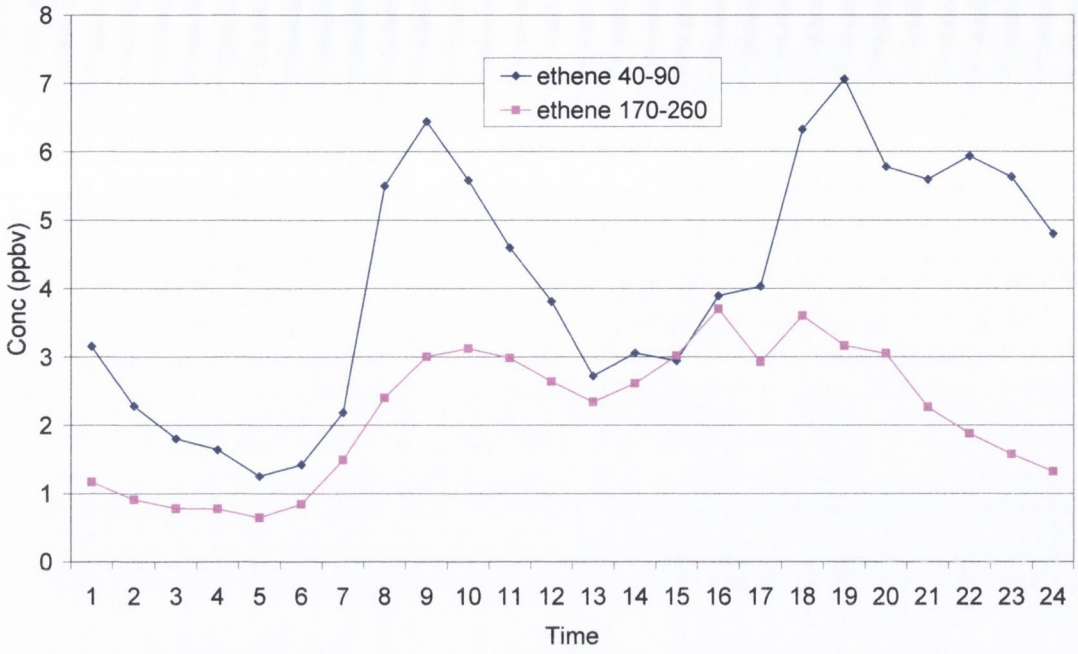


Figure 7.19 Diurnal plot for ethene for 2 main wind direction sectors

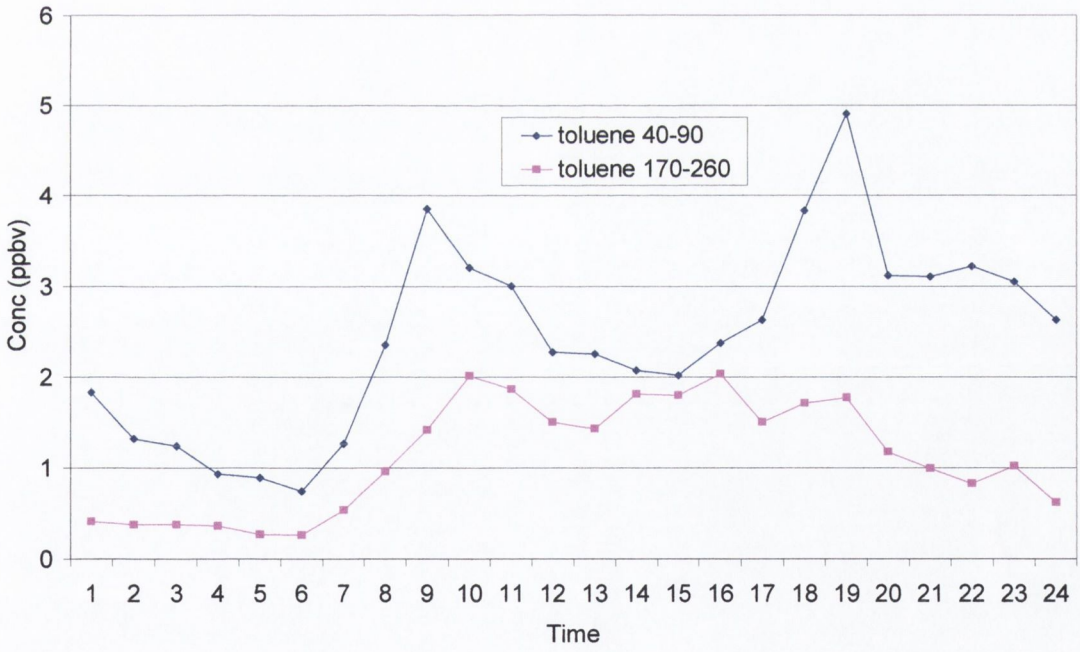


Figure 7.20 Diurnal plot for toluene for 2 main wind direction sectors

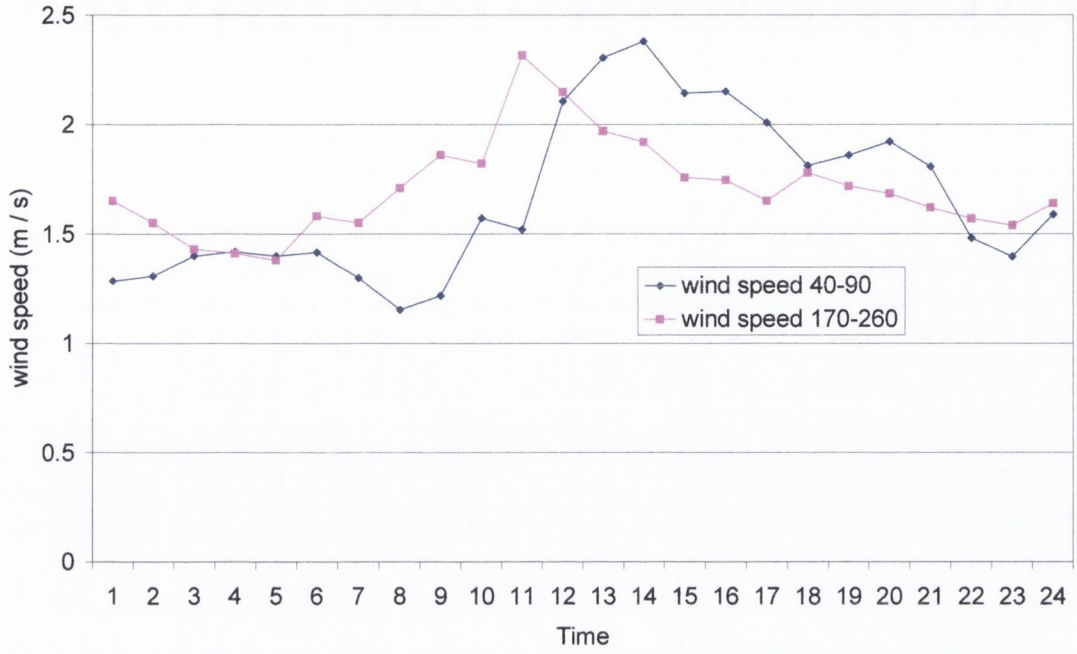


Figure 7.21 Average hourly local wind speeds (m / s), for wind direction sectors 40-90° and 170-260°

7.3.4 Comparison with international studies

Table 7.2 presents a summary of similar studies carried out world-wide. Columns (a) to (c) show the results obtained for this study, (a) outlines the average values at the receptor, while (b) and (c) present the averages obtained for the main wind direction sectors, representing roadside and urban background averages respectively.

Columns (d) to (f) present urban average concentrations for Cardiff, Edinburgh and London, obtained form the UK Hydrocarbon Monitoring Network (www.airquality.co.uk), from which only London data was available for 2003. Cardiff and Edinburgh represent urban background monitoring sites, whereas the Marleybone road in London, is a roadside monitoring location. Columns (g) and (h) outline average concentrations observed by Borbon *et al.* (2002), over a 4 year period at two separate urban monitoring sites in Lille, Northern France. Column (g) refers to urban roadside concentrations observed at Liberte, between 1997 and 1999, whereas column (h) refers to an urban background receptor at Fives, giving concentrations observed between 1999 and 2000.

Column (i) relates to urban background levels observed in Helsinki during 2001, by *Helien et al.* (2003). Columns (j) to (p) present average concentrations observed at locations outside of Europe, where (j) shows urban background Hong Kong concentrations obtained in 2001 by Guo *et al.* (2004), and (k) outlines the BTEX concentrations observed in 2001 by Hwa *et al.* (2002), at an urban Taiwanese roadside location.

Columns (l) to (p) show a selection of studies carried out in the United States, with column (l) depicting 2001 BTEX concentrations observed in San Berdino (California) at an urban background site (Pankow *et al.*, 2003). Columns (m) to (p) present average BTEX concentrations in 2003 for four separate states in the US. These data were obtained from the USEPA Air Quality System database (AQS), (www.epa.gov/air/data/reports.html).The AQS database is updated regularly by states and local environmental agencies that operate the monitoring stations. All four sites were located in what were defined as urban / city centre locations. Columns (m) to (p) relate to Bronx County (New York City), El Paso (Texas), Los Angeles (California) and Claremont (New Hampshire), respectively.

Comparing the overall averages from our study (a) to the two sites at Lille (g) and (h), it is apparent that the Dublin values lie between those observed at the two French sites. However, both French sites have higher Pearson's correlation co-efficients when compared with Dublin averages associated with wind directions from the junction (40-90°). The highest correlation, as expected, is observed between the Dublin 40-90°sector (b) and the roadside French monitor (g), suggesting road traffic as the primary pollutant source for both data sets compared.

In contrast, when considering the urban background-monitoring site in Helsinki (i), the correlation is higher between the data associated with Dublin wind directions 170-260°. The concentrations observed with winds from the 170-260° sector are similar to those obtained in Helsinki, with the Dublin concentrations usually slightly higher (the Helsinki receptor was located on a roof-top).

The concentrations observed in column (j) are in the main very similar to those seen for wind directions between 40° and 90° in Dublin. The Hong Kong toluene and m+p-xylene concentrations are however much higher than those observed in Dublin. This leads to the

lower correlations observed. It these two compounds are omitted, much improved Pearson's correlation's of 0.94 and 0.96 are obtained for wind sectors 40-90° and 170-260° respectively. The common usage of organic solvents in the building and industrial sectors was cited by Chan *et al.* (2002), as possible reason for the elevated Hong Kong concentrations of these compounds. The concentrations observed in Taiwan (k) are also similar to those observed in Dublin, except for the higher levels of toluene observed in Taiwan.

Comparisons of the BTEX compound concentrations in US studies (columns l to p) and Dublin, suggest good agreement, with concentrations similar at all locations. The high correlations observed are due to the relatively few compounds being compared.

The comprehensive nature and the proximity of the country involved makes comparisons with the UK Hydrocarbon Network monitoring results (columns d to f) most relevant (www.npl.co.uk/hcn/hchome.htm). For the Cardiff and Edinburgh sites (2001 data), better correlation is achieved with Dublin wind directions between 40° and 90°. The concentrations in Dublin are in general higher, and significantly so for the alkenes. As these two UK locations are classified as urban background sites, it is not surprising that the concentrations observed at these sites are closer to those observed for Dublin wind directions between 170° and 260°.

The UK site most similar to the monitoring location of this study, is located at Marleybone road in London (f). The data available at this site was also the most recent (2003). The London roadside monitoring data show excellent correlation with Dublin concentrations associated with wind directions between 40° and 90°, this is illustrated in Figure 7.22, where a scatter plot of Dublin and London average concentrations is shown. The lower correlation observed between Dublin concentrations associated with wind directions 170-260° and London values is illustrated by the scatter plot in Figure 7.23. In both scatter plots, ethane has been excluded due to its minimal association with road traffic emissions. The London concentrations are on average 44% higher than those observed in Dublin with wind directions between 40° and 90°, but the relative proportions of the individual hydrocarbons are very similar, suggesting similar sources at both sites, namely road traffic emissions, as cited by Derwent et al (2000) for London.

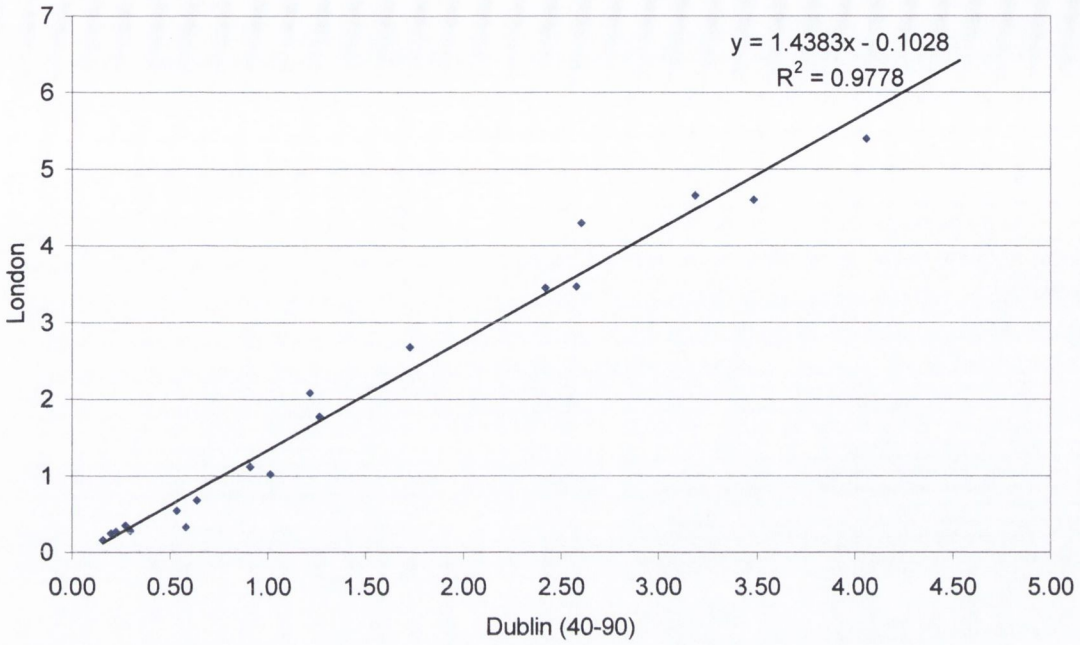


Figure 7.22 Scatter plot of Dublin (40-90°) and London average HC concentrations

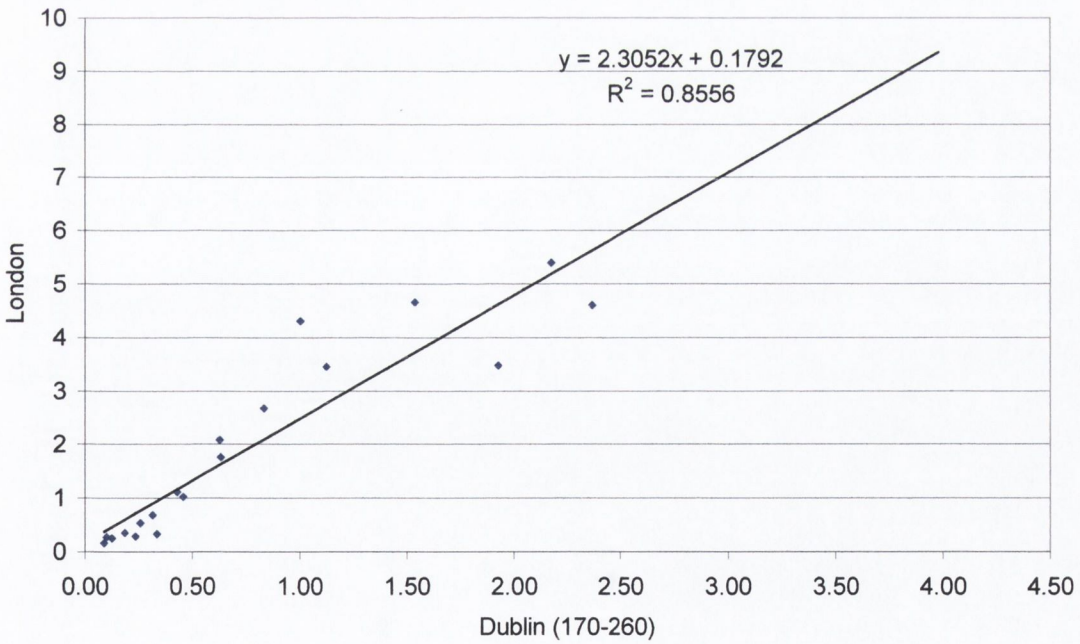


Figure 7.23 Scatter plot of Dublin (170-260°) and London average HC concentrations

Table 7.2 Comparison of Dublin city centre concentrations to similar studies world-wide

	This study (overall)	This study (40-90°)	This study (170-260°)	Cardiff (2001)	Edinburgh (2001)	London (2003)	Lille (97-99)	Lille (99-2000)	Helsinki (2001)	Hong Kong (01)	Taiwan (02)	CA (2000)	NY (2003)	TX (2003)	CA (2003)	NH (2003)
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)	(n)	(o)	(p)
ethan	4.98	5.31	3.98	5.80	3.70	8.51	4.86	3.96	3.36	-	-	-	-	-	-	-
prop	2.58	2.98	1.93	2.24	3.60	3.47	2.48	1.80	1.80	2.62	-	-	-	-	-	-
n-but	2.52	3.19	1.54	2.63	2.49	4.66	3.07	1.61	2.24	3.65	-	-	-	-	-	-
i-but	1.41	1.73	0.83	0.91	1.36	2.68	1.64	0.87	0.66	1.49	-	-	-	-	-	-
n-pen	0.70	0.91	0.43	0.72	0.70	1.12	1.51	0.54	0.37	0.74	-	-	-	-	-	-
i-pen	1.86	2.61	1.00	1.76	1.11	4.30	5.23	1.43	0.77	1.57	-	-	-	-	-	-
eth	3.42	4.06	2.17	2.99	1.33	5.40	7.83	2.72	1.80	-	-	-	-	-	-	-
pro	1.03	1.27	0.64	1.11	1.06	1.77	2.01	0.67	0.40	1.11	-	-	-	-	-	
1-but	0.47	0.58	0.34	0.14	0.09	0.33	0.61	0.19	0.09	-	-	-	-	-	-	-
1,3 b	0.28	0.30	0.24	0.12	0.09	0.28	0.40	0.11	0.08	0.18	-	-	0.12	0.20	0.20	0.10
t-2-b	0.25	0.27	0.19	0.15	0.16	0.35	0.59	0.37	0.02	-	-	-	-	-	-	-
c-2-b	0.18	0.19	0.12	0.09	0.08	0.25	0.43	0.16	0.06	-	-	-	-	-	-	-
t-2-p	0.18	0.22	0.10	0.09	0.06	0.27	0.32	0.05	0.05	-	-	-	-	-	-	-
c-2-p	0.14	0.15	0.09	0.05	0.03	0.16	0.16	0.03	0.02	0.17	-	-	-	-	-	-
tol	1.84	2.42	1.12	1.49	1.14	3.45	5.12	2.32	1.07	3.42	7.53	2.30	1.10	1.80	3.30	2.30
o-xyl	0.49	0.64	0.31	0.29	0.23	0.68	0.99	0.25	0.23	0.14	0.66	0.43	0.21	0.20	0.40	0.20
m+p	0.96	1.21	0.63	0.83	0.66	2.08	2.56	0.71	0.54	0.41	0.91	1.21	-	-	-	-
benz	0.77	1.01	0.46	0.54	0.41	1.02	2.43	0.78	0.59	0.78	1.53	0.95	0.40	0.80	0.90	0.40
ethb	0.41	0.53	0.26	0.33	0.19	0.54	0.81	0.26	0.18	0.27	0.71	0.37	0.20	0.30	0.50	0.30
acet	2.91	3.48	2.36	1.36	1.60	4.60	5.13	1.54	2.13	-	-	-	-	-	-	-
Correlation with Dublin (40-90°)				0.94	0.93	0.99	0.98	0.94	0.96	0.84	*0.95*	*1.00*	*1.00*	*0.99*	*0.99*	*0.98*
Correlation with Dublin (160-270°)				0.86	0.90	0.94	0.91	0.86	0.99	0.88	*0.93*	*1.00*	*1.00*	*0.98*	*1.00*	*0.99*

7.4 M+P XYLENE / ETHYLBENZENE RATIO

Section 5.7.2 described how the difference in photochemical degradation rates of m+p-xylene and ethylbenzene can be used to gather information on the relative age of different air masses. Specifically, the average concentration ratio in hourly data for wind direction sectors 40-90° and 170-260° gives a general indication of the average air mass age for either sector. A ratio of 2.26±0.03 at 95% confidence was obtained for sector 40-90° while a value of 2.42±0.05 at 95% confidence was obtained for sector 170-260°. These values show that although the concentration levels are much lower for wind sector 170-260°, the compounds detected have been present in the air for less time than for wind direction sector 40-90°.

Due to local obstructions associated with local wind directions 40-90°, it is not certain where exactly this older air has originated, but it can be said with a high degree of certainty, that it emanated from the wind direction sector 0-160° (Figure 7.5). This regional wind direction sector is associated with the United Kingdom and continental Europe beyond. It is therefore possible that the older average air mass from this wind direction can be attributed to transboundary pollution with emissions originating in the U.K or continental Europe. This is further substantiated when one considers how close the receptor is to the Irish sea (approximately 1km eastwards).

To corroborate this suggestion that air masses with local wind directions between 40-90° often originate from the UK or continental Europe, Figures 7.17 to 7.20 may be re-examined. The profiles between 00:00 and 05:00, when relatively little traffic activity is observed, are in stark contrast.

On average, the concentrations obtained with wind directions between 40° and 90° are more than double those obtained for wind directions 170-260°. Differences in wind speeds and hence atmospheric turbulence are not anticipated to be the cause, as both wind sectors experienced similar average wind speeds of 1.7 m/s for 40-90° and 1.8 m/s for 170-260° and similar average hourly wind profiles as illustrated in Figure 7.21.This suggests that for local wind directions 40-90°, a relatively high level of pollutants was already present in the air prior to the air passing through the junction of interest.

Figures 7.24 and 7.25 show the variation in average hourly m+p xylene / etylbenzene ratio over the course of the average day. Two contrasting trends are observed. In Figure 7.24 very little variation occurs over the course of the average day for wind sector 40-90°. Hence, although the emissions from traffic activity at the junction are relatively high during morning and evening peak times, they (perhaps unexpectedly) have a limited effect on the relative age of the average air mass sampled. Ethene concentrations obtained for the same wind sector are also plotted to illustrate this point.

For wind direction sector 170-260° we observe a marked change in the trend. Similar to observations made at the M4 site in Leixlip (Figure 5.37), road traffic emissions are seen to impact on the relative age of the average air mass over the course of the average day.

From Figure 7.25 we can see the relative age of the air mass is younger for morning periods associated with morning peak road traffic emissions. Ethene concentrations are again plotted on the same graph to outline the similarity in increased road traffic emissions and relative air mass age.

Although the concentrations for this wind direction are much lower than those for sector 40-90° we can see they have a greater effect on the relative age of the air mass, possibly due to the considerably higher background concentrations observed for wind sector 40-90°.The relative air mass age over the course of the average day for wind sector 170-260° and the M4 at Leixlip are both seen to be effected by road traffic emissions, where concentrations monitored are relatively low, and pollutants well mixed.

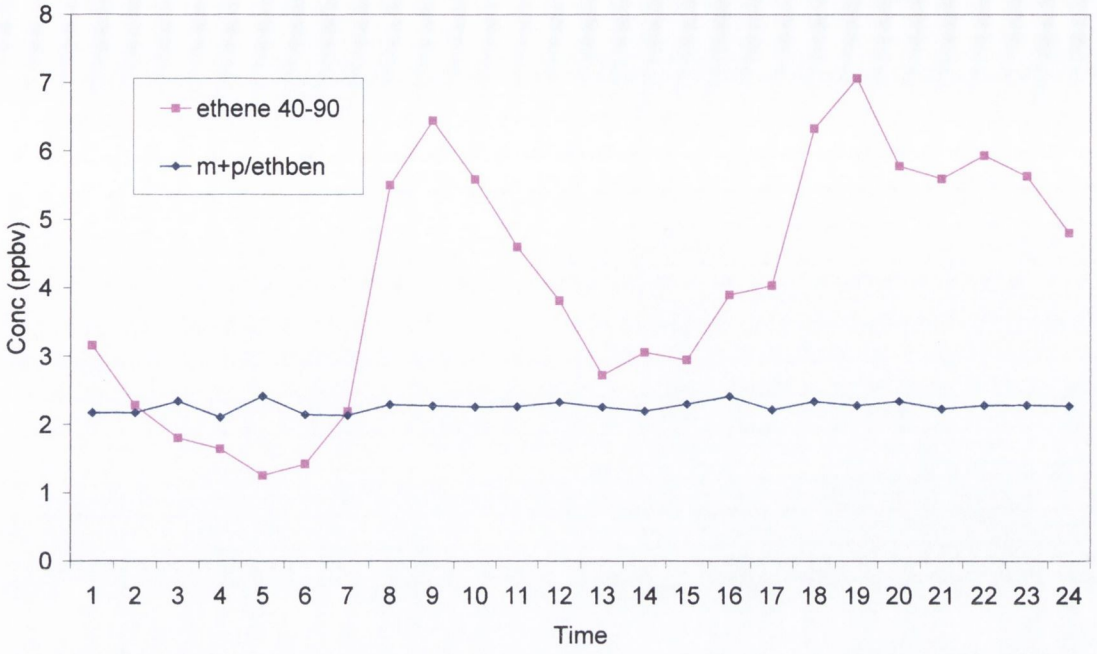


Figure 7.24 Average age of air mass for each hour allied to ethene diurnal profile for wind direction sector 40-90°

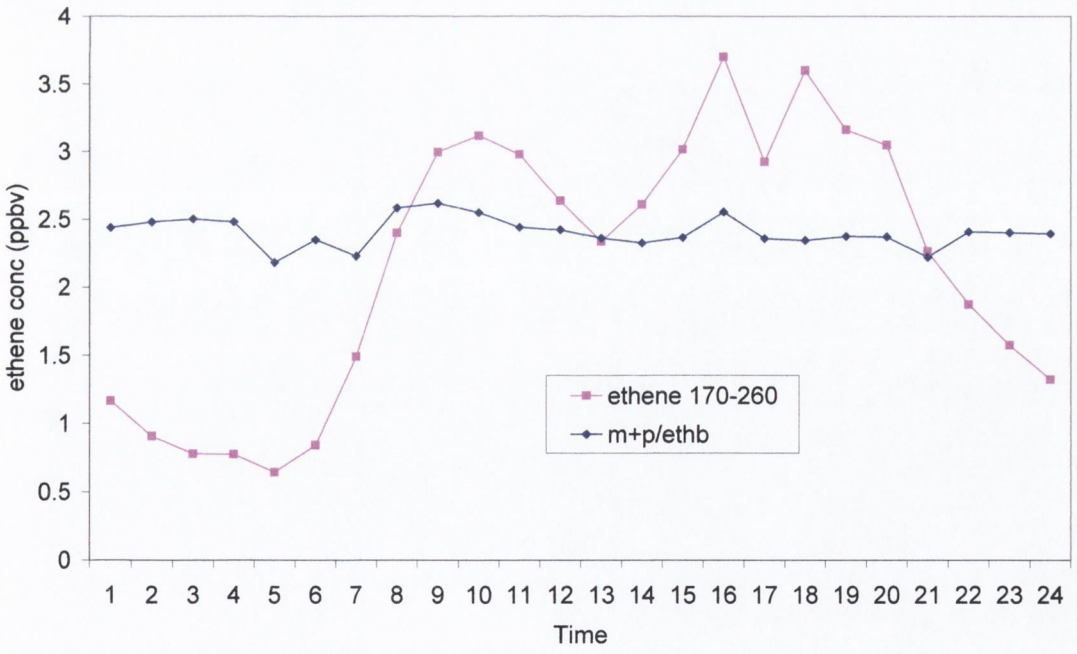


Figure 7.25 Average age of air mass for each hour allied to diurnal profile observed for ethene for wind direction sector 170-260°

7.5 ETHENE / ACETYLENE RATIO

The ethene / acetylene ratio again used to investigate road traffic emission trends and to further corroborate conclusions made in the previous chapter on the validity of using this ratio as an absolute indicator of catalytic converter efficiency. For wind sector 170-260°, an average ratio of 0.99 was obtained, a value which relates very well to the back ground ratios observed in Chapter 6 at the M50 site. As expected a higher ratio of 1.23 was obtained for wind sector 40-90°.

The ratio is more useful in giving an indication of the contribution of nearby road traffic sources to ambient concentrations. In chapter 6, with an average wind speed of 1.06 m/s, the ratio had decreased to its background value (approximately 1.0) within 240 metres. Higher ratios can therefore be viewed as being directly associated with nearby local road traffic emissions, whereas lower average ratios are associated with road traffic emissions from less local sources. If this hypothesis is true, higher average ratios should correlate with higher traffic activity for nearby sources. To analyse this, the variation in the average hourly ratio was plotted for each wind sector, the results being shown in Figures 7.26 and 7.27.

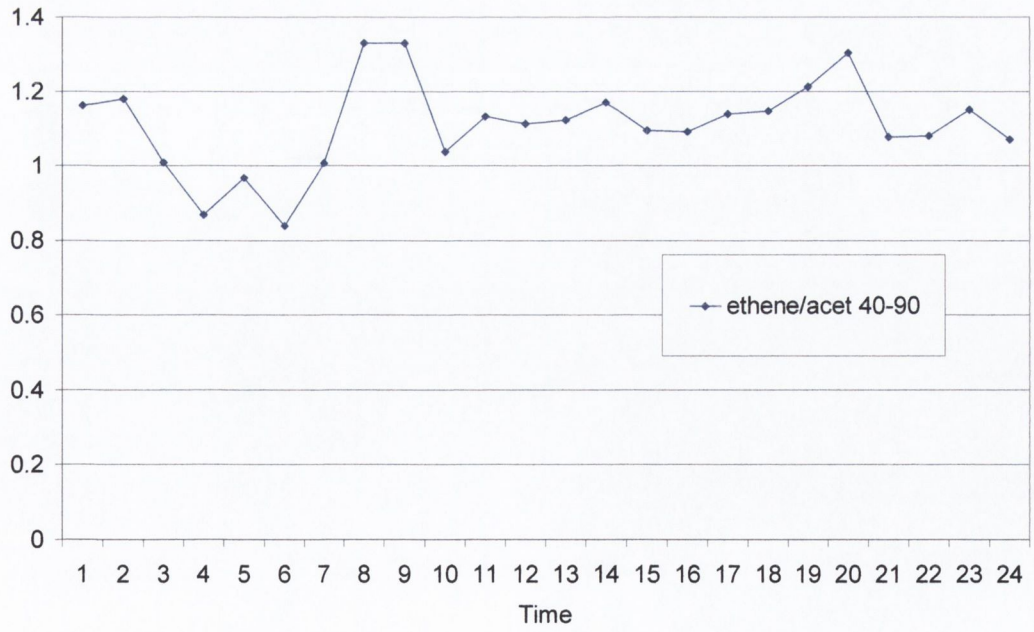


Figure 7.26 Average 24 hour ethene / acetylene ratio for wind direction sector 40-90°

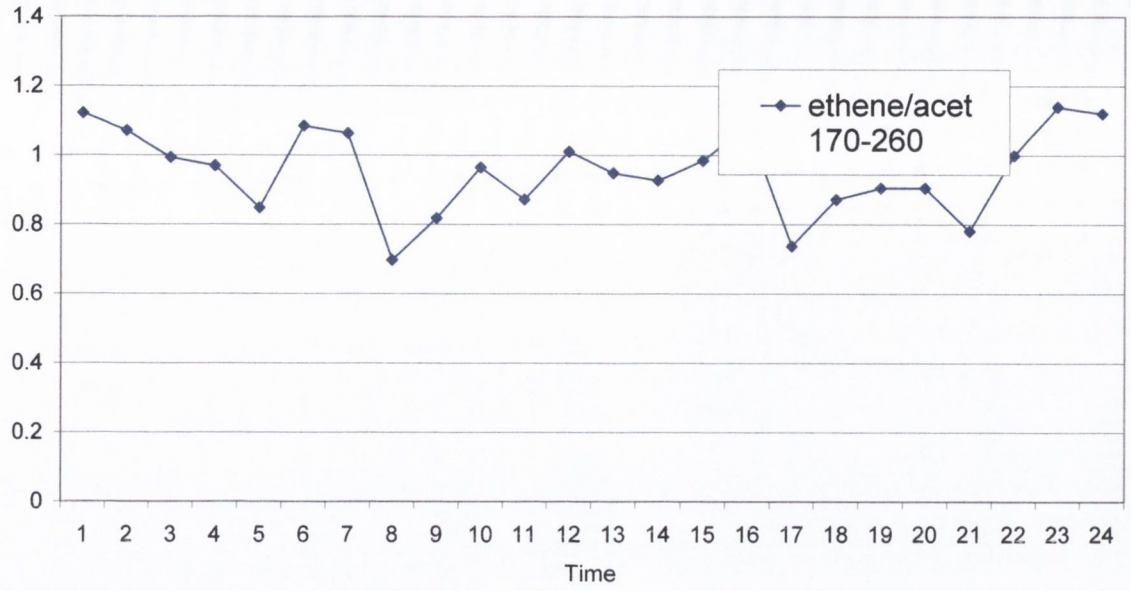


Figure 7.27 Average 24 hour ethene / acetylene ratio for wind direction sector 170-260°

Figure 7.26 shows a clear correlation with traffic flow at the junction. A distinct morning peak between 07:00 and 10:00 and an evening peak around 20:00 are evident. This suggests that when a strong local road traffic emissions source is nearby, an increase in traffic activity will produce an increased E:A ratio.

In contrast, for wind sector 170-260° in Figure 7.27, the average hourly ratio is not greatly affected by anticipated traffic flow. The 16:00 peak coincides with evening peak emissions, but the overall deviation over the course of the day is very limited.

To illustrate how this ratio can be used to ascertain the impact of local road traffic emissions, data associated with high (top 10%) and low (ratio < 1) ratios were examined for each wind sector. Figures 7.28, 7.29 and 7.30 compare the frequency of high and low ratios and the observed ethene concentrations for each wind sector.

For wind sector 40-90°, the 90^{th} percentile value of the E:A ratio is 1.3, hence, Figure 7.28 plots the number of times ratios greater than this value were observed in each hour. The hourly frequencies of these higher ratios correlate very well with peak ethene concentrations and peak traffic flow at the junction. For ratios less than 1, the hourly frequencies of occurrence

correlate very poorly with peak traffic flows, the highest frequencies occurring between the hours of 02:00 and 07:00.

For wind direction sector 170-260°, the 90th percentile ratio is 1.15. The hourly occurrences of ratios greater than this were plotted against the average ethene concentration, and m+p xylene / ethylbenzene ratio in each hour for this wind sector (Figure 7.29). The m+p xylene / ethylbenzene ratio (representing the relative air mass age) was not included in Figure 7.28 for the wind sector 40-90°, as no noticeable trend was seen over the 24 hour period.

In Figure 7.29, the frequency of higher ethene / acetylene ratios correlates well with both ethene concentrations and the average age of the air mass. The relatively "older" air between 04:00 and 06:00 has the lowest frequency of ratios above 1.15 and the lowest actual ethene concentrations. All three morning peaks correlate well showing that the relatively young air is associated with a high hourly frequency of ethene / acetylene ratios above 1.15. The correlation between the three graphs is less certain for the evening peak at 16:00, but is still evident.

Figure 7.30, shows that for wind sector 170-260°, by far the highest hourly frequencies of ratios less than 1 occur between 04:00 and 06:00, a period associated with relatively old air. During traffic-active times of between 07:00 and 23:00, a relatively high frequency of ratios less than 1 is observed, compared to wind direction sector 40-90°.

For 40-90°, the frequency never exceeds 2 for this time period, but for 170-260°, all frequencies are 2 or above for the same time. This is to be expected as the wind sector 170-260° is associated with more distant emissions, and as seen in Chapter 6, the ethene / acetylene ratio decreases with distance travelled from the source.

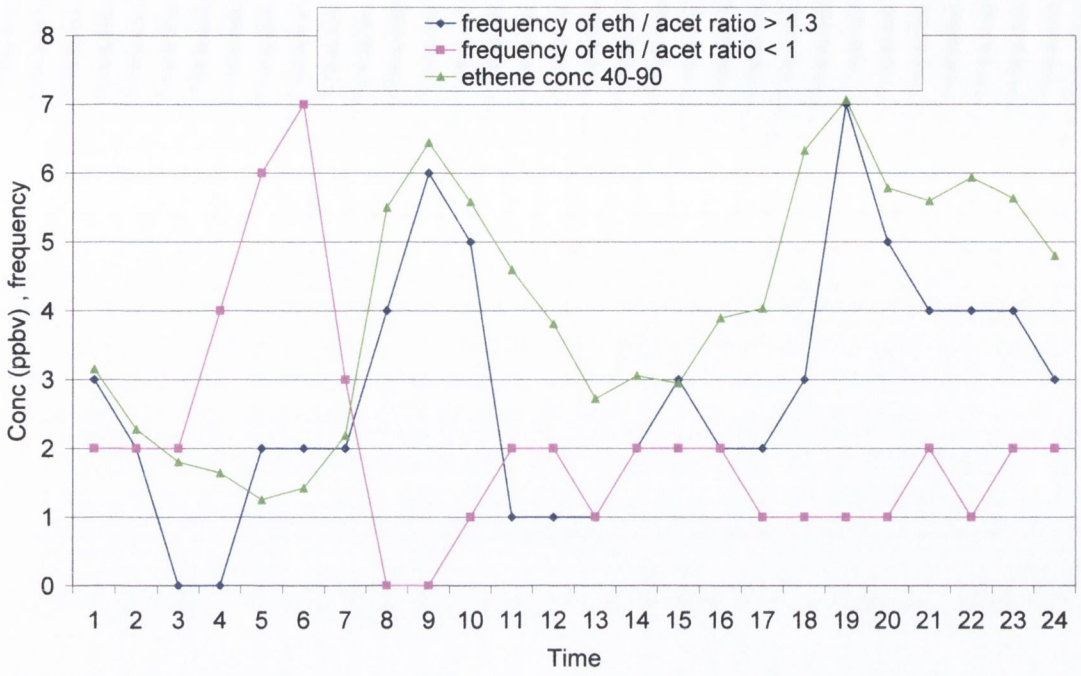


Figure 7.28 Hourly frequencies of ethene / acetylene ratios for values >1.3 and<1 in addition to ethene diurnal profile, for wind directions 40-90°

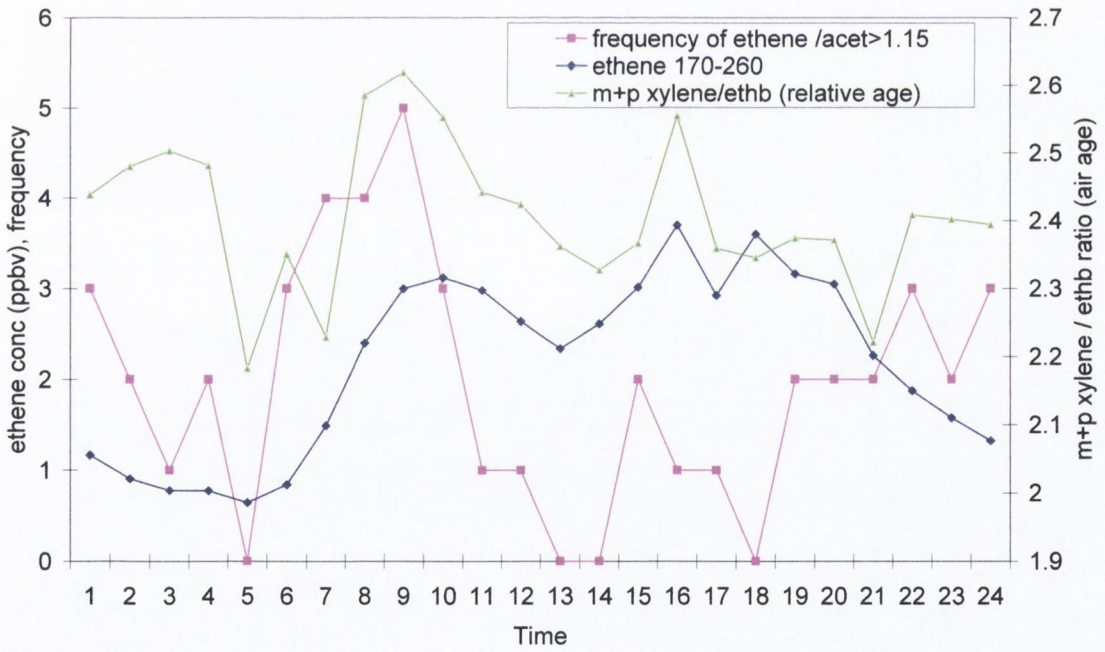


Figure 7.29 Hourly frequencies for ethene / acetylene ratios > 1.15, diurnal profile for ethene and average relative air mass age for wind direction sectors 170-260°

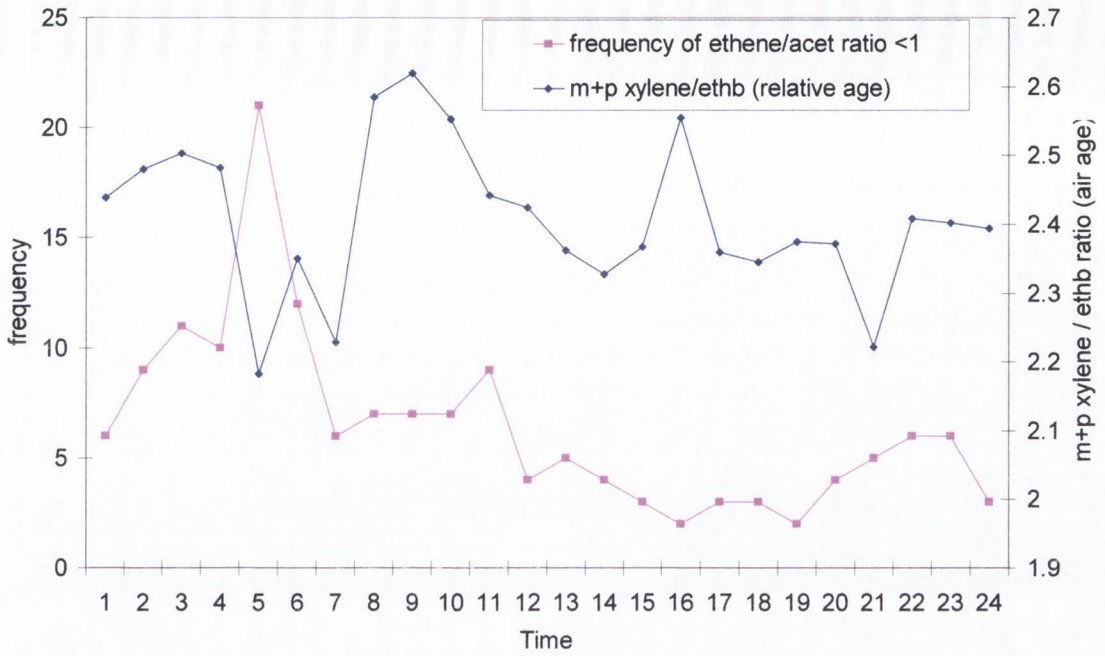


Figure 7.30 Hourly frequencies for ethene / acetylene ratios <1 and average relative air mass age for wind directions 170-260°

7.6 EVAPORATIVE EMISSIONS

The analysis techniques used to determine the impact of evaporative emissions at the M4 motorway site at Leixlip were applied at the city centre. The same three parameters were examined, namely:

- correlation between hourly concentrations and temperatures.
- correlation between hourly HC / acetylene ratio and temperatures.
- distribution of HC / acetylene ratio over the course of the average day.

These techniques were applied to both main wind direction sectors, 40-90° and 170-260°. The correlations between concentration and temperature and between HC / acetylene ratio and temperature are shown in Table 7.3.

Compound	Correlation between conc. and temp. for 40-90° sector	Correlation between ratio and temp. for 40-90° sector	Correlation between conc. and temp. for 170-260° sector	Correlation between ratio and temp. for 170-260° sector
ethane	- 0.80	- 0.65	-0.94	- 0.01
propane	- 0.73	- 0.61	-0.85	- 0.36
n-butane	- 0.19	- 0.13	-0.63	0.05
iso-butane	- 0.43	- 0.13	-0.61	0.03
n-pentane	0.08	0.32	-0.64	0.37
iso-pentane	0.54	0.84	-0.36	0.63
1-butene	0.32	0.67	-0.47	0.58
1,3 butadiene	- 0.23	- 0.36	-0.90	- 0.47
trans-2-but	- 0.62	- 0.51	-0.74	- 0.26
cis -2 -butene	- 0.40	- 0.21	-0.44	- 0.35
trns -2 -pent	0.60	0.65	-0.32	0.61
cis -2 -pentene	0.43	0.58	-0.09	0.62
toluene	0.01	0.30	-0.32	0.61
o-xylene	0.11	0.32	-0.30	0.53
m+p xylene	0.12	0.36	-0.30	0.62
benzene	- 0.26	- 0.29	-0.64	0.09
ethylbenzene	0.09	0.35	-0.39	0.49

Table 7.3 Correlations for concentrations and ratios versus temperature for wind direction sectors 40-90° and 170-260°

Due to the differing source effects associated with both main wind sectors, contrasting evaporative trends are observed. For wind sector 40-90°, the pattern is very similar to that observed at the M4 site at Leixlip, namely, all compounds which display positive correlations between concentration and temperature also show positive correlations between the HC / acetylene ratio and temperature.

For wind sector 170° to 260°, only negative correlations between concentration and temperature are observed, and only the HC / acetylene ratios indicate which compounds show evaporative tendencies (n-butane, iso-butane, n-pentane, iso-pentane, 1-butene, trans-2-pentene, cis-2-pentene, toluene, o-xylene, m+p-xylene, benzene and ethylbenzene). The data suggests evaporative behaviour from the butanes and benzene from emissions emanating from this sector. However, the correlations are so weak that evaporative emissions are not anticipated to be significant, as confirmed in Figure 7.31 which shows the variation in benzene / acetylene ratio with temperature.

Graphical illustrations of 2 compounds showing positive correlations between the HC / acetylene concentration ratios and temperature are shown in Figure 7.32 for both wind sectors. The expected trend is observed, with the ratio increasing with temperature above 10°C, the temperature above which significant evaporative emissions are known to occur (Field *et al*, 1994).

Figures 7.33 and 7.34 compare the average diurnal profiles of the toluene / acetylene ratio and temperature for the different wind sectors. Mid-day peaks relating to ambient evaporative emissions are evident as are early evening (19:00) peaks associated with running losses.

For sector 40-90°, the peaks corresponding to running losses, seen at 08:00-09:00 and 19:00 are less well defined (Figure 7.33). As has been discussed the average age of the air from this wind sector is considerably older than that from wind sector 170-260° which tends to mask the influence of local evaporative emissions.

The large peaks observed at 09:00 and 16:00 for sector 170-260° (Figure 7.34) correlate very well with the morning and evening peak traffic emissions observed for this wind sector (Figure 7.19). This suggests that running losses make a substantial contribution to evaporative emissions for this wind sector.

In general temperatures in the UK and Dublin are similar and episodes of high temperature are likely to be experienced at the same times in both countries. Given suitable meteorological conditions, in particular wind speeds high enough to transport the pollutants before sufficient atmospheric degradation has occurred, evaporative emissions could travel from the UK and be detected at our receptor. This would have the effect of raising the background HC / acetylene ratio. This effect is evident when comparing the daily trends of Figures 7.33 and 7.34. This same behaviour is displayed by all compounds exhibiting evaporative behaviour. This adds further evidence of the importance of emissions emanating from the UK and continental Europe.

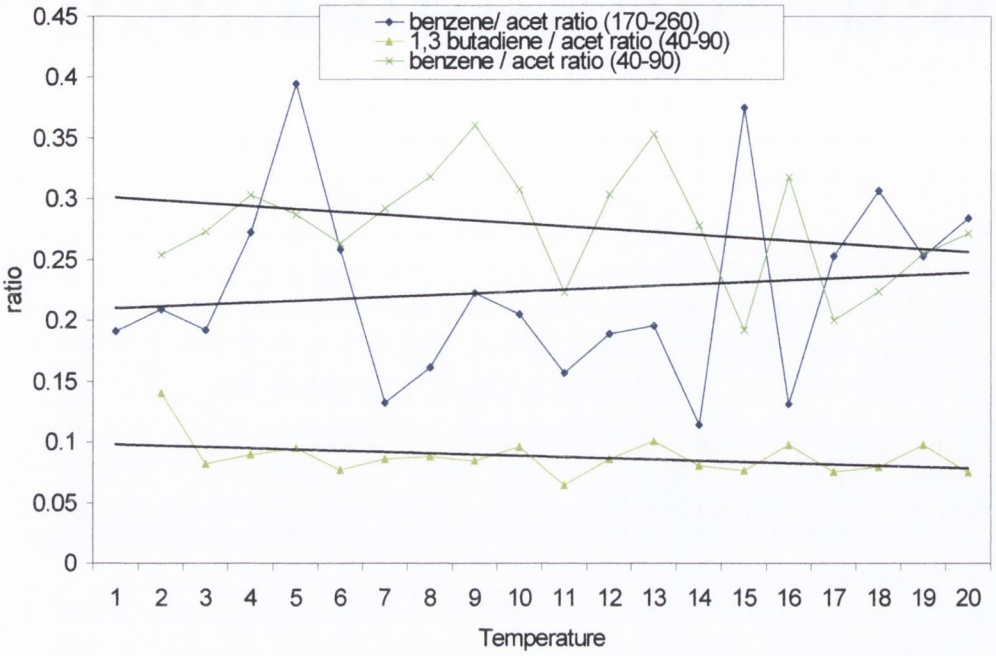


Figure 7.31 Examples of compounds exhibiting little or no evaporative trends for both main wind direction sectors

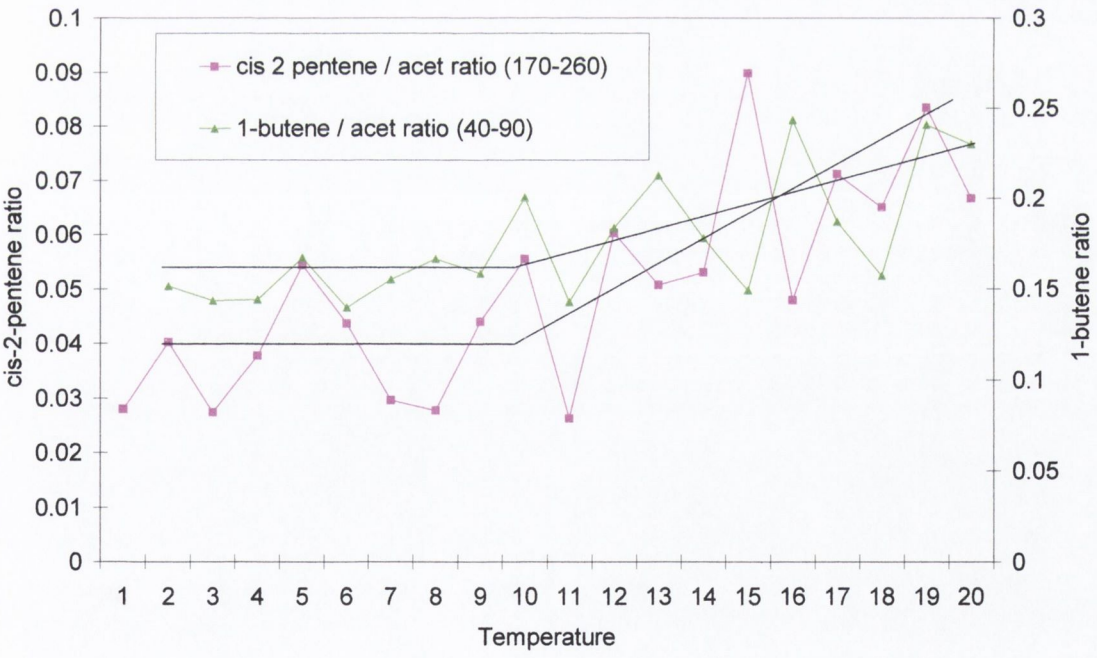


Figure 7.32 Examples of compounds exhibiting evaporative trends for both main wind direction sectors

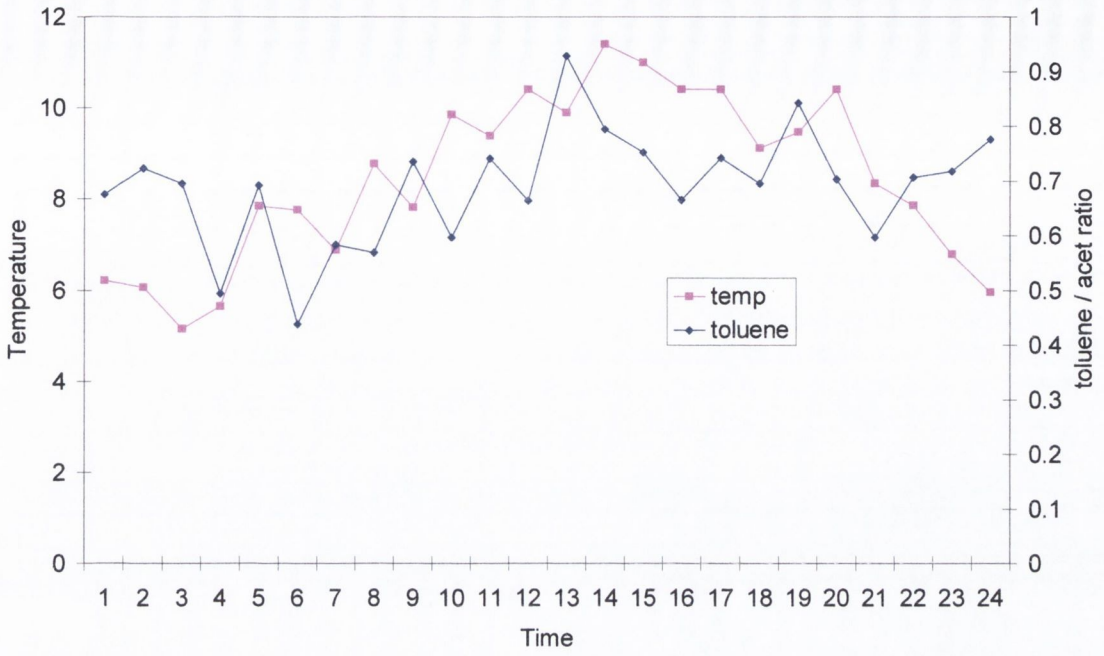


Figure 7.33 Diurnal variations of toluene / acetylene ratio and temperature for wind direction sector 40-90°

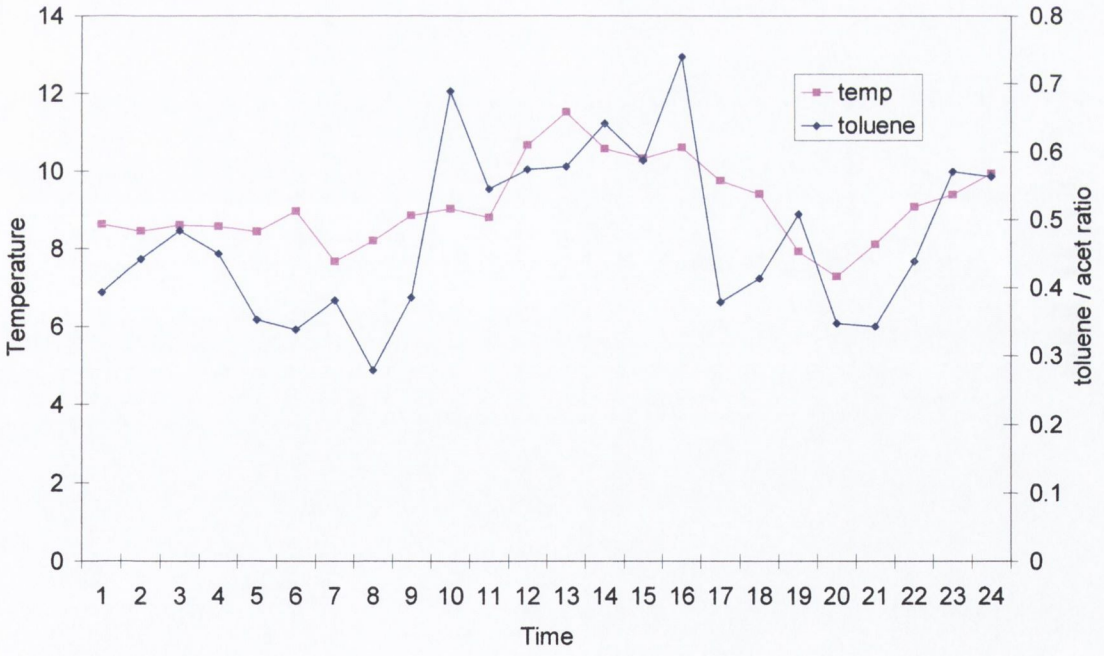


Figure 7.34 Diurnal variations of toluene / acetylene ratio against temperature for wind direction sector 170-260°

7.7 COMPARISON WITH CONCENTRATIONS OBTAINED IN 1998

A period of monitoring was carried out at the same location using the same pre-cursor system from March to August 1998. Statistical comparisons between results obtained in 1998 and the present are summarised in Table 7.6.

Most compounds have decreased in concentration from 1998 to 2003. The exceptions being ethane, propane, trans-2-butene, 1-butene and acetylene.

The concentrations of toluene and benzene were seen to decrease by more than any other compound: toluene reduced by on average 44%, while that of benzene was seen to decrease by 57%. The toluene decrease can be explained by the relocation of Independent Newspapers printing press from Middle Abbey Street in Dublin City centre to Citywest in sub-urban Dublin. This source was cited in 1998 as the reason for the elevated toluene concentrations monitored at the receptor (Marnane, 2000). The reduction in benzene is probably due to changes in fuel regulations since 1998 requiring benzene content in fuel to be less than 1% v/v (CEC, 1998a). In 1998, the average fuel was found to have 2.98% v/v benzene.

If these two compounds are removed from a scatter plot comparing 1998 to 2003 concentrations, an R^2 value of 0.99 is obtained suggesting a near uniform reduction in concentrations (Figure 7.35).

As can be seen in Table 7.6, the majority of compounds strongly related to traffic activity have decreased in concentration between 1998 and 2003. Two of the exceptions, 1-butene and trans-2-butene, can be discounted as a large number of zero values were obtained in the 1998 study due to analytical problems. This had the effect of lowering the average 1998 concentrations of these compounds, making a comparison with 2003 unhelpful.

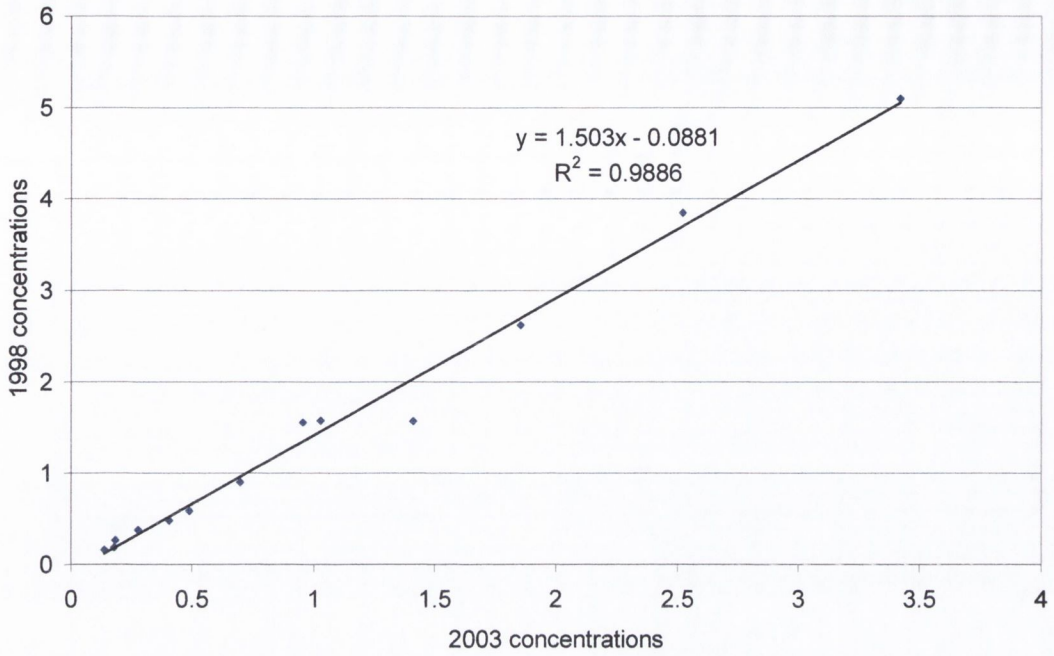


Figure 7.35 Scatter plot of 2003 concentrations against 1998 concentrations for those compounds which were seen to decrease

Acetylene is the only strongly traffic-related compound for which a significant lowering of average concentrations did not occur between 1998 and 2003. As acetylene is almost exclusively associated with road traffic emissions, a reduction similar to those observed for all other traffic-related compounds could have been expected. One possible explanation is an alternate acetylene source raising ambient concentrations relative to 1998. This is however highly improbable due to the aforementioned, well documented, almost exclusive association of ambient acetylene with road traffic emissions (Derwent *et al.*, 2000; Barletta *et al.*, 2002, Borbon *et al.*, 2002).

A second possible reason relates again to long range transport of emissions from other countries. Figure 7.36 compares the diurnal profiles obtained for acetylene in 2003 and 1998. For both years, the complete data set is employed, i.e. unfiltered data including times of low wind speed and stable atmospheres. It is quite evident that the background levels (01:00-07:00) in 2003 are considerably higher than those obtained in 1998. In contrast both morning and evening peaks have decreased substantially over the same period, in line with all other strongly traffic-related compounds, for which m+p xylene is shown as an example in Figure 7.37. The early morning (01:00-07:00) levels of all other traffic-related compounds, where

limited traffic activity is observed, are lower in 2003 than in 1998. The unique behaviour of acetylene is attributable to its relatively long atmospheric lifetime (approximately 20 days as opposed to several hours for m+p xylene) which gives it the capacity to be transported over much greater distances than most hydrocarbons. The only other hydrocarbon monitored with a strong association with road traffic emissions and a similar degradation time is benzene, with an atmospheric lifetime of approximately 18 days (Atkinson, 1995). However, changes in fuel content of benzene from 1998 to 2003, dominate the behaviour of this compound, preventing direct comparison with acetylene.

Table 7.4 shows that regional winds from a 0-160° sector were much more frequent in 2003 than in 1998. These wind directions are likely to have emanated from the UK or continental Europe, resulting in higher background concentrations of compounds possessing the ability to travel long distances. Table 7.4 also compares the average age of the air for both monitoring periods (m+p xylene / ethylbenzene ratio). The relative age of the air in 2003 is much older than that observed in 1998, giving further evidence that distant sources play a significant role in the higher levels of acetylene observed in 2003.

	Frequency of regional winds from 0-160° (%)	Frequency of regional winds from 170-260° (%)	Relative age of air mass (m+p xyl. / ethbenz.)
1998	26%	69%	3.3
2003	50%	36%	2.4

Table 7.4 Frequency of occurrence of regional winds from 0-160° and 170-260° wind direction sectors and relative air mass age for monitoring periods in 1998 and 2003

A comparison of the average daytime concentrations (08:00-20:00) of acetylene in both years, when traffic activity is highest and background concentrations have a less significant effect, reveals a reduction in acetylene levels from 1998 to 2003 of 12%. A correction for the increased background acetylene concentrations arising due to long range transport can be made, by subtracting the average difference in values between 01:00 and 07:00 (0.6ppbv). This gives an overall reduction of 18% from 1998 to 2003, which compares reasonably to the overall average decrease seen of 24% for all compounds strongly related to traffic emissions (toluene and benzene excluded due differences in sources for 98 and 03).

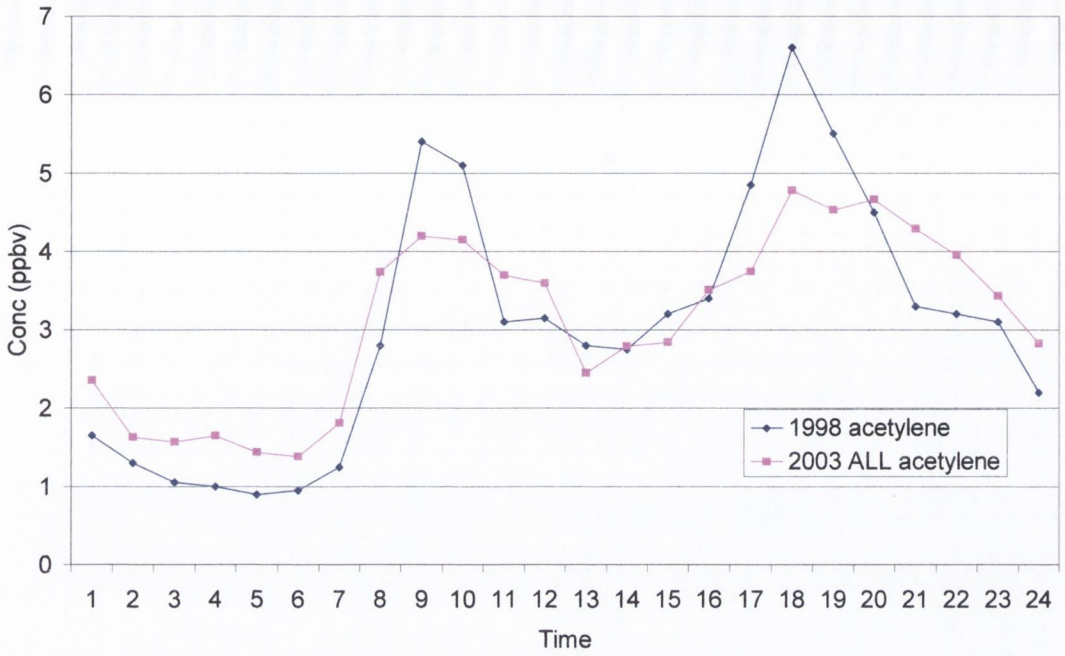


Figure 7.36 Comparison of diurnal trends of acetylene concentrations obtained in 1998 and 2003

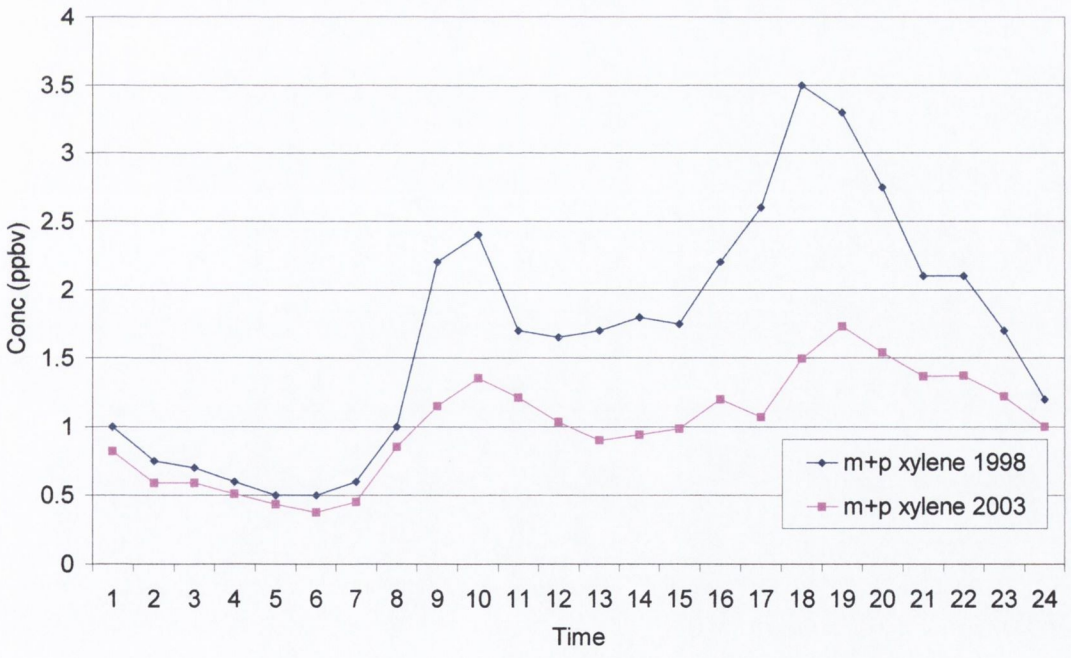


Figure 7.37 Comparison of diurnal trends for m+p-xylene obtained in 1998 and 2003

Figure 7.37 is representative of the trend displayed by compounds strongly related to road traffic emissions. The morning and evening peaks are seen to occur at similar times in both

years, but the 2003 morning peak extends over a longer time period. The diurnal profiles obtained in 1998 display more variation over the course of the average day, suggesting a stronger influence from local road traffic. In addition, the 2003 morning peak is extended over a longer period due to more staggered morning peak traffic. The two other compounds which showed a rise in mean concentrations from 1998 to 2003, but are not strongly associated with road traffic emissions, are ethane and propane. As both compounds have relatively long atmospheric lifetimes (approximately 60 days for ethane and 13 days for propane; Atkinson, 1995), the increase in their concentrations can also be explained by long range transport from relatively more polluted regions. Figure 7.38 shows the behaviour of ethane. The background levels are seen to be much higher in 2003, but again, the values between 08:00 and 20:00 (traffic active hours) are generally slightly higher in 1998 than 2003. This is evidence of the contribution from local road traffic emissions to ambient ethane levels. The reduction in this contribution between 1998 and 2003 can be seen in the background corrected plot of Figure 7.38, which shows how road traffic emissions for ethane have decreased over the 5 year period.

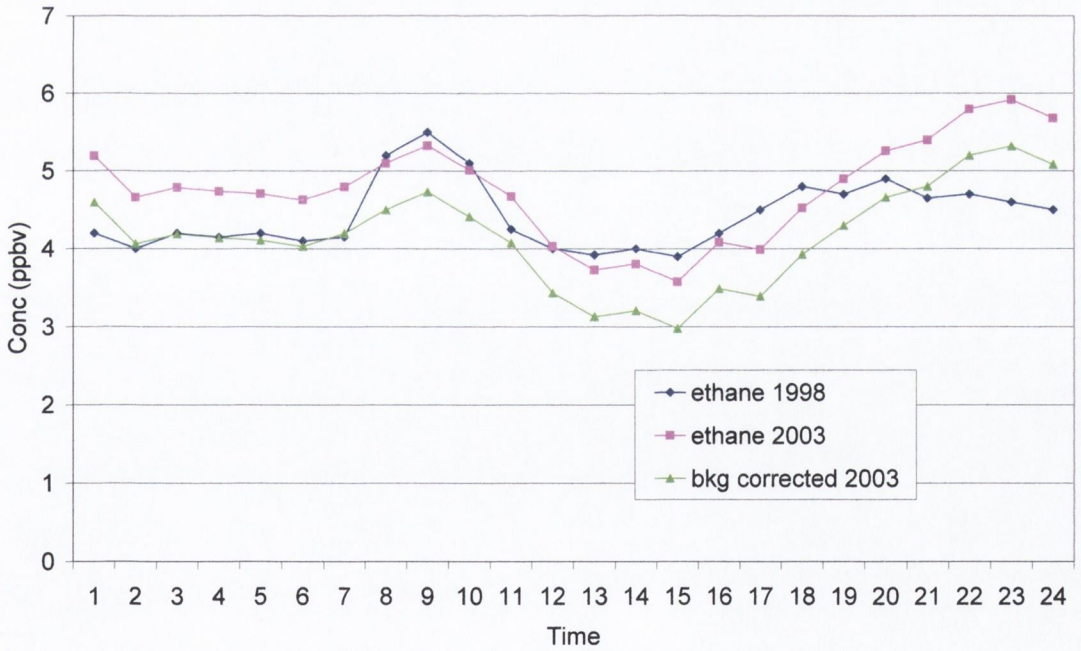


Figure 7.38 Diurnal profile for ethane for 1998 and 2003, with background corrected profile also shown

To further investigate the effect of long-range transport of pollutants relative to 1998, we plotted the ratio of average (2003 / 1998) concentrations against the natural log of atmospheric lifetime (days) for 12 compounds (Figure 7.39). Toluene and benzene were excluded due to the previously discussed difference in sources from 1998 to 2003. The compounds included and their associated atmospheric lifetimes are shown in Table 7.6.

The overall trend is quite apparent (Figure 7.39) and adds further evidence to the hypothesis of long range transport contributing substantially to the changes in concentrations observed. The relatively high R^2 seems to suggest a strong relationship between the concentration ratios and atmospheric lifetime. In general, the shorter lived the compound, the lower the ratio and hence greatest reduction since 1998, due to limited effect from long range transport.

	Approximate atmospheric lifetimes (due to reaction with OH radical), days
ethane	60.0[a]
propane	13[a]
n-butane	5.0[b]
i-butane	5.0[b]
n-pentane	2.9[b]
i-pentane	2.9[b]
ethene	1.7[a]
propene	0.3[a]
1,3 butadiene	0.2[c]
m+p xylene	0.3[d]
ethylbenzene	2.0[d]
acetylene	20.0[e]

a = Atkinson (1995), b = Doskey (1999), c = Dollard et al (2001), d = Monod et al (2001), e =Kanakidou et al (1988)

Table 7.5 Atmospheric lifetimes of HC compounds of interest

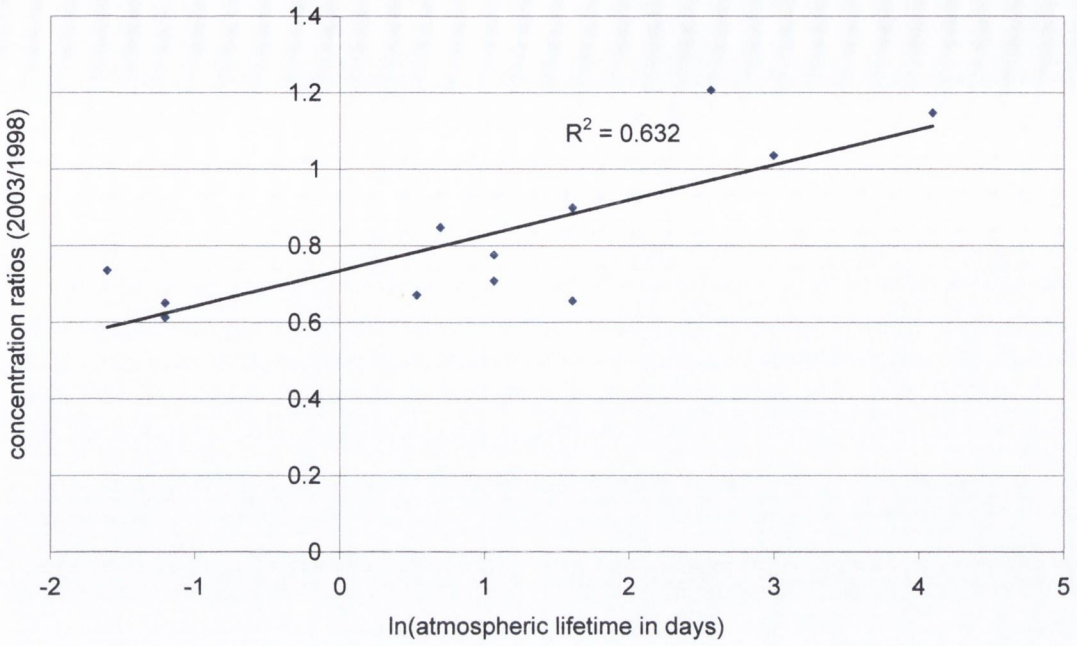


Figure 7.39 Concentration ratios (2003 / 1998) against the natural log of atmospheric lifetime (days) for HC compounds of interest

A recent EPA report on Ireland's environment (EPA, 2004) outlined the trend in overall VOC emissions from transport, in which a significant decrease from 1998 to 2002 was reported. Emissions from road traffic were estimated from fuel sales, disaggregated by vehicle category and their annual average mileage, and by applying emission factors that take account of engine capacity, applicable control technology, speed and other factors.

Figure 7.40 from that report illustrates the dominant contribution from transport to total VOC concentrations and the extent to which VOCs were estimated to have decreased since 1998. The report estimates a reduction in transport emissions of approximately 50% from 1998 to 2003, almost double the average value of 24% observed during this study.

This difference between the two estimations is possibly due to the difference in meteorological conditions observed at the monitoring site between 1998 and 2003. If the 1998 meteorological conditions had been repeated in 2003, significantly lower average ambient concentrations would have been observed. In addition, the EPA report does not take into account real world driving conditions and the effect vehicle condition has on emissions. However, the overall

trend of emission reduction is consistent in both the EPA report and the 2003 study in Dublin City.

Data obtained form the UK Hydrocarbon Monitoring Network at Marlyborne road for 1998 and 2003 was also analysed and compared with the trend observed in Dublin. The average 1998 and 2003 concentrations for London are shown in Table 7.6.

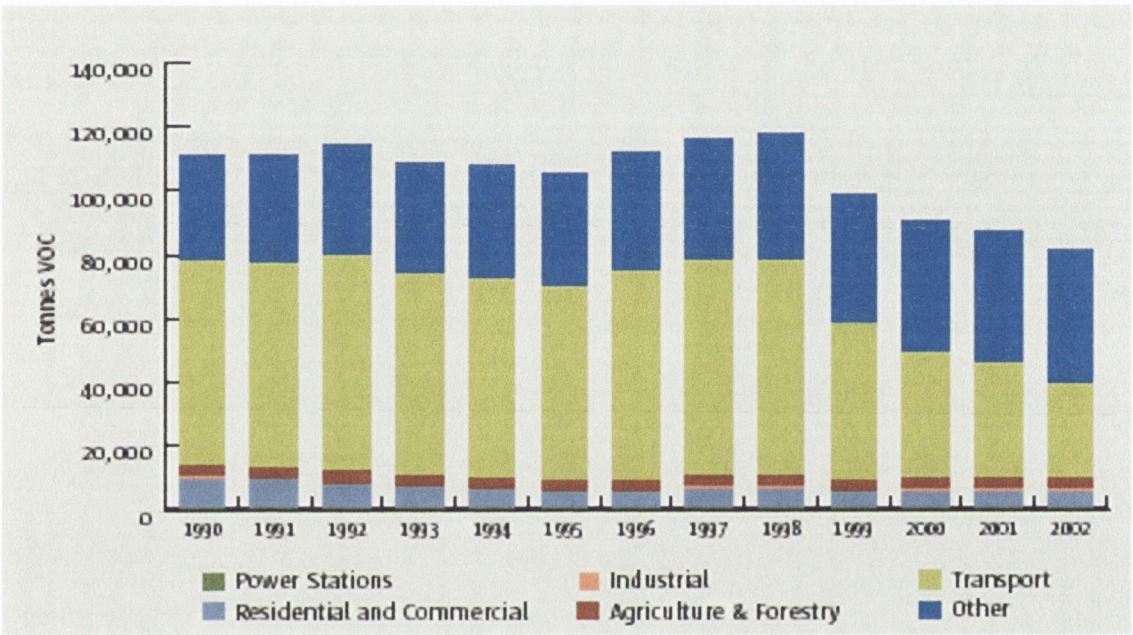


Figure 7.40 (EPA, 2004) Emissions of VOCs from 1990 to 2002

Figure 7.41 illustrates the decreasing trend in ambient concentrations in London for benzene and 1,3 butadiene, observed from January 1999 to December 2001 (Dumitrian, 2002a). The sharper decrease in benzene concentrations in 2000 is due to the change in benzene content in fuel to a mandatory level of no greater than 1% v/v.

If ethane and propane are omitted due to their strong association with natural gas emissions, an overall decrease of 57% is seen in London as opposed to 26% in Dublin. The trends observed at both locations illustrate the effect that control technology on newer vehicles has had on hydrocarbon emissions over the period of interest. The most interesting comparison between the two locations is the behaviour of acetylene, where a small increase in average

concentrations has been observed at both sites. Acetylene data was also obtained for 2001 at Marlyborne Lane where an even higher average value of 5.24ppbv was observed. This oscillating trend of acetylene concentrations is inconsistent with the continuously decreasing trends displayed by all other traffic related hydrocarbons.

Derwent *et al.* (2000), cited that road traffic is the only significant source of acetylene in London and analytical error due to co-elution of compounds was a probable cause for the high London levels observed. As the same trend was observed in Dublin with the present study, where no such analytical resolution problems were encountered, this explanation is unlikely to account for the trend observed. As in Dublin, a possible cause for the fluctuating trend observed in London is long range transport of acetylene from continental Europe.

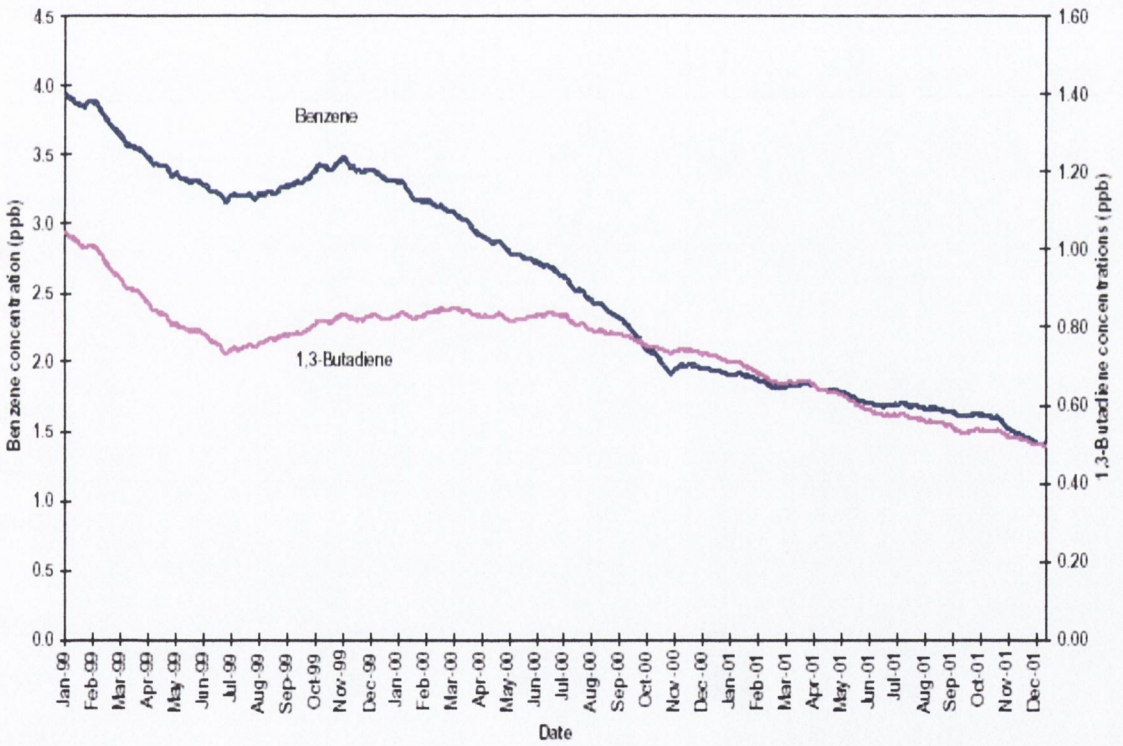


Figure 7.41 Concentrations of 1,3 butadiene and benzene observed at Marlyborne road, London between Jan 1999 and Dec 2001 (Dumitrian et al, 2002a)

There are several contributory reasons for the reductions in the concentrations of traffic-related compounds from 1998 to 2003. The main one is anticipated to be an increase in the

percentage of active catalytic converters in the Irish car fleet in 2003 compared to 1998.The percentage of petrol vehicles in 1998 with catalytic converter technology installed was approximately 57% (Marnane, 2000). However in 2003, this figure rose to a much greater 95%, estimated from the 2003 traffic fleet discussed in detail in Chapter 6. The meteorological conditions were vastly different in both monitoring periods. As a result, consideration of the ethene / acetylene ratio for catalytic converter efficiency is not useful as this ratio was shown conclusively in chapter 6 to vary with wind speed (atmospheric dilution capability).

A reduction in traffic volume at the junction is also a possible contributing factor to the decrease in concentrations observed. The morning peak time traffic flow passing the monitoring site, from the junction towards Pearse Street was determined in 1998 by Reynolds and Broderick (2000), where on average a flow of 2898 vehicles was observed between 08:00 and 09:00. From data obtained from the Dublin Transportation Office, the 2003 flow in the same location was estimated at 2014 vehicles between 08:00 and 09:00.

However, this lower traffic flow could be an indicator of increased congestion at the site, the effects of which are more than compensated for by the increase in catalytic converters. Using the equations described in Chapter 7, from COPERT3, a decrease in average speed of 10km/hr would lead to an increase in ethene composite emissions (using the 2003 fleet estimates) of 25%. Therefore, if average speeds were to drop a further 10km/hr at the receptor, the gains made in emissions reduction (on average 24% from 1998 to 2003) due to emissions control technology would become negligible. In addition, the lower vehicle velocities will effect the associated wake and hence limit pollutant dispersion (Seakins *et al.*, 2002).

Another major factor in the reduction of concentrations is the relative importance of local traffic sources in 1998 compared to 2003. As shown in Table 7.4, the majority of wind direction observations were from the 170-260° sector in 1998. In 1998 hydrocarbon data associated with this wind direction sector would have elevated HC concentrations to a much higher degree than would have been observed for similar conditions in 2003.

The reason for this is, in 1998 the area in the immediate vicinity of the receptor in this general wind direction was a car park facilitating Trinity College Dublin. The peak time traffic

movement would have undoubtedly effected the concentrations obtained. This source effect is most probably the reason for the much sharper diurnal profile seen in Figures 7.36 and 7.37 for 1998 data. Unfortunately it was not possible to compare results from different sectors as no sector analysis was done in 1998.

If meteorological conditions observed in 1998 has been repeated during our course of sampling in 2003, the resultant concentrations obtained would have been even lower, as the car park is now not in use, and a higher proportion of values would have emanated from this region, now more associated with Dublin city background levels.

	Mean		Minimum		Maximum		St. deviation		% Rel. st. dev		50th percentile		95th percentile		98th percentile		**London**	
	2003	1998	2003	1998	2003	1998	2003	1998	2003	1998	2003	1998	2003	1998	2003	1998	**2003**	**1998**
ethan	**4.98**	**4.34**	1.27	1.47	50.93	19.29	3.59	1.89	0.72	0.44	4.14	4.03	10.89	7.38	14.17	10.45	8.51	22.25
prop	**2.58**	**2.14**	0.27	0.39	18.72	22.09	2.51	1.48	0.97	0.69	1.92	1.79	6.92	4.53	10.36	6.63	3.47	27.49
n-but	**2.52**	**3.85**	0.11	0.24	31.05	29.00	3.10	3.33	1.23	0.86	1.59	3.08	7.73	10.27	10.13	12.89	4.66	6.3
i-but	**1.41**	**1.57**	0.05	0.11	26.34	13.34	1.93	1.33	1.37	0.85	0.80	1.26	4.67	3.83	6.37	5.05	2.68	6.47
n-pen	**0.70**	**0.90**	0.02	0.11	6.31	7.05	0.68	0.78	0.97	0.87	0.50	0.72	1.89	2.46	2.27	2.99	1.12	2.23
i-pen	**1.86**	**2.62**	0.06	0.04	29.85	22.71	2.41	2.51	1.30	0.96	1.11	1.99	5.57	7.61	7.02	9.77	4.3	10.64
eth	**3.42**	**5.10**	0.13	0.20	21.48	35.29	3.11	4.51	0.91	0.88	2.43	3.81	9.68	13.91	11.72	18.72	5.4	16.1
pro	**1.03**	**1.58**	0.07	0.03	6.88	13.57	0.94	1.48	0.92	0.94	0.70	1.15	2.99	4.35	3.56	5.84	1.77	5.28
1-but	**0.47**	**0.07**	0.06	0.00	3.08	1.23	0.35	0.18	0.74	2.57	0.36	0.00	1.18	0.48	1.36	0.75	0.33	0.93
1,3 but	**0.28**	**0.38**	0.03	0.03	1.61	2.85	0.18	0.33	0.66	0.87	0.25	0.29	0.63	1.03	0.79	1.30	0.28	1.04
t-2-b	**0.25**	**0.11**	0.02	0.00	2.29	1.68	0.21	0.18	0.83	0.86	0.19	0.16	0.67	0.55	0.78	0.71	0.35	0.88
c-2-b	**0.18**	**0.19**	0.01	0.00	1.92	1.56	0.16	0.17	0.87	0.89	0.13	0.14	0.50	0.52	0.57	0.65	0.25	0.7
t-2-p	**0.18**	**0.27**	0.03	0.00	2.05	3.13	0.19	0.28	1.03	1.04	0.12	0.21	0.50	0.74	0.70	0.96	0.27	0.75
c-2-p	**0.14**	**0.16**	0.03	0.00	1.19	1.54	0.12	0.16	0.84	1.00	0.10	0.12	0.32	0.46	0.42	0.68	0.16	0.43
tol	**1.84**	**3.30**	0.09	0.20	14.45	30.87	1.78	3.61	0.97	1.09	1.21	2.10	5.31	9.88	6.70	13.78	3.45	8.62
o-xyl	**0.49**	**0.59**	0.03	0.05	3.44	4.82	0.45	0.54	0.93	0.92	0.34	0.43	1.40	1.62	1.76	2.13	0.68	1.65
m+p	**0.96**	**1.56**	0.06	0.16	6.30	12.49	0.86	1.42	0.90	0.91	0.65	1.14	2.67	4.29	3.40	5.52	2.08	4.55
benz	**0.77**	**1.80**	0.03	0.18	5.01	16.97	0.69	1.66	0.89	0.92	0.54	1.37	2.16	4.90	2.67	6.40	1.02	3.93
ethb	**0.41**	**0.48**	0.03	0.03	2.78	3.93	0.37	0.43	0.90	0.90	0.28	0.35	1.14	1.33	1.42	1.70	0.54	1.39
acet	**2.91**	**2.81**	0.17	0.14	30.90	23.70	2.69	2.66	0.88	0.95	2.29	1.90	8.04	8.54	9.81	10.76	4.6	4.48

Lond = Average concentrations for Marlyborne road monitoring site, London.

Table 7.6 Statistical summary comparing concentrations obtained in 1998 to the present study

7.8 SUMMARY

- Local and regional meteorological data was compared, and the effect of local obstructions on wind speed and direction were explored.

- For unfiltered Hydrocarbon data, clear diurnal trends were observed for all compounds with the exception of ethane and propane. Morning and evening peaks associated with peak time traffic flow were observed.

- With HC data associated with stable atmospheric conditions and windspeeds less than 1 m/s filtered out, more pronounced diurnal profiles are obtained, with ethane and propane also showing improved profiles.

- The concentration wind roses show source effects relating to two main wind direction sectors, 40-90° and 170-260°, associated with the junction and background Dublin values respectively. Sectional analysis, profiling the diurnal trends associated with each wind sector emphasise this, with concentrations for all compounds relating to wind directions 40-90°, significantly higher than those for 170-260°. Similar average hourly wind speed profiles were obtained for both sectors.

- The concentrations and trends observed compare favourably to recent studies presented elsewhere in the world, most notably Marlyborne road in London.

- The m+p xylene / ethylbenzene ratio was investigated for both wind direction sectors, with the relative age of HC's for wind sector 40-90° older than those observed for wind sector 170-260°, likely due to long range transport of pollutants.

- A higher ethene / acetylene ratio was observed from wind direction sector 40-90° due to the proximity of the road traffic emissions.

- Evaporative emissions were investigated using the HC acetylene ratio, where higher evaporative ratios were observed for wind direction sector 40-90°, due to transboundary pollution.

- Concentrations for all compounds except ethane, propane and acetylene decreased substantially from values reported in 1998, mainly due to a lower percent of high emitting vehicles in the 2003 vehicle fleet relative to that of 1998. It was hypothesised that the rise in acetylene concentrations was due to long range transport from Continental Europe and the UK, due to its relatively long atmospheric lifetime. Similar trends were noted over the same period at Marlyborne road in London.

- The objectives outlined in section 7.1 were completed, namely, the ambient concentrations of the Hydrocarbons of interest were estimated over a six month period, and as expected, the main source was found to be road traffic emissions. The significant difference in relative air mass age (40-90°, older) for both main wind directions allied to the higher evaporative emissions and non-traffic hours background concentrations observed with sector 40-90° points toward an alternate distance source other than the Pearse street junction, most likely the UK or continental Europe. In addition ,the influence of HC lifetime (and hence ability to travel long distances) on 2003 / 1998 ratios, where, in 2003 a much greater proportion of easterly winds were observed relative to 1998, also serves to highlight the effect of long range transport of pollutants, influencing the 2003 ambient levels found.

8. BACKGROUND HC MONITORING IN DUBLIN CITY CENTRE

The main objectives of this monitoring programme were to determine representative background concentrations of hydrocarbons for Dublin City centre, and to ascertain which monitoring site gives a more accurate estimation of background hydrocarbon concentrations: a green-park site or rooftop monitoring site. To this authors knowledge, no monitoring campaign has been carried out for such an array of traffic related hydrocarbons in Dublin City. The results should be of special interest to those involved in urban dispersion modelling of hydrocarbons and other traffic-related pollutants in Dublin City.

8.1 MONITORING LOCATION AND PROGRAMME

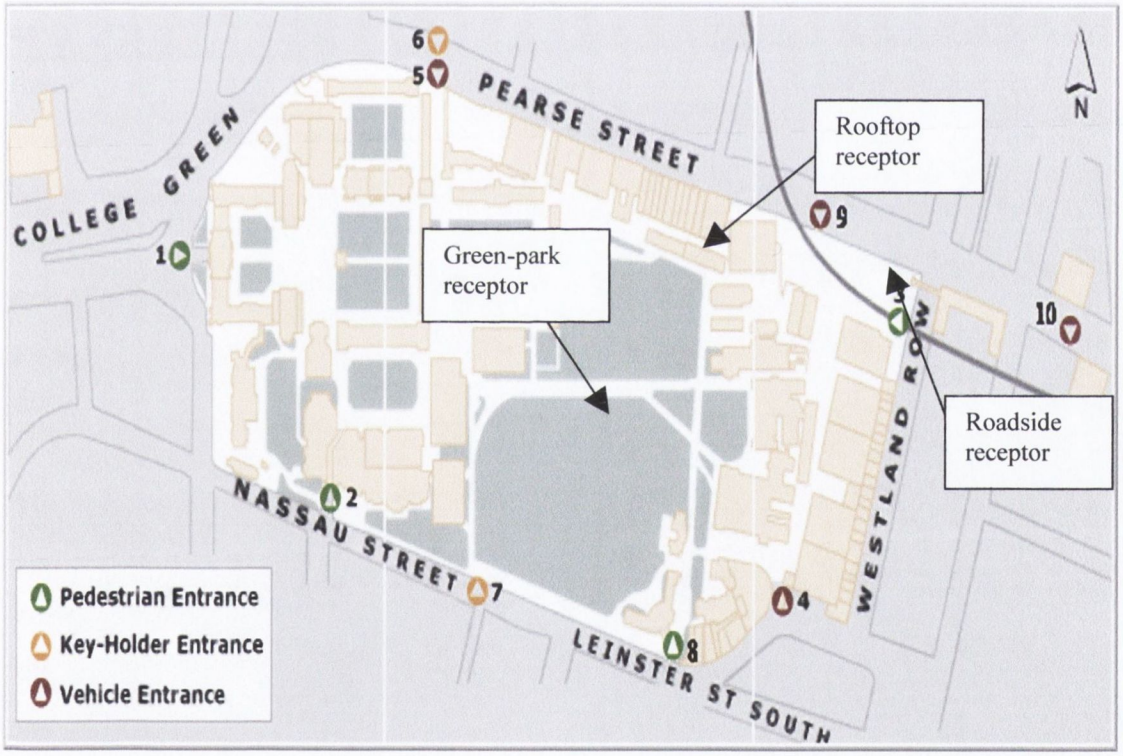


Figure 8.1 Map of receptor locations

The 11 hydrocarbons for which the sampling method was validated in chapter 4 were monitored over a five week period from the 16th May until the 30th June 2003, at three separate receptor locations; roadside, rooftop and green-park. All 3 sites were monitored for an initial period of 3 weeks, followed by an additional 2 weeks of sampling at the roadside site and receptor location considered to give the more accurate estimation of city centre background concentrations.

All 3 receptor locations were within the grounds of Trinity College Dublin campus. The roadside receptor site was described in chapter 7, on the online monitoring of City centre HC concentrations. The rooftop site was situated on the Department of Civil, Structural and Environmental Engineering building, approximately 35 metres high and 40 metres from the nearest road traffic source of Pearse Street. The green-park site was located centrally in TCD campus, surrounded by sports playing pitches and approximately 100 metres from the nearest road traffic source of Nassau street.

Samples were collected at the rooftop and green-park sites using the mobile sampling method, while the roadside measurements were taken using the online Perkin Elmer Ozone Precursor system, run in the conventional way. Sampling periods of 20 minutes at the rooftop and green-park and 40 minutes for the online system were employed. It was not anticipated that this difference in sampling time would have a significant effect on average hourly results.

The rooftop and green-park samples were taken within the same hour, always between 10:00 and 19:00 on a weekday. Roadside samples were taken concurrently for the purposes of comparison. Samples could, at best, be taken every three hours, as it took 2 hours to analyse the two background samples (mobile method samples) following the sampling and analysis of the online roadside sample. In total, over the five-week monitoring period, fifty-eight hours of samples were obtained.

Wind speeds, wind directions and temperature were estimated at the background sites using the equipment described in Chapter 6, which discussed the monitoring of HC concentrations at the M50 motorway. As samples were taken at all three sites within the same hour, meteorological effects at each receptor were very similar. The only notable exception was the

consistently higher wind speed observed at the rooftop site, the difference ranging from 0.5-1.0 m/s. An average difference of 0.8 m/s over the initial three-week period was observed, with average ground level and roof-top wind speeds of 1.1m/s and 1.9 m/s, respectively. Hourly wind directions and temperatures were very similar at the three receptors. Local wind directions fell into the same 2 major wind directions observed in chapter 7, namely 40-90° and 170-260°. Temperatures ranged from 17-23°C, with the majority of values between 18-19°C. An overall average temperature of 19°C was observed.

8.2 ANALYSIS OF RESULTS

Local urban background concentrations can be considered as a combination of regional background concentrations onto which contributions from sources in the more immediate area are added. Results from dispersion or other models can be used to estimate the impact of individual sources on local air quality. Ambient air quality near to sources, such as at the edge of a busy road, can be estimated by calculating the sum of this local impact and the background concentration (DoE, 1997). In addition, estimates of population exposure can be combined with dose response relationships for the health impact of air pollutants to provide estimates of the magnitude of health impacts across the country (Stedman *et al*, 1997a, Department of Health, 1997). It was anticipated that whichever monitoring site showed the lowest average HC concentrations, with the lowest relative standard deviation, would represent the most accurate estimation of city centre background concentrations. This background site would represent a conservative estimate for city centre exposure levels and also a local background site relative to the 4 surrounding main roads when the wind direction is travelling towards each road and the background receptor is upwind. The average results obtained over the initial 3 weeks of monitoring are summarised in Table 8.1. As expected, the average roadside concentrations are always highest due to the proximity of road traffic emissions. With the exception of ethane (Figure 8.2), rooftop levels are consistently higher than those obtained at the ground level green-park site. As discussed in Chapters 5, 6 and 7, ethane has a relatively weak association with road traffic emissions, resulting in relatively minor local source effects. This limited local source effect results in a relatively well mixed compound. It is therefore no surprise to observe the lowest average ethane concentrations on the rooftop site, where the highest average wind speeds are observed.

The higher average rooftop wind speed did not dilute the concentrations of traffic related compounds to levels lower than those observed at the green field site. The relative standard deviation (%) is also consistently lower for all compounds (except ethane) at the green-park receptor. Benzene is shown in Figure 8.3, representing the trend displayed by all traffic-related compounds monitored. It is evident from this illustration how little variation in concentrations occurs at the green park site compared to the roadside and roof top receptors. The rooftop site is somewhat intermediary between the park and roadside receptors, suggesting an influence from road traffic emissions from Pearse Street (approximately 40m North). A clear evening concentration peak can be observed at the roadside monitor, relating to evening peak road traffic emissions. This trend is less obvious at the green park site, where a relatively smooth profile is observed, outlining the limited effect local traffic emissions have on concentrations observed at this receptor. At 15:00, very similar average concentrations were observed at all three sites, probably due to the absence of wind directions from 40-90° observed during this time period. Chapter 7 described how this wind direction is associated with road traffic emissions from Pearse Street. From Figure 8.3 and Table 8.1, it is evident that the green-park site displayed the lowest average concentrations and relative standard, giving the most accurate measure of Dublin City background concentrations. However, due to the influence of wind direction on the concentrations observed between 14:00 and 15:00, the effect of wind direction on the concentrations obtained at each site was investigated further.

	Average conc. (ppbv)			Standard deviation (ppbv)			Rel. standard deviation (%)		
	road	park	roof	road	park	roof	road	park	roof
ethane	2.49	1.78	1.77	0.48	0.28	0.16	19%	16%	9%
propane	0.76	0.58	0.78	0.18	0.10	0.24	24%	17%	31%
n-butane	1.18	0.62	1.09	0.37	0.04	0.69	31%	7%	63%
iso-butane	0.58	0.30	0.55	0.13	0.03	0.39	23%	9%	70%
n-pentane	0.49	0.20	0.27	0.26	0.04	0.12	54%	19%	46%
iso-pentane	1.35	0.54	0.68	0.77	0.07	0.26	57%	12%	37%
ethene	2.44	0.82	1.04	1.52	0.06	0.27	62%	7%	26%
propene	0.74	0.26	0.32	0.45	0.01	0.06	61%	2%	20%
1,3 butadiene	0.20	0.10	0.13	0.10	0.01	0.05	49%	12%	37%
acetylene	1.95	0.76	0.97	1.14	0.12	0.27	58%	16%	28%
benzene	0.50	0.19	0.26	0.32	0.04	0.08	64%	19%	32%

Table 8.1 Average hydrocarbon concentrations and relative standard deviations for 3 receptors over 3 week monitoring period

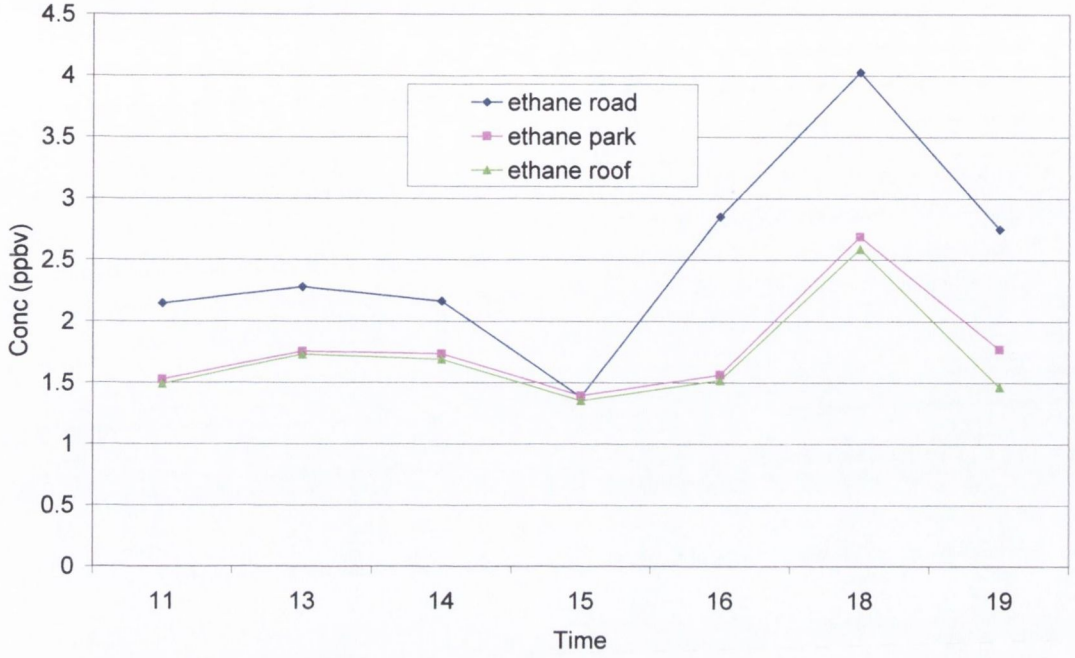


Figure 8.2 Average hourly concentrations for ethane at each receptor site

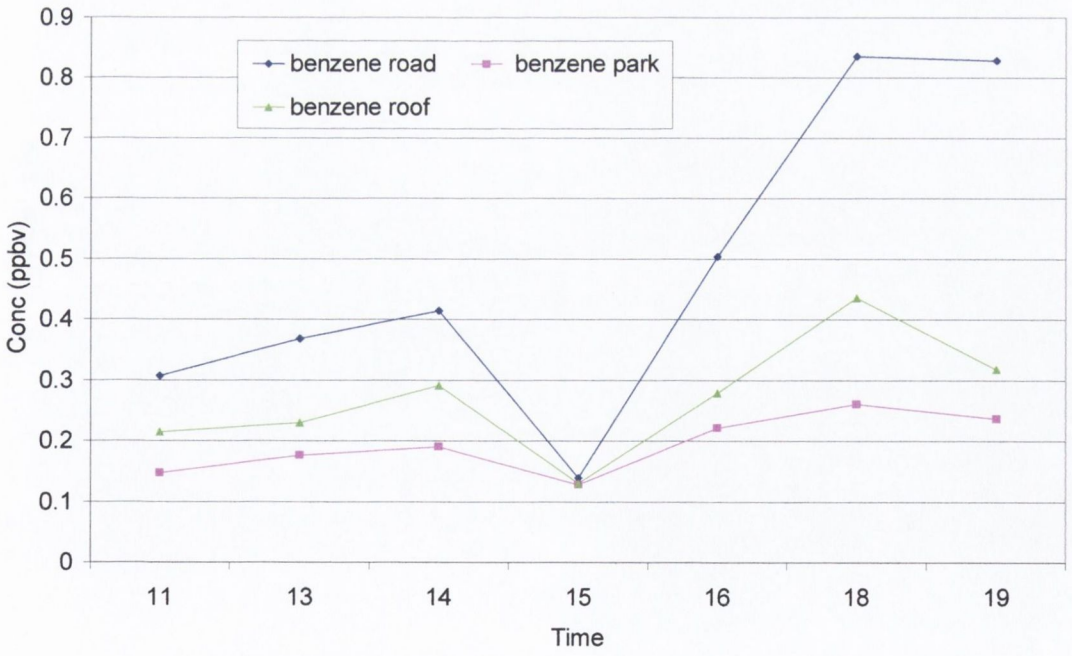


Figure 8.3 Average hourly concentrations for benzene at each receptor site

8.3 WIND SECTOR ANALYSIS

The data obtained was grouped into two main wind direction sectors, 40-90° and 170-260°, as in Chapter 7. Comparison of average concentrations for each wind sector are not helpful due to the different frequencies of peak time traffic hours sampled for each sector. A higher proportion of hours associated with evening peak time traffic were sampled for wind direction sector 170-260, thereby raising its overall average relative to the 40-90° sector. Therefore, the following observations, relate to concentrations and deviations at each site *within* each wind sector, treated separately.

For wind sector 40-90°, the differences between the 3 sites are very pronounced, with roadside concentrations much higher than rooftop concentrations, which are in turn higher than green-park concentrations. An example plot of the average hourly ethene concentrations at each site is shown in Figure 8.4. The lower concentrations, allied to the limited deviation over the course of the day can be clearly seen for the green-park site.

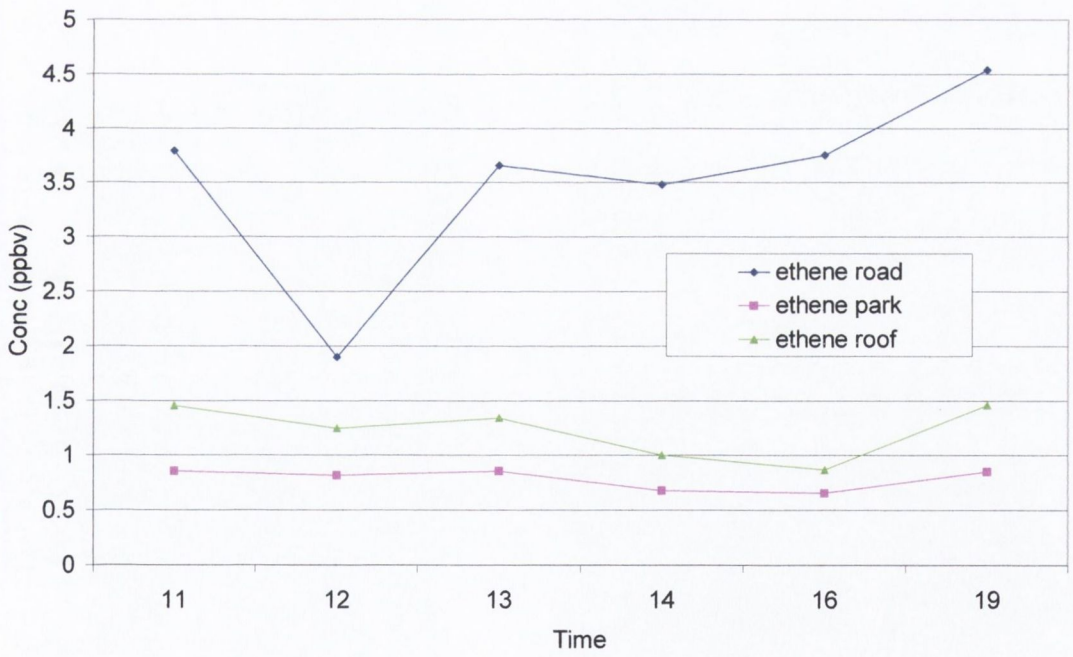


Figure 8.4 Average hourly concentrations for ethene at the 3 sites, for wind directions 40-90°

	40-90°		170-260°	
	Average conc (ppbv)	Relative standard deviation (%)	Average conc (ppbv)	Relative standard deviation (%)
ethane road	2.15	14%	2.83	47%
ethane park	1.58	7%	1.98	32%
ethane roof	1.66	11%	1.89	30%
propane road	0.63	17%	0.89	34%
propane park	0.51	20%	0.65	31%
propane roof	0.95	47%	0.61	24%
n-but road	1.44	26%	0.92	33%
n-but park	0.59	25%	0.65	22%
n-but roof	1.58	70%	0.61	15%
iso-but road	0.68	24%	0.49	27%
iso-but park	0.28	29%	0.32	25%
iso-but roof	0.83	57%	0.28	18%
n-pent road	0.67	30%	0.30	34%
n-pent park	0.23	22%	0.18	19%
n-pent roof	0.35	28%	0.18	20%
iso-pent road	1.89	28%	0.80	37%
iso-pent park	0.58	32%	0.49	24%
iso-pent roof	0.87	37%	0.50	21%
ethene road	3.52	25%	1.37	31%
ethene park	0.78	13%	0.86	22%
ethene roof	1.23	20%	0.85	19%
propene road	1.06	32%	0.42	34%
propene park	0.26	25%	0.25	24%
propene roof	0.37	33%	0.28	29%
1,3 but road	0.27	38%	0.13	42%
1,3 but park	0.11	56%	0.10	37%
1,3 but roof	0.17	66%	0.10	45%
acetylene road	2.75	28%	1.14	31%
acetylene park	0.74	11%	0.84	23%
acetylene roof	1.10	44%	0.78	19%
benzene road	0.73	45%	0.27	37%
benzene park	0.22	22%	0.17	34%
benzene roof	0.32	13%	0.20	31%

Table 8.2 Average concentrations at each receptor location for each wind direction sector

In Table 8.2 the behaviour of each hydrocarbon at each of the three monitoring sites for wind direction sector 40-90° is summarised. The first observation is the atypical behaviour of propane, n-butane and iso-butane for this wind sector. For these compounds, the roof top concentrations are seen to be the highest, suggesting contribution from sources other than road traffic emissions. The trends observed for the 7 strongly-traffic related compounds are all similar, with average green park levels consistently the lowest with the smallest associated relative deviation. The average of these 7 HC concentrations at each site, in conjunction with the overall relative deviation for the three sites can be seen in Table 8.3. This illustrates clearly the overall trend observed at each of the 3 receptors, where the highest average concentrations and relative deviations are observed at the roadside and roof-top sites.

	Average HC conc. for 7 traffic related compounds (ppbv)	Average relative std. deviation for 7 traffic related HC compounds
Roadside	1.56	32%
Green-park	0.42	26%
Rooftop	0.63	34%

Table 8.3 Average HC concentrations for n-pentane, iso-pentane, ethene, propene, 1,3-butadiene, acetylene and benzene with average relative standard deviation for both background receptors, for wind direction sector 40-90°

For wind direction sector 170-260°, the roadside monitor again yields the highest concentrations for all compounds, but these values are, as expected, considerably lower than those observed for wind sector 40-90°. For this sector the differences between the rooftop and green-park site concentrations are smaller. Table 8.2 shows the individual trend for each for each hydrocarbon at each receptor, while Table 8.4 shows the overall trend for this wind direction for the 7 strongly related traffic compounds. The average HC concentration for these 7 compounds are equal for the green-park and rooftop site, with identical overall standard deviations. From this it can be assumed that both sites offer a similar representation of the overall background concentrations when the wind direction is from this sector. This also confirms the source effect from Pearse street observed at the rooftop site when the wind direction is from 40-90°.

As no significant road traffic emission source lies between the green-park receptor and the roadside monitor, concentrations could be anticipated to be similar at both sites when wind directions emanate from this sector (170-260°). Mechanical turbulence and dispersion is, however, seen to have a significant effect on roadside concentrations, which are on average 50% higher for the 7 traffic related compounds (Table 8.3).

From the analysis carried out we can see that the green-park site is overall the most representative background monitoring location. It provides the lowest concentrations with the lowest standard deviation regardless of time of day or wind directions.

Attempting to facilitate a more quantitative estimate of Dublin city background concentrations, a further 2 weeks of monitoring was carried out at the roadside and green-park receptors. The results are discussed in the proceeding section.

	Average HC conc. for 7 traffic related compounds	Average relative std. deviation for 7 traffic related HC compounds
Roadside	0.63	35%
Green-park	0.41	26%
Rooftop	0.41	26%

Table 8.4 Average HC concentrations for n-pentane, iso-pentane, ethene, propene, 1,3-butadiene, acetylene and benzene with average relative standard deviation for background receptors, for wind direction sector 170-260°

8.4 ADDITIONAL GREEN-PARK MONITORING

The results obtained for the entire five-week sampling period for the roadside and green-park site are considered and the summarised results are presented in Table 8.5. With the two additional weeks of sampling, all concentrations (except ethane) were seen to increase, by on average 12% at the green park site and 24% at the roadside receptor. Both background and roadside concentrations increased in very similar proportions, as evidenced by the scatter plots in Figures 8.5 and 8.6.

Figure 8.5 shows the initial 3 week average concentrations at the road and park sites plotted against the entire 5 week average concentrations obtained at both sites. When ethane is excluded, an R^2 value of 0.995 is obtained showing how the concentrations of all hydrocarbons (except ethane) increased in similar proportions at both sites. This general increase in concentrations is due to a higher proportion of evening peak time traffic samples, during the additional two weeks of sampling. This was achieved by increasing the sampling rate from every 3 hours when the road, roof and park were being sampled, to every 2 hours for just the road and park. The very limited increase in concentrations observed for ethane emphasises the limited contribution from road traffic emissions to ambient levels observed.

A scatter plot of concentration increases at both sites due to the two additional weeks of sampling is shown in Figure 8.6, this plot shows more definitively how the proportional increases at both sites are very similar. Ethane is again excluded from this plot due to its atypical behaviour.

The average hydrocarbon values observed over the initial 3 week period were seen to increase significantly (18% on average) when an additional 2 weeks of sampling was carried out due to the increased number of peak traffic hours sampled.

	3 week average conc. (ppbv)		5 week average conc. (ppbv)		% increase due to additional 2 weeks of sampling	
	road	park	road	park	road	park
ethane	2.56	1.82	2.65	1.89	4%	3%
propane	0.79	0.58	0.93	0.63	19%	9%
n-butane	1.13	0.61	1.38	0.66	23%	9%
iso-butane	0.56	0.29	0.64	0.31	13%	6%
n-pentane	0.45	0.19	0.54	0.22	20%	13%
iso-pentane	1.24	0.50	1.54	0.56	24%	11%
ethene	2.23	0.82	3.00	0.93	35%	13%
propene	0.68	0.24	0.84	0.28	24%	15%
1,3 but	0.19	0.10	0.23	0.12	24%	14%
acetylene	1.79	0.75	2.30	0.84	29%	12%
benzene	0.44	0.19	0.55	0.21	25%	12%

Table 8.5 Average concentrations obtained over 3 and 5 week monitoring period at roadside and green-park sites

With 5 weeks of monitoring and a larger sample pool, more representative diurnal profiles of HC concentrations at both sites, for the 2 main wind direction sectors, were obtained. The example of ethene is shown in Figures 8.7 and 8.8. The trends observed with 3 weeks of data are confirmed with the additional 2 weeks of sampling. For the 40-90° sector, a large difference in average hourly values at the roadside relative to the green-park is observed (Figure 8.7).

For 170-260°, the differences between 10:00 and 15:00 are minimal, but the roadside values increase to a greater extent with evening peak traffic emissions, verifying the effects of local turbulence and mechanical dispersion on concentrations at the roadside site for this wind sector. Once again there is little variation over the course of the sampling day at the green-park site (Figure 8.8).

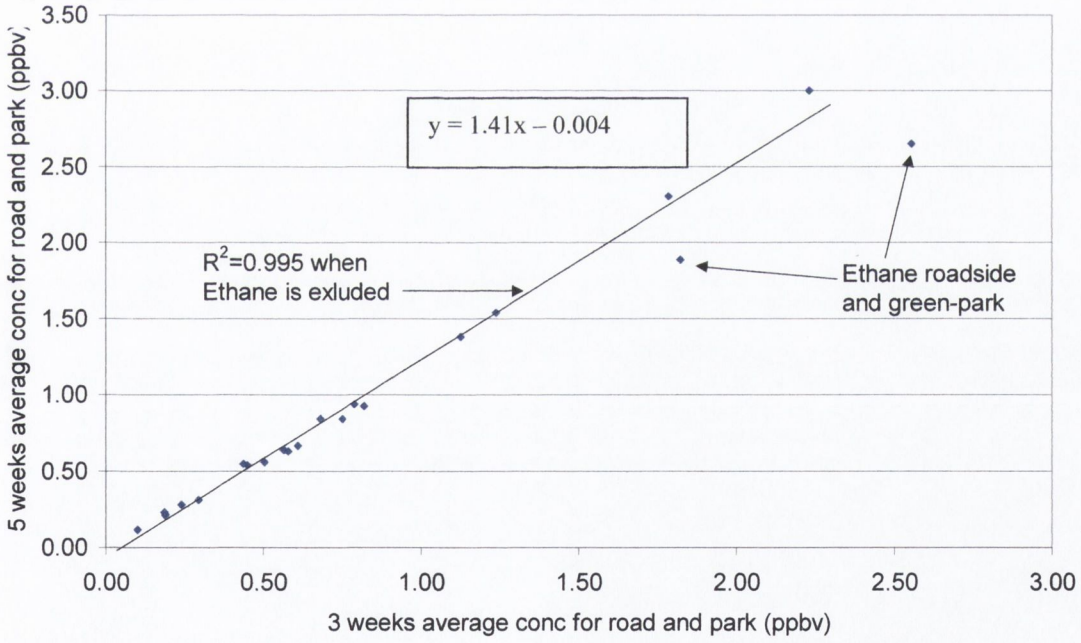


Figure 8.5 Scatter plot of 3 week average concentrations at both sites against 5 week average concentrations at both site

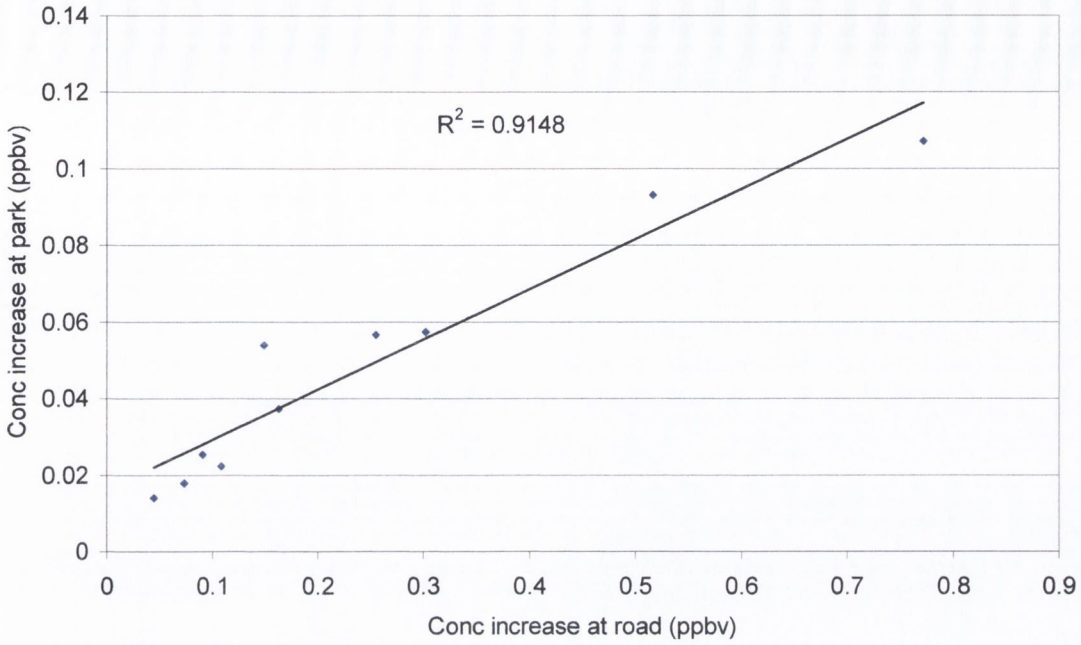


Figure 8.6 Scatter plot of increase in concentrations observed at both sites for additional 2 weeks of sampling

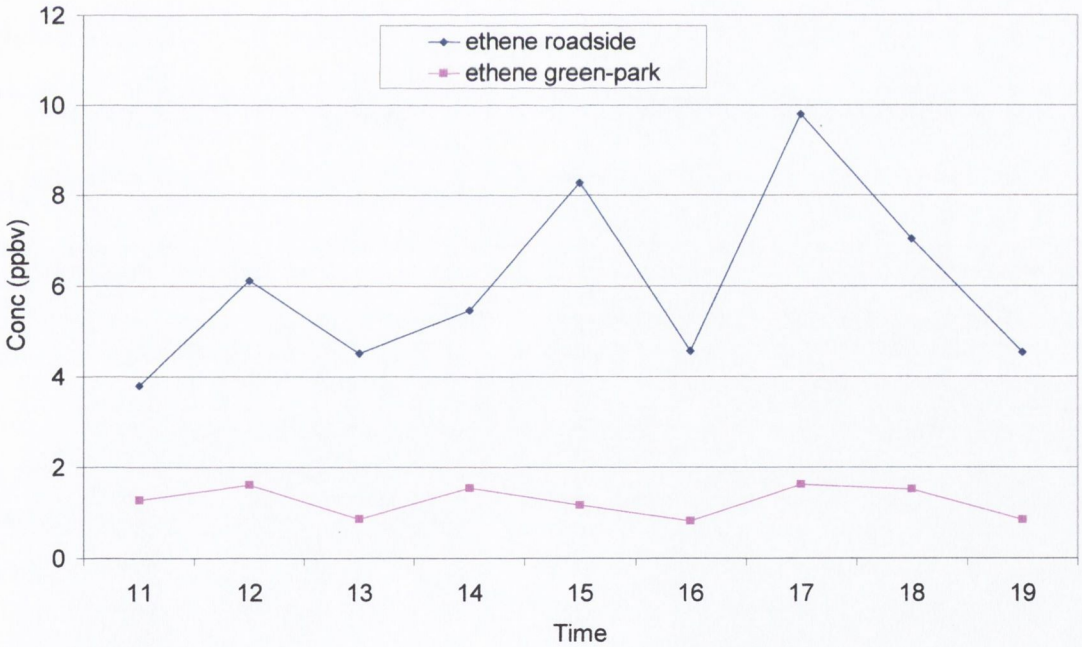


Figure 8.7 Average hourly concentrations over 5 week monitoring period at both sites for wind direction sector 40-90°

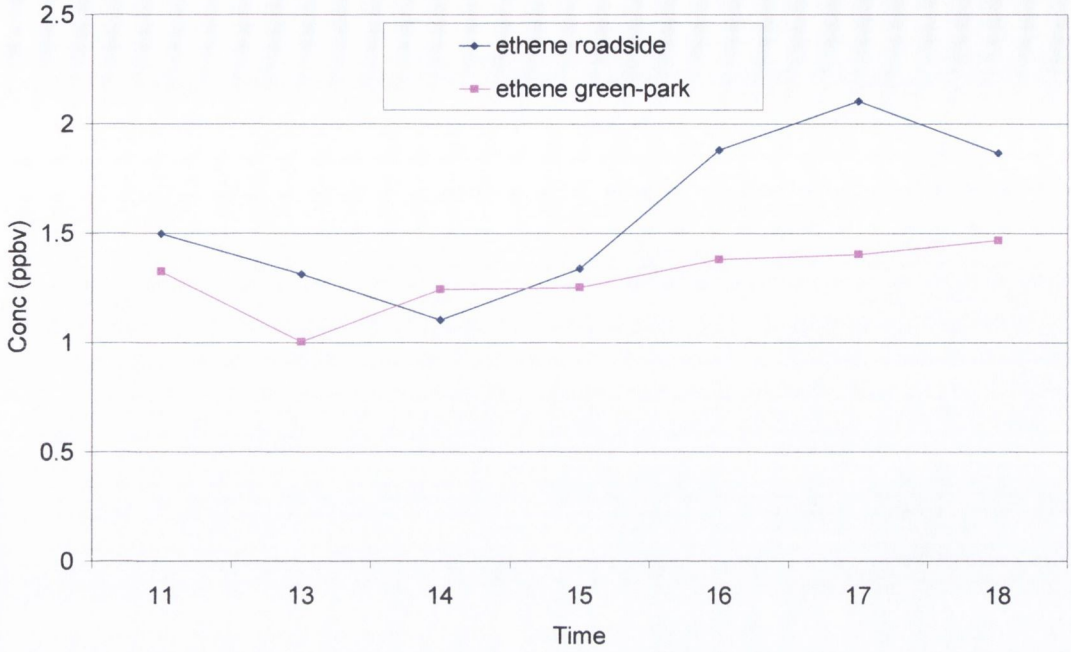


Figure 8.8 Average hourly concentrations over 5 week monitoring period at both sites for wind direction sector 170-260°

The sampling and analysis carried out shows that site location is paramount when deciding where to sample for background concentrations. The selection of any rooftop site will not necessarily yield a representative background concentration for that area. This is due to the relatively low average building height in Dublin city and hence the ability of nearby heavily trafficked roads to affect rooftop concentrations. The rooftop site should therefore be either far enough away from local road traffic sources or high enough not to be significantly affected by temporal variations in local road traffic emissions.

It seems clear from our study that the green-park site offers the most representative background site. The location was of sufficient distance from local sources not to be affected to any great affect by increases in traffic flow (time of the day), or changes in wind direction.

8.5 EVAPORATIVE EMISSIONS

Investigations were carried out into which of the 3 monitoring sites was most affected by changes in temperature. Similar to observations at the M50 monitoring site in Chapter 6, the amount of analysis and the resultant conclusions are limited due to the relatively narrow

temperature range observed over the 3 week monitoring period. Again, changes in the HC / acetylene ratio with temperature were used to ascertain trends in evaporative emissions.

As in Chapter 6, due to iso-pentanes association with evaporative emissions, we analysed the iso-pentane / acetylene ratios behaviour with temperature at each of the 3 receptor sites. The overall average ratio was ascertained at each site, in conjunction with the ratio at each site for both main wind direction sectors. The results can be seen summarised in Table 8.6. The average temperature for each wind direction sector was 19°C.

	iso-pentane / acetylene ratio		
	Roadside receptor	Green-park receptor	Rooftop receptor
overall	0.66	0.64	0.70
40-90° wind dir.	0.70	0.67	0.76
170-260° wind dir.	0.61	0.59	0.64

Table 8.6 Average iso-pentane / acetylene ratios at each site overall and for each main wind direction sector

The trend of higher ratios observed from wind direction sector 40-90° are similar at each site. This same evaporative behaviour was noted in chapter 7, where a much larger sampling pool was used.

Roadside and green-park receptors behave very similarly, with average ratios in broad agreement. The rooftop site however, consistently shows the highest average ratios, both overall and for each separate wind direction sector. This suggests a greater relative contribution from evaporative emissions to levels obtained at this receptor location. A possible reason for this is due to increased vertical air mass movement with increased temperature, resulting in higher evaporative emissions at the rooftop site.

Figure 8.9 shows the trend of the average iso-pentane / acetylene ratio with increased temperature (°C) for the roadside and rooftop sites. A higher rate of increase in ratio with temperature is clearly seen for the rooftop site, verifying the greater affect temperature has on concentrations obtained at this elevated site.

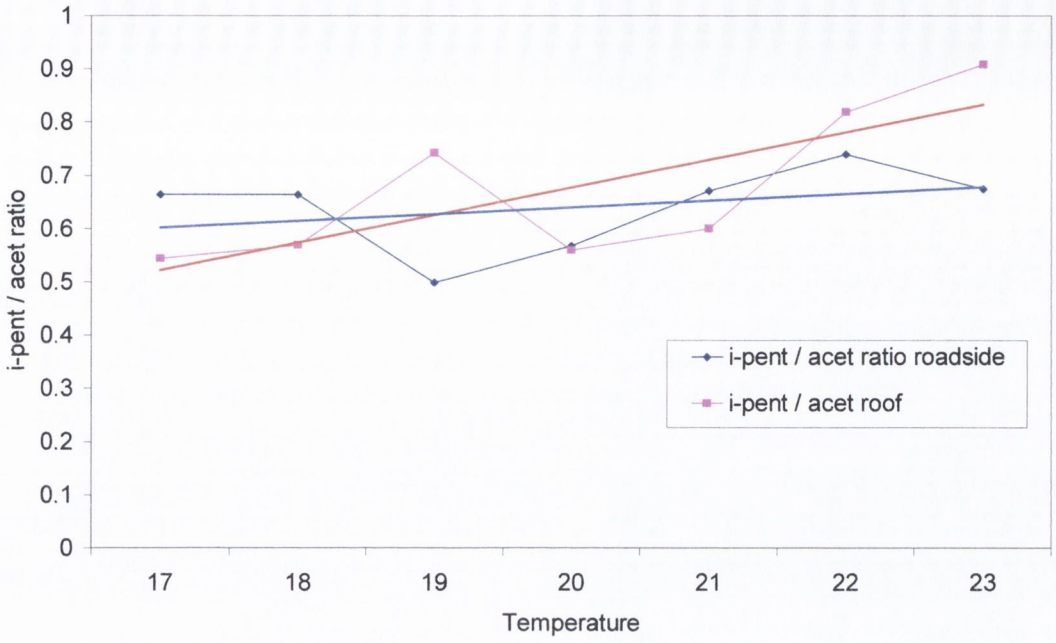


Figure 8.9 Increase in iso-pentane / acetylene ratios observed with increased temperature for the roadside and rooftop sites

8.6 ETHENE / ACETYLENE RATIO

As has been established previously (Chapters 5, 6 and 7), this ratio is more useful in determining the extent of local traffic emission sources, rather than the extent of catalytic converter efficiency.

We have ascertained that the higher the relative ethene / acetylene ratio obtained the nearer the road traffic emission source. Ratios of approximately 1 are more associated with background levels, where the air parcel has had sufficient time (distance travelled) to dilute to the approximate background ratio. The distance required will vary depending on source strength and atmospheric dilution capability.

Table 8.7 shows the overall average ratios obtained at each receptor site and also the ratios associated with each main wind direction sector.

	ethene / acetylene ratio		
	overall average	wind sector 40-90°	wind sector 170-260°
Roadside site	1.24	1.28	1.20
Green-park site	1.04	1.06	1.03
Rooftop site	1.10	1.12	1.07

Table 8.7 Average ethene / acetylene ratios for each receptor site

The observations made in section 8.3 on sector analysis are verified by the ratios obtained for the 3 sites. The green park has consistently the lowest average ratio, with all values close to 1, indicative of background concentrations. For wind direction's 40-90°, the ratios obtained for the rooftop site are once again intermediary between the park and roadside receptor, highlighting the effect local road traffic emissions from Pearse Street have on the concentrations observed at the elevated site.

For 170-260°, the similarity in ratios at the rooftop and green-park sites is evident. This is due to the rooftop receptor being more representative of a background site for this wind direction sector as seen in section 8.3.

Comparing the ratios obtained at the roadside and green-park sites for the initial 3 week period and the total 5 week period, we obtain the results shown in Table 8.8.

	Average ethene / acetylene ratio for 3 week period	Average ethene / acetylene ratio for 5 week period
Roadside site	1.25	1.30
Green-park site	1.09	1.09

Table 8.8 Comparison of average ethene / acetylene ratios for 3 week and 5 week sampling periods

From the 3 weeks to 5 weeks sampling period the roadside E:A ratio increased due to the increase in evening peak hours sampled. However, the ratio at the green-park site remained relatively constant, even though the concentrations were seen to increase in similar proportions to those at the roadside site (Figure 8.6). The trend in ratios over the course of the

average sampling day for the 5 week period associated with wind direction sector 40-90° can be seen for both roadside and green-park receptors in Figure 8.10.

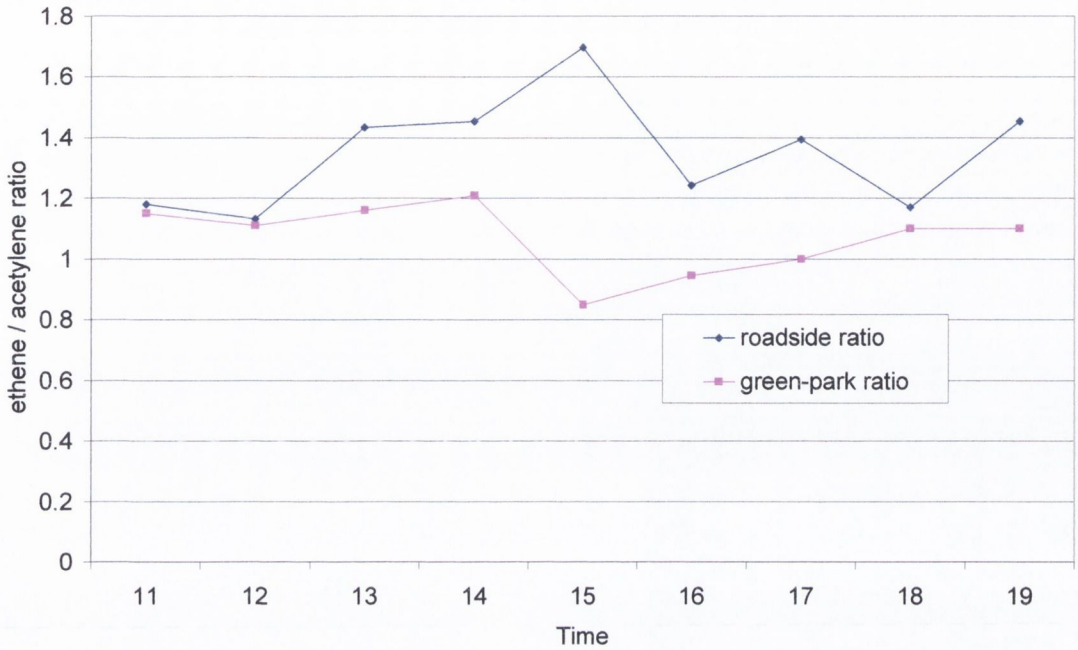


Figure 8.10 Average hourly ethene / acetylene ratios for the 5 week sampling period at the roadside and green-park sites for wind direction sector 40-90°

Comparing Figure 8.10 to Figure 8.7, we can see that roadside E:A ratios are highest at times where peak ethene concentrations are obtained. The ratios and concentrations for the green-park site are relatively constant.

From the analysis carried out we can see that this ratio can be used to assess the required distance from a source, in order to monitor local background concentrations. From our studies of ratio trends in Dublin city and suburbs, when a value of approximately 1 is obtained, you can predict with a relatively high degree of certainty that you are sufficient distance from local road traffic sources for measuring road traffic background concentrations.

8.7 COMPARISON OF CAMPAIGNS

Direct comparisons are difficult between the various monitoring campaigns carried out during this course of this research, due to the difference in site locations and sampling conditions experienced at each location. The sampling duration, meteorological conditions and site topography differed significantly between each separate monitoring campaign location. Table 8.9 compares the average concentrations of the HC compounds monitored during the background monitoring study described in this Chapter, the Dublin City online monitoring study (Chapter 7) and the motorway studies (Chapters 5 and 6).

	Dublin city centre				M4, Leixlip		M50, Tallaght		
	Green area bkg	Roadside monitor			ovrll. avg	bkg. corr. morn. Peak (105-285°)	Easterly 25m average	Westerly 25m average	bkg. corr. M50 source effect
		ovrll. avg	Wind dir 40-90°	Wind dir 160-270°					
eth.	1.89	4.98	5.31	3.98	1.43	0.11	1.98	1.35	-
prop.	0.63	2.58	2.98	1.93	0.72	0.06	1.18	0.51	-
n-but	0.66	2.52	3.19	1.54	0.46	0.11	1.61	0.59	-
i-but	0.31	1.41	1.73	0.83	0.33	0.10	0.59	0.21	-
n-pen	0.22	0.7	0.91	0.43	-	-	0.44	0.24	0.17
i-pen	0.56	1.86	2.61	1.00	0.28	0.09	1.07	0.68	0.52
ethe	0.93	3.42	4.06	2.17	0.78	0.36	1.58	1.38	0.84
prope	0.28	1.03	1.27	0.64	0.22	0.10	0.48	0.5	0.28
1,3 b	0.12	0.28	0.3	0.24	0.24	0.02	0.11	0.19	0.10
acet	0.84	2.91	3.48	2.36	0.52	0.10	1.17	0.87	0.45
benz	0.21	0.77	1.01	0.46	0.16	0.02	0.40	0.31	0.15

bkg=background, ovrll=overall, avg=average, dir=direction, corr=corrected

Table 8.9 Concentrations (ppbv) obtained for various monitoring campaigns during this project

In the City centre, the green area background concentrations are significantly lower than the roadside values, even for concentrations associated with wind directions 160-270°. This is probably due to both the influence of mechanical turbulence at the road side site and also the time of year the monitoring campaign was carried out at the green area, namely, warm Summer conditions as opposed to Winter/Spring for the roadside period.

The green area concentrations are, in the main higher, than those obtained for the M4 (with no filtering of data), the exception being 1,3 butadiene for reasons discussed in chapter 5. The

concentrations at the M50 were slightly higher than the Dublin City green area background values. The background corrected M50 values are all close to the City green area background values with the notable exception of acetylene which shows a higher relative background concentration at the City green area, due to its longer atmospheric lifetime.

The M50 source effect observed is up to seven times higher than the background corrected M4 morning time peak concentrations. This is due to the nature of the data presented for the M4, where only wind speeds greater than 1 m/s were used as opposed to all wind speeds at the M50, the majority of which were less than 1 m/s. In addition, the background concentrations used at the M4 were only estimations, based on observed early morning average values. The M50 background measurements were observed almost concurrently to windward measurements, giving a far more representative motorway source effect.

As expected, the highest concentrations were observed during the city centre roadside monitoring campaign, within which, the concentrations associated with winds from the heavily trafficked junction (wind directions 40-90°) were greatest.

Higher peak time values were found not to impact greatly on average ambient concentrations, where, overall, the air quality monitored in Dublin and surrounding suburbs was found to be good, with no location exhibiting average concentrations greater than the legislated air quality standards.

9. CLOSURE

9.1 CONCLUSIONS

The research completed represents an experimental investigation of atmospheric hydrocarbon concentrations in the Dublin area. Several separate monitoring campaigns were carried out using both the Perkin Elmer Ozone Pre-cursor System, run as standard and the newly validated mobile sampling method. Approximately eighteen months were spent monitoring air quality at various locations and six months validating the mobile sampling method. The collected data was analysed and compared with traffic and meteorological conditions.

Chapter 4

A new mobile sampling method was developed based on EPA methods TO-14 and TO-15 which utilise stainless steel canisters as the sample vessel. The mobile method applied employs Tedlar bags as sampling vessels and the method was validated under the following headings: specificity, linearity, method detection limits, precision, accuracy, robustness and sample stability. With the exception of benzene, the aromatic compounds were found to contaminate the Tedlar vessels and the sampling method was deemed unsatisfactory for their quantitative assessment. Results obtained for 1-butene also showed this compound is unsuitable for the proposed mobile method. For the remaining compounds, ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, ethene, propene, 1,3-butadiene, acetylene and benzene, the mobile sampling method was observed to perform very well when compared to the online system, run as standard. A wide linear concentration range was achieved with low method detection limits and acceptable precision and accuracy over the desired range. A 1-point calibration procedure was shown to be adequate for routine system calibration and samples stored in the Tedlar vessels were found to be stable for at least 24 hours. In addition, variations in sample vessel volume (above 400cm^3) or sample time (between 5 and 40minutes) did not adversely affect result accuracy. The method allows greater flexibility in sampling location and sample time. It also facilitates concurrent sampling with the online system run as standard. These points allied to the mobile method's ease of use significantly extend the hydrocarbon sampling capability of the Department.

Chapter 5

The monitoring campaign carried out at the M4, Leixlip, represented the longest single monitoring study undertaken in this research project. Approximately eight months of online-sampling was carried out to investigate the road traffic source-effect, emanating from the M4 at the sub-urban / rural location chosen.

The effect a nearby building had on funnelling local winds was estimated and accounted for, resulting in the omission of data pertaining to wind directions 0 and 80°.

HC compounds which showed a higher mean than median value were found to be associated with a greater local source effect. These compounds also showed the highest Pearson's correlation coefficients with acetylene and ethene, known traffic emission markers.

Peak concentrations in Winter were found to be significantly higher than in Summer and values obtained all year round were highly dependant on local wind speed.

Local atmospheric inversions and associated low wind speeds were seen to obscure 24 hour diurnal trends and concentration wind roses. With the HC data associated with these meteorological conditions removed, more defined plots were obtained. The aromatics, acetylene, ethene, propene and 1-butene all showed strong diurnal trends associated with traffic flow on the M4. The greatest source effect was observed from near-parallel wind directions relative to the M4, in approximately easterly directions. Higher traffic flow and lower wind speeds associated with these wind directions were seen to contribute to this source effect.

Sectoral analysis was carried out, where wind directions associated with the M4 (105-285°) were treated in isolation. The number of compounds exhibiting strongly traffic related diurnal trends increased using for wind directions, where iso-butane, n-butane and iso-pentane showed significantly improved 24 hour average profiles. Background corrected morning and evening peak concentrations were estimated for these wind directions, and as expected, ethene displayed the highest diurnal range of concentrations.

For comparison, diurnal plots were examined for wind directions not associated with emissions from the M4, but with Leixlip village (285-345°). No obvious source effect was noted, and the trends observed were more dependant on local average wind speeds than anticipated peak time traffic flow in the area.

Various trends in HC ratios were examined for data associated with wind directions 105-285°. An alternate 1,3 butadiene source other than the M4 was hypothesised, based on the high 1,3 butadiene / propene ratio observed. The m+p xylene / ethylbenzene ratio was used to investigate the relative age of hydrocarbons sampled, from which it was observed that the youngest HC's were sampled during the morning peak traffic time when near-parallel winds were observed. A morning peak was also observed for the ethene / acetylene ratio, with the highest ratio again associated with near-parallel winds. Evaporative emissions were also investigated using the HC / acetylene ratio and by analysing correlations with temperature. Some evidence of diurnal, running and hot soak losses was obtained.

The results obtained compared favourably with reported studies in other countries. Most notably, excellent agreement was observed between the M4 site and the Harwell background monitoring site in the UK.

Chapter 6

Hydrocarbon concentrations were measured on a daily basis during the morning peak traffic period at six different receptor locations, three on either side of a busy sub-urban Motorway. Both sets of receptors were located at equal distance from the motorway source, at 30, 120 and 240 metres from the M50. Hydrocarbon data was grouped according to two main wind direction sectors (345-135° and 165-315°), which produced source effects on opposite sides of the road.

A very low average wind speed of 1.1 m/s was observed over the course of the 5 week monitoring campaign.

For both wind direction sectors, a clear and well-defined M50 source effect was observed for n-pentane, iso-pentane, ethene, propene, 1,3 butadiene, benzene and acetylene. The affect of

traffic flow on concentrations was seen to be minimal due to the relatively constant flow observed over the monitoring period. However, wind speed was seen to affect concentrations significantly. Background corrected concentrations compared very well for both wind direction sectors, with higher dispersion observed for winds between 165° and 315°, due to the higher average wind speed observed for this sector. Pearson's correlation coefficients were highest between the compounds showing a strong M50 source effect, for windward data sets.

For all compounds, average background values for both wind sectors were significantly different. This highlights the need for thorough investigations to be carried into background concentrations to isolate the desired source effect.

The temporal variation in the ethene / acetylene ratio was also examined. Higher ratio values were observed nearer the M50, on the downwind side, with the ratio reducing to the background ratio value of approximately 1 within 240 metres.

The evaporative behaviour of iso-pentane was examined, the results of which compared favourably to those presented in Chapter 7.

The measured results were compared on a day-to-day basis with the Gaussian dispersion model, CALINE4. To do this, the 2003 traffic fleet was estimated, from which composite emission factors were calculated using formulas and procedures outlined in COPERT3.

On a day-to-day basis, the model performance was acceptable, with agreement between the predicted and measured concentrations best at the receptor, closest to the M50 source. The model was found to slightly underpredict concentrations associated with cross-winds and slightly overpredict those for near-parallel winds. The model behaviour improved significantly for long term (5 week) average predictions, where the average modelled / measured concentration ratio varied from 0.9 to 1.05 for 25 to 250 metres respectively.

Chapter 7

Ambient hydrocarbon concentrations were monitored over a six-month period, using the online system, at a heavily trafficked junction in Dublin City centre.

Local and regional meteorological data were compared, and the effect of local obstructions on wind speed and direction were explored.

For unfiltered hydrocarbon data, clear diurnal trends were observed for all compounds with the exception of ethane and propane. Morning and evening peaks associated with peak time traffic flow were observed.

When HC data associated with stable atmospheric conditions were filtered out, more pronounced diurnal profiles were obtained, with ethane and propane also showing improved profiles.

Concentration wind roses showed source effects relating to two main wind direction sectors, 40-90° and 170-260°, associated with the junction and background Dublin values, respectively. Sectoral analysis, profiling the diurnal trends associated with each wind sector emphasise this, with concentrations for all compounds relating to wind directions 40-90°, significantly higher than those for 170-260°.

The concentrations and trends observed compare well with recent studies presented elsewhere in the world, most notably Marlyborne road in London.

A higher ethene / acetylene ratio was observed from wind direction sector 40-90° due to the proximity of the road traffic emissions.

Evaporative emissions and the m+p xylene / ethylbenzene ratio were investigated for both wind direction sectors, where higher evaporative ratios and relatively older HC's were associated with wind sector 40-90°, most likely due to long range transport of pollutants

Concentrations of all compounds except ethane, propane and acetylene decreased substantially from values reported in 1998, mainly due to a lower percent of high emitting vehicles in the 2003 vehicle fleet relative to that of 1998. It was hypothesised that the rise in acetylene concentrations was due to long range transport from Continental Europe and the UK, due to its relatively long atmospheric lifetime. Similar trends were noted over the same period at Marlyborne road in London.

Chapter 8

A 5 week monitoring campaign was carried out in Dublin City centre, to establish which site gave a more accurate background city centre estimation: a roof-top or green field site. This background represented a conservative estimate of HC exposure in Dublin City centre, useful for quantifying health effects related to this form of pollution.

Over the entire monitoring campaign, the lowest concentrations and relative standard deviations were observed at the green field site.

The rooftop concentrations were significantly higher for data associated with wind directions of between 40-90°, outlining the greater source effect Pearse Street traffic emissions have on the roof-top relative to the green field site. For 170-260°, similar results were observed for both background monitoring sites.

Evaporative emissions were found to be greater at the roof-top location regardless of wind direction.

The ethene / acetylene ratio was consistently lower at the green park site, outlining the relatively weaker local traffic related source effect observed at this receptor.

Overall

Utilising both the online system and mobile sampling method, a comprehensive assessment of Dublin air quality was possible. As expected, the highest concentrations were observed during the City centre roadside monitoring campaign, within which, the concentrations associated with winds from the heavily trafficked junction (40-90°) were greatest. This study also

emphasised not only the positive effect legislative and engineering controls have had on ambient HC concentrations since 1998, but also the effect long range transport of pollutants has on ambient concentrations and hence exposure. The green area background concentrations were significantly lower than the City roadside values. These concentrations represented a conservative estimate of HC exposure levels within Dublin City Centre. As no filtering was applied to these values, the concentrations presented can be used to quantify health effects associated with these background HC concentrations. Coincidentally, these were found to be very similar to the background corrected M50 values. On a day-to-day basis CALINE4 performed adequately for the M50 site, however, as the model did not predict values within a factor of two on every occasion, caution must be exercised when applying this model to situations where it is envisaged that HC emissions from the modelled road will be near to that of legislated air quality standards (i.e 6-8 lane motorways). Excellent agreement was observed between measured and modelled values over the entire monitoring campaign, mainly due to the over and underestimating nature of the model (associated with near parallel and perpendicular winds) cancelling itself out over the 5 week period. The M50 source effect was up to seven times higher than the background corrected morning peak time concentrations observed at the M4 site, where, unsurprisingly the lowest overall concentrations were observed. Study at the M4 site served to highlight the influence road orientation along with meteorological and topographical effects have on roadside concentrations. This form of information should aid planners in regard to road orientation, limiting the exposure of traffic related pollution, by maximising conditions for effective pollution dispersion. Higher peak time values were found not to impact greatly on average ambient concentrations, where, overall, the air quality monitored in Dublin and surrounding suburbs was found to be good, with no location exhibiting average concentrations greater than the legislated air quality standards for benzene or the guide value for 1,3-butadiene. Although this may be the case, it is naïve to assume the concentrations to which Dublin City and suburbs inhabitants are exposed have no adverse effects on health. However, it is difficult to estimate the health effects of exposure to such concentrations of hydrocarbons (other than benzene), as relatively little information is available in relation to their effects due to long term exposure, at the relatively low concentrations ascertained (in both urban and sub-urban studies).

9.2 RECOMMENDATIONS FOR FURTHER RESEARCH.

- The online system and mobile sampling method should be applied to a variety of long-term monitoring campaigns, such as estimating the effects of a newly built town by-pass, by assessing the concentrations at both the town and proposed bypass site before and after the road is complete.
- Further studies should be carried out into background concentrations in Dublin city, using additional roof-top and green field sites, to ascertain if the trends presented in Chapter 8 are consistently observed.
- An additional mobile sampling method should be developed to incorporate stainless steel canisters, which would facilitate the sampling of mono-aromatic hydrocarbons such as toluene and the xylene monomers. A thorough validation of this method should be undertaken to ensure acceptable performance.
- The Tedlar bag mobile method should be employed to investigate the "real world" exhaust emissions from a selection of Irish fleet vehicles of various age and condition, tested in different driving environments and conditions.
- The Tedlar bag mobile method and online system should be employed in an Irish tunnel study, to ascertain real world composite emission factors for the Irish fleet. The soon to be completed Dublin port tunnel, would present an ideal opportunity to ascertain emission factors for heavy goods vehicles.
- Comparisons between alternate road traffic dispersion models, as applied to Irish conditions, should be carried out, within which comparisons between emission factors derived from COPERT3, real world exhaust and real world tunnel studies can be undertaken.
- Using long range dispersion models such as the UK meteorological office model; NAME, and back trajectory techniques, long range transport of pollutants should be estimated and compared to rural ambient concentrations, ascertained using the online system over an extended period. In addition, mobile sampling should be carried out at a marine site on the east coast to provide additional information into the extent of long range transport of pollutants from primarily the UK.

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40 CFR Appendix B to part 136, Definition and procedure for the determination of the Method Detection Limit, revision 1.11.

APPENDIX A : Method parameters for ATD400 and GC

ATD400 method parameters :

Mode	2	Oven temp	250°C
First tube	1	Desorb time	1.0 min
Last tube	1	Valve temp	175°C
Inj/tube	99	Trap low	-30°C
Trap fast	YES	Trap high	325°C
Cycle time	60min	Trap hold	5.0 min
Inlet split	NO	Line temp	200°C
Outlet split	YES	Min PSI	43psig
Recycle	NO	Std inj	40min

Outlet split flow = 3 to 5ml/min
Desorb flow = 15 to 20ml/min
Inlet split (not used) – needle valve fully anti-clockwise (open)

Sample collection rate (adjusted using mass flow controller) set to 10 ml/min.

Autosystem GC method parameters

Oven temp 1	45°C	Oven temp 2	170°C	Oven temp 3	200°C
Oven time 1	15min	Oven time 2	0 min	Oven time 3	6min
Oven rate 1	5°C/min	Oven rate 2	15°C/min	Oven rate 3	END
Det 1 temp	250°C	Det 1 range	1	Det 1 attenuation	1
Det 2 temp	250°C	Det 2 range	1	Det 2 attenuation	1
Int output 1	FID 1	Autozero 1	ON	FID 1 offset	10
Int output 2	FID 2	Autozero 2	ON	FID 2 offset	10
Carrier 2	17.0 psig	Valve 2 (initial)	ON		
Events	10.5min	Valve 2	OFF		

APPENDIX B : Online system maintenance and Quality Control

It is imperative that helium carrier gas is kept flowing through the analytical columns at all times to maintain the columns in good working order. To facilitate this, a second spare helium cylinder should be kept on standby for rapid attachment to the system if required. Gases should in general be ordered a week before it is anticipated that they will run empty, as it usually takes several days for new cylinders to be delivered.

ATD400

If the zero air is not sufficiently dry (dewpoint <-100°F), the sample air cannot be purged of moisture, which may lead to icing of the peltier cooling system at the cold trap. This is usually manifested as a difficulty cooling rapidly to the setpoint of -30°C on the ATD.

You may observe data being acquired at successively later times in the hour, e.g.:

File 1 Collected at 12:22 p.m.
File 2 Collected at 13:24 p.m.
File 3 Collected at 14:26 p.m.
File 4 Collected at 15:28 p.m.
File 5 Collected at 16:30 p.m.

Notice the minutes increasing. If this phenomena is observed, sampling should be halted and the problem resolved. Failure to do so will damage the ATD. Check for the cause of the failure of the dry zero air (such as broken or split tubing, broken compressor, stuck drain valve on the compressor or zero air generator, etc.). Procedures for drying the peltier cooler on the cold trap are complicated. The easiest way is to re-establish a dry zero air supply, then leave the ATD 400 turned OFF for two hours or more (or *as long as possible*). Resist the temptation to open the peltier cooler housing, as this damages the sealing gaskets. The dry air will remove any moisture as long as the ATD is not powered on.

The sorbent trap material is held in the trap by a glass wool plug at the entrance/exit end, and a glass wool plug and spring at the other end. During the collection and analysis cycles, the system pressure cycles from a vacuum to ~48psi. This can cause eventual failure of the trap if the packing becomes loose. Material displaced from the trap will contaminate the sample lines within the ATD. The onset of failure is manifested by the degradation of peak shape on the BP-1 column (excessive tailing of peaks), while the PLOT column peaks remain relatively sharp. In addition, there may also be the loss of recovery of some compounds, especially the higher molecular weight hydrocarbons (C6, benzene and up). The sorbent should be replaced if the above is observed.

The ATD will test itself for leaks at the start of sampling. Thereafter, no leak checking is performed since the tube is not unloaded. If system leaks occur, they will be from devices such as the rotary valve or fittings, resulting in poor recovery of all analytes from both columns.

GC autosystem

If no signal for the FIDs is observed, several possible explanations should be examined. Check that you have the FID flames lit. This is commonly done by holding a cold surface (mirror or shiny wrench) over the FID chimney to observe the condensation from the moisture in the flame. Common reasons for the flame to be extinguished are humidity (inadequate drying) and lack of hydrogen or air fuel gases, or the wrong ratio of hydrogen to air. If the flame goes out consistently during a run, it is very likely that the incoming sample contains too much water. The water on a GC column will expand with such force during temperature programming that it will literally blow the flame out. Check that a column has not broken. If necessary, open the oven, disconnect the column from the detector, put the end in a non-polar solvent such as pentane and see if you get bubbles. If no bubbles are observed there is a leak in the column, if it can not be isolated and resolved the column must be replaced. Finally, check the midpoint pressure. If it is too high the carrier gas cannot flow down the BP-1 column.

If a baseline disturbance is noted on one chromatogram it may be due to a bad hydrogen regulator (there is one for each FID). The particular regulators used in the Perkin-Elmer GC's have a diaphragm that can become displaced when the control knob is turned. The displaced diaphragm prevents the regulator from working properly, causing pulses in pressure from 1 to

10 minutes in duration. Other causes of baseline cycling, including the zero air system, can cause confusing diagnoses. A good baseline is achievable.

A baseline disturbance on both chromatograms may be may be due to a bad air supply (there is one for both FIDs). This can be very difficult to diagnose, and difficult to resolve as there are many possible causes. Expert technical help should be sought to aid the resolution of this problem.

900 series interface and Turbochrom software

If the "under range" and "over range" LEDs are continuosly lit on the 900 interface, the interface may not be properly configured. Turbochrom should be restarted and a new sequence downloaded. In addition, baseline disturbances can cause the interface to signal under and over range. Under range could indicate that the FID might not be lit, causing a very low or under-range signal. Over range could indicate that the analog cables are not connected the right way round.

If a date like October 32nd is observed on a report, it is because a new sequence has not been downloaded in more than a month. To avoid this do not generate sequences of more than one month.

If poor peak integration has been observed, it can be ascribed to a variety of factors that include baseline noise and other disturbances, poor peak shape, faulty A/D interface, wrong sampling rate, wrong noise and baseline threshold values, poor peak separation, poor column performance. All of these factors should be considered when attempting to integrate the chromatogram.

APPENDIX C: Mobile sampling method pump

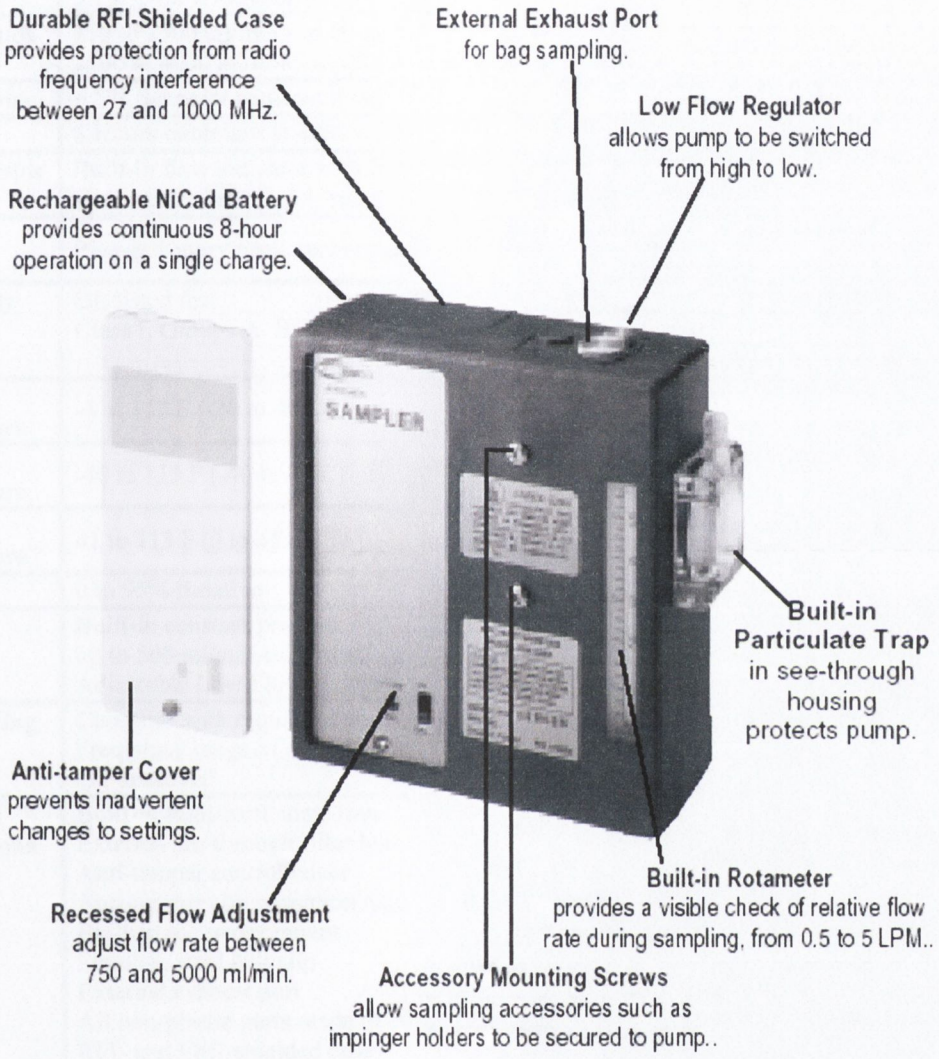

Figure C.1 SKC Universal Pump

Operating Range	5 to 5000 ml/min (5 to 500 ml/min requires the 224-26 series Adjustable Low Flow Holder) 5 to 3000 ml/min (MSHA -approved model)
Weight	34 ounces (964 grams)
Dimensions	5.1 x 4.7 x 1.9 inches (13 x 11.9 x 4.8 centimeters)
Compensation Range	750 to 2500 ml/min - to 40 inches water back pressure 2500 to 4000 ml/min - to 20 inches water back pressure
Flow Control	± 5% Set point constant flow
Run Time	8 Hours minimum at 4000 ml/min and 20 inches water back pressure
Flow Indicator	Built-in flow indicator with 250 ml/min divisions; scale marked at 1,2,3,4, and 5 liters per minute
Battery Assembly	Plug-in battery pack, rechargeable NiCad 2.0 Ah, 6.0 V, UL-listed
Intrinsically Safe	UL listed for: Class I, Groups A, B, C, D; Class II, Groups E, F, G and Class III. Temperature Code T3C
Operating Temperature	-4 to 113 F (-20 to 45 C)
Storage Temperature	-40 to 113 F (-40 to 45 C)
Charging Temperature	41 to 113 F (5 to 45 C)
Humidity	0 to 95% Relative
Multiple Sampling	Built-in constant pressure regulator allows user to take up to four simultaneous air samples of up to 500 ml/min each (total combined flow 1350 ml/min maximum) using the optional Adjustable Low Flow Holder accessory
RFI Shielding	Complies with requirements of EN 55022, FCC Part 15 Class B, EN 50082-1 Frequency range of the radiated susceptibility test was 27 to 1000 MHz CE-approved
Additional Specifications	Built-in fluid/particulate trap External see-through filter housing Anti-tamper control cover Anti-tamper compensation adjustments Built-in accessory mount Stainless steel belt clip External exhaust port All non-plastic parts made of corrosion-resistant materials RFI- and EMI-shielded case
Additional Features	One-year warranty Ultra-quiet operation Pulsation-free flow Impact-resistant case
Year 2000 Compliant	The 224-44XR air sampling pump has no date functions and is unaffected by the Year 2000 problem

Table C.1 specifications for universal pump

APPENDIX D: Tedlar bag connections and low flow controller

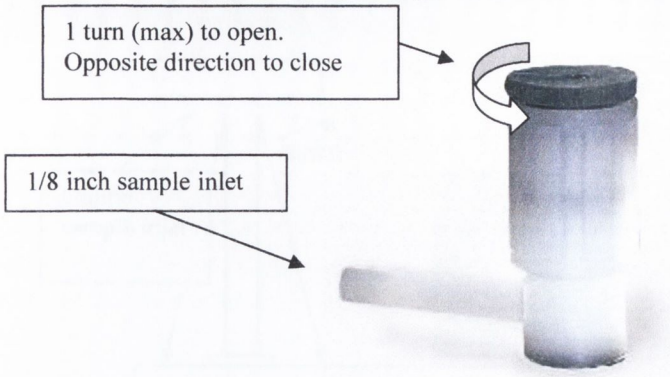

Figure D.1 polypropylene single fitting on 1 litre tedlar bags used

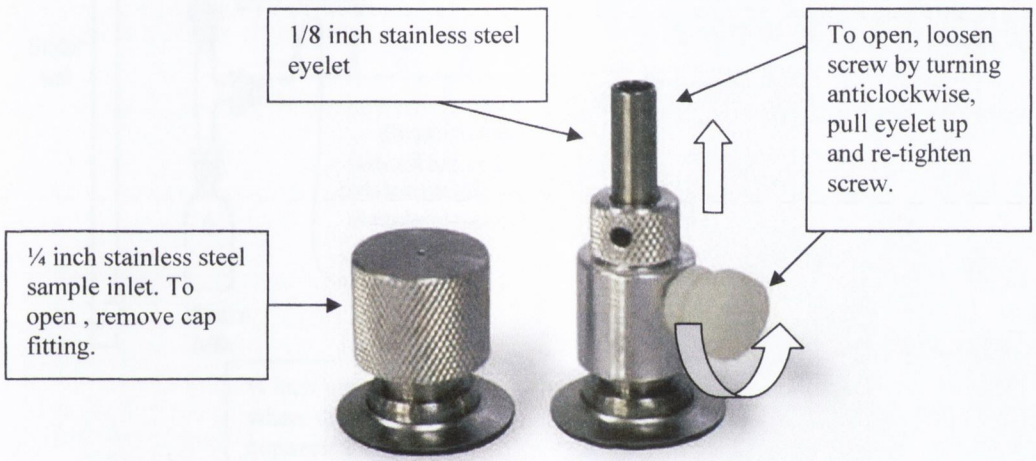

Figure D.2 Dual stainless steel fittings on 5litre tedlar bag used

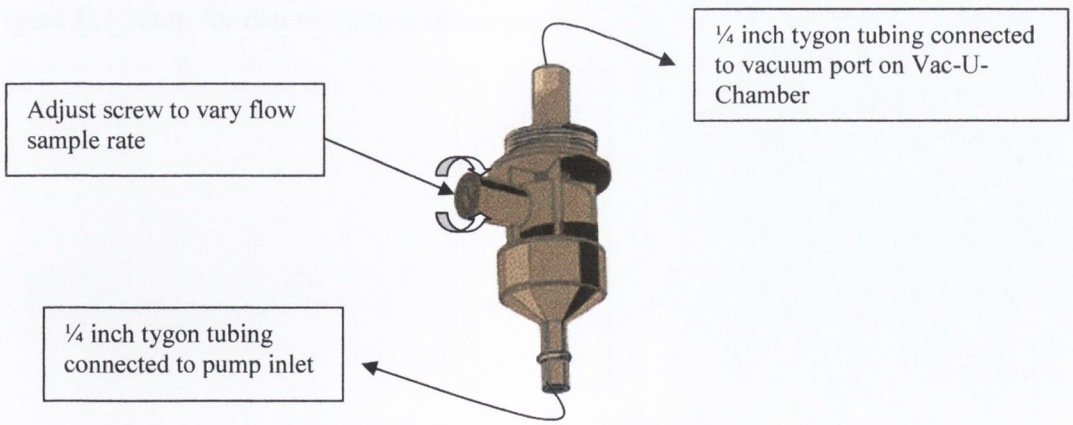

Figure D.3 low flow controller

APPENDIX E: Set-up for accuracy determination

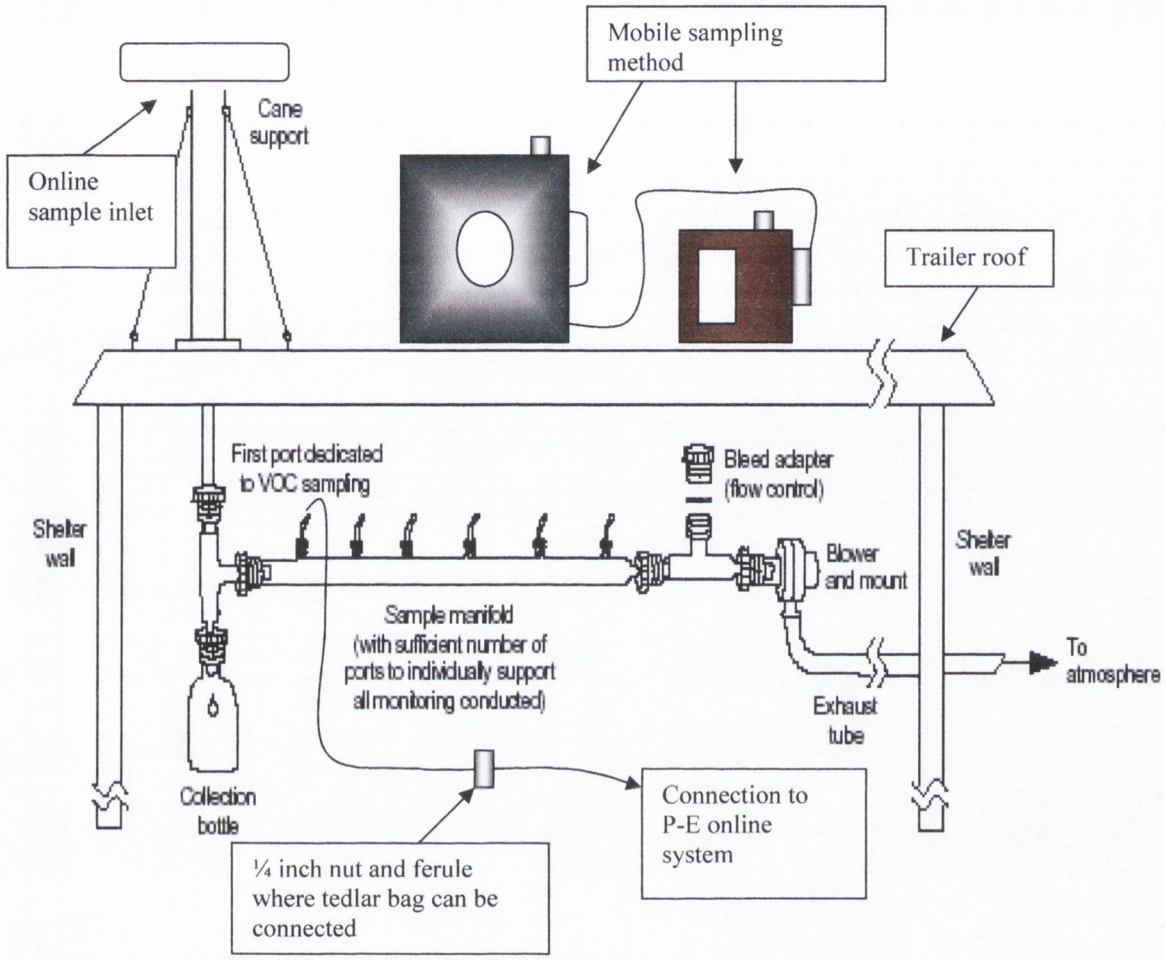

Figure E.1 setup for determination of accuracy, showing mobile sampler placed on the trailer roof

APPENDIX F: Calibration curves

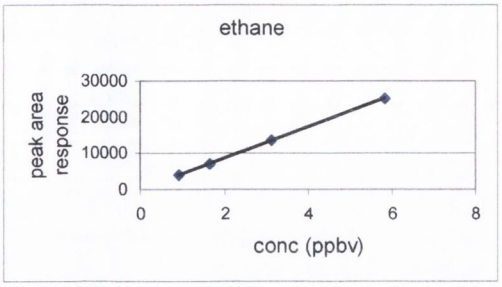

Figure F.1 ethane calibration curve

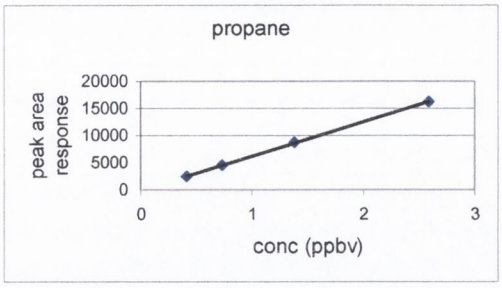

Figure F.2 propane calibration curve

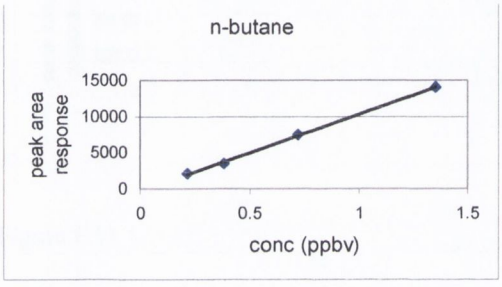

Figure F.3 n-butane calibration curve

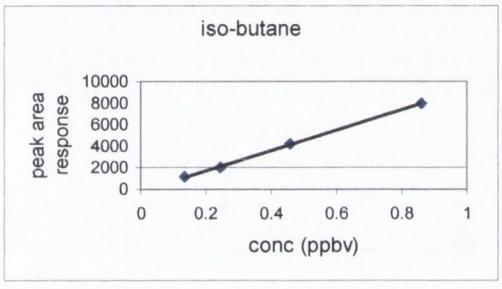

Figure F.4 iso-butane calibration curve

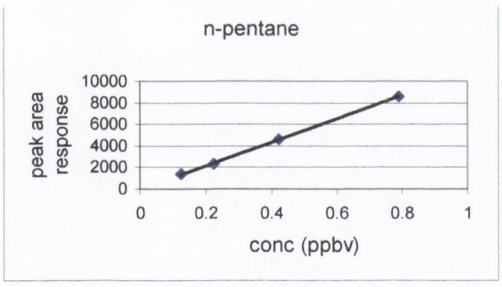

Figure F.5 n-pentane calibration curve

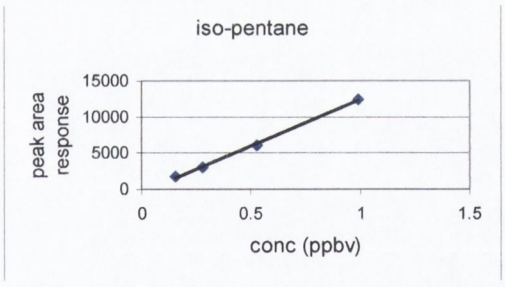

Figure F.6 iso-pentane calibration curve

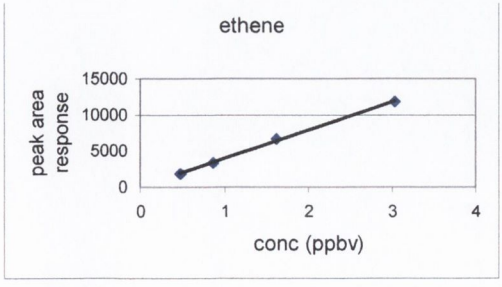

Figure F.7 ethene calibration curve

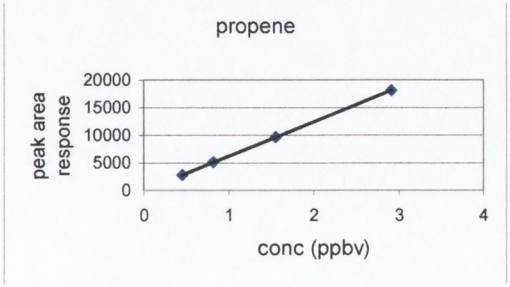

Figure F.8 propene calibration curve

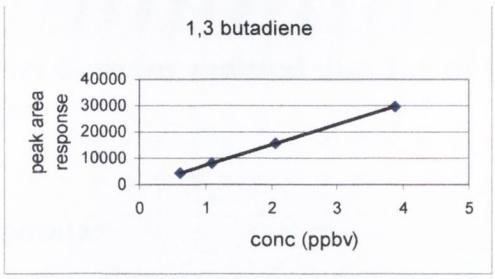

Figure F.9 1,3 butadiene calibration curve

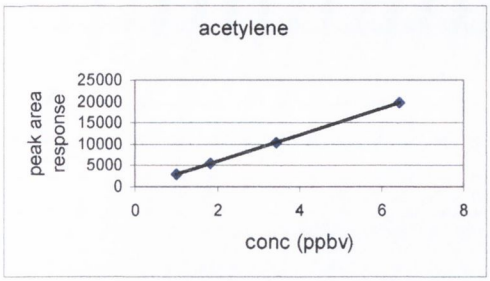

Figure F.10 acetylene calibration curve

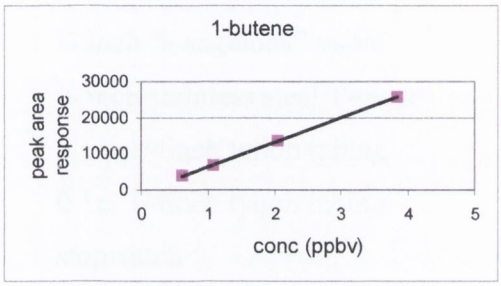

Figure F.11 1-butene calibration curve

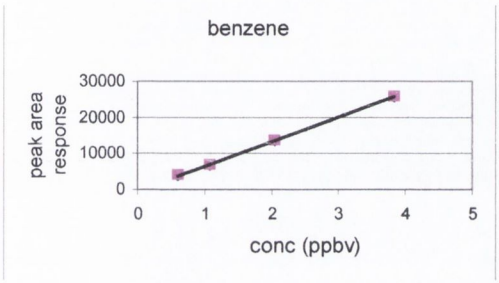

Figure F.12 benzene calibration curve

APPENDIX G:

Procedure for manual dilution of traceable calibration standard gas mix.

Apparatus

- specially adapted gas flow regulator
- 1/16 inch stainless steel tubing
- ¼ inch "swagelock" valve
- ¼ inch stainless steel T-piece
- 0.1m 1/4inch teflon tubing
- 0.1m 1/4inch tygon tubing
- stopwatch
- 5litre tedlar sampling vessel
- Digital flow meter

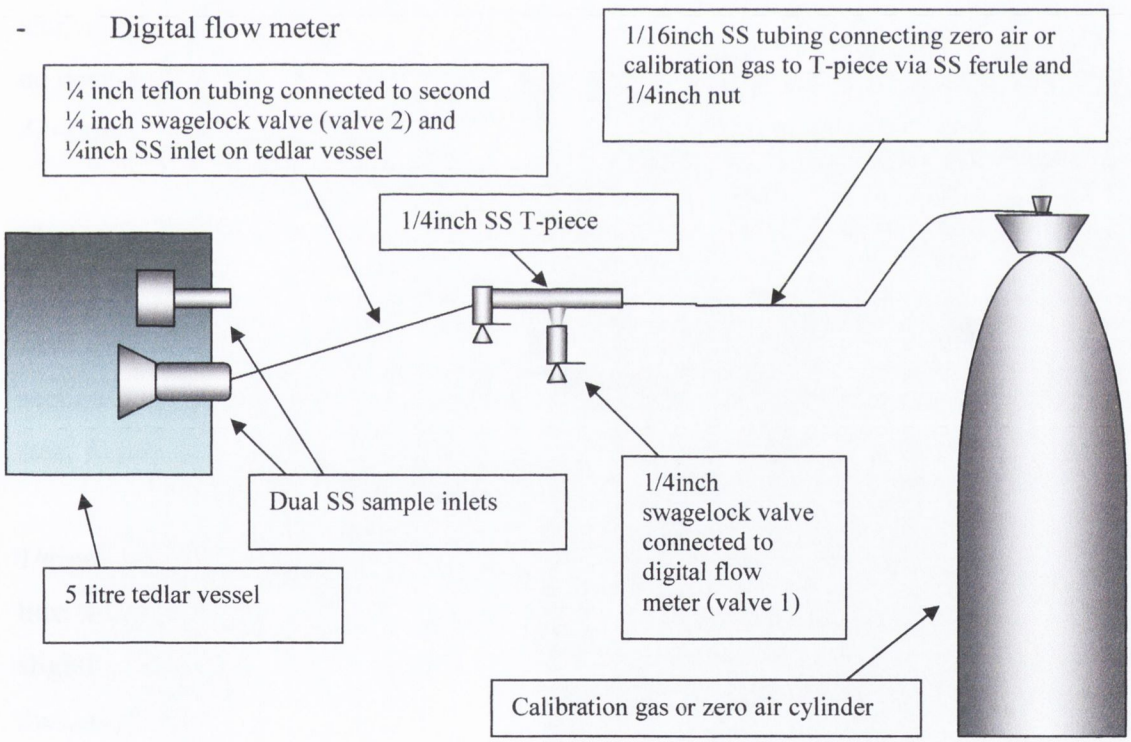

Figure G.1 manual dilution of calibration gas setup

The rational behind the procedure can be explained as follows. To achieve a 5 times dilution of the gas concentrations in the cylinder, for equal flow rates, zero air should be passed into the tedlar vessel for 4 times longer than the calibrant gas. A volume of approximately 4litres in the vessel was required, hence 2 minutes sampling of calibrant gas at a flow rate of 400ml/min and 8 minutes sampling of zero air at a flow rate of 400ml/min gave the required volume and dilution. The absolute flow rate was not of prime importance, the critical consideration being that the flow rate for the calibrant gas and zero air through the system be the same. The absolute flow rate was chosen to obtain the required volume in a total sampling time of 10 minutes.

Procedure

Prior to any dilution, the 5 litre tedlar bag was flushed 15 times with zero air, a blank reading was taken by attaching the vessel to the online system as per section 3.1.3 and analysis taken as per section 3.1.2. The chromatogram was visually examined to ensure no contamination of the 5 litre tedlar by the compounds of interest in vessel prior to dilution.

The apparatus was set up as in Figure G.1.

Zero air / calibration gas cylinder was first attached to the adapted regulator discussed in section 3.5. The 1/16 inch S.S line was connected to the ¼ inch T-piece via a stainless steel ferule and ¼ inch nut.

1/4inch teflon tubing was connected to the ¼ inch stainless steel sample inlet on the 5 litre tedlar bag. This was done by heating the teflon tubing to expand the diameter slightly, the tubing was then attached by applying pressure and rotating the tubing over the sample inlet. ¼ inch flexible tygon tubing was placed over the joint to ensure a good seal. For rapid sample evacuation and 5 litre tedlar vessel cleaning, the second sample inlet was used.

The 5 litre tedlar bag was connected to the second ¼ inch swagelock valve (valve 2) via ¼ inch teflon tubing, flexible ¼ inch tygon tubing was placed over the joint to prevent leaks. The swagelock valve was simply screwed onto the T-piece.

A digital flow meter was connected to the first ¼ inch swagelock valve (valve 1) via flexible rubber tubing attached to the flow meter. This swagelock was screwed onto the T-piece.

The entire setup was then checked for leaks by passing zero air through the setup at a high flow rate and applying an inert soapy solution to each connection point, a lack of bubbles suggested a leak free setup. The setup was left to room dry before continuing.

After completing the above setup, it was necessary to clean the tedlar bag again, as its interior had been exposed to outside air when attaching the ¼ inch teflon tubing to the sample inlet and then to the swagelock valve. To reclean the bag, valve 2 was closed and zero air flushed in and out of the vessel using the second stainless steel inlet. A blank reading was again taken from the vessel by connecting this inlet to the P-E system as per section 3.1.3 and non-contamination of the vessel was verified. The vessel was then evacuated completely, the second sample inlet closed and the dilution process could begin.

The calibration gas was first attached to the adapted regulator. The cylinder was opened and with valve 2 closed, valve 1 was opened and the flow of calbrant gas measured. The regulator was adjusted until a flow of 400mls/min was obtained. This was observed for several minutes to ensure that the flow remained constant. When satisfied that the flow was constant, valve 1 was closed and valve 2 simultaneously opened, at which point the stopwatch was started and the calibrant gas flushed into the tedlar bag for a period of exactly 2 minutes. Assistance was required at this stage of the procedure, to employ ues of the stopwatch. After the required time, valve 2 was closed and valve 1 opened. The calibration gas cylinder was closed and disconnected from the regulator. Zero air was

then attached and the procedure was repeated, with the exception that zero air was flushed into the vessel for 8 minutes as opposed to 2.

The gases in the Tedlar bag were mixed by lightly squeezing the 5litre vessel for several minutes. The mix was left for several hours before analyzing.

Numerous errors are associated with this procedure for diluting gasses. The setup is prone to leaks as gases are being forced through the system at pressure. Minor leaks occurring during sampling will give different flow rates and hence incorrect dilution. The turning on and off of valves has to be carried out precisely to ensure accuracy and most time consuming of all, for every mistake made, the vessel must be re-cleaned and a contamination free blank established.

APPENDIX H: Sampling set-up for Precision estimation

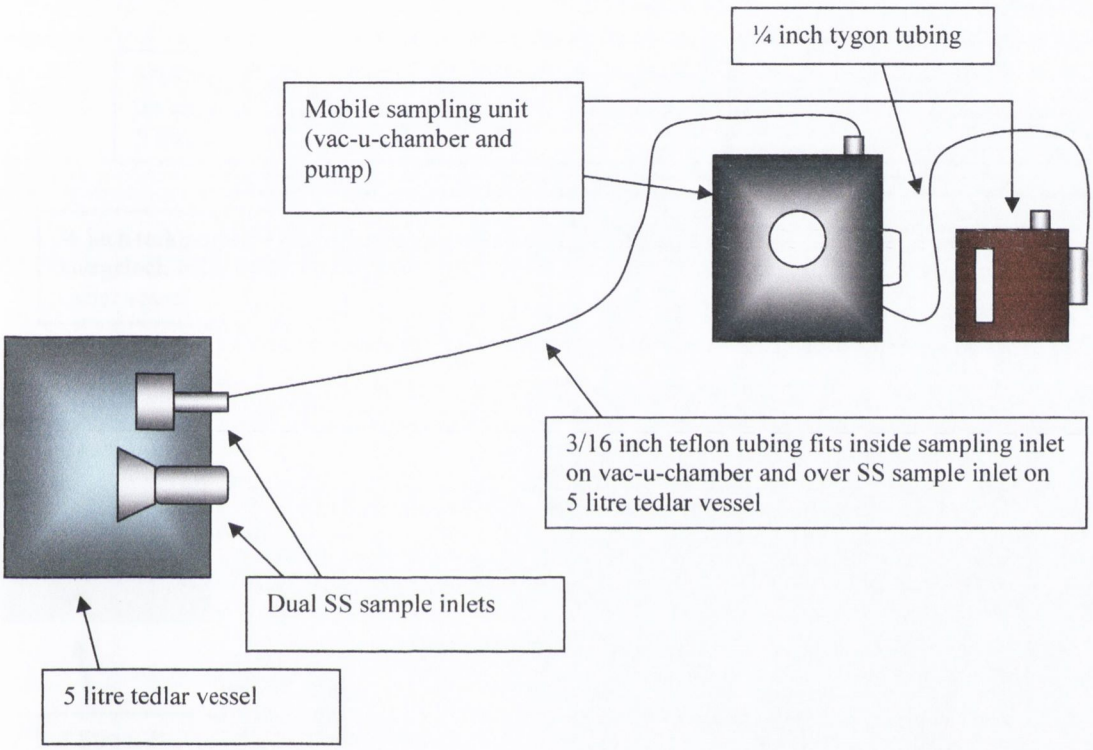

Figure H.1 setup used for determination of replicate precision of ambient samples

APPENDIX I: Sampling set-up for robustness tests

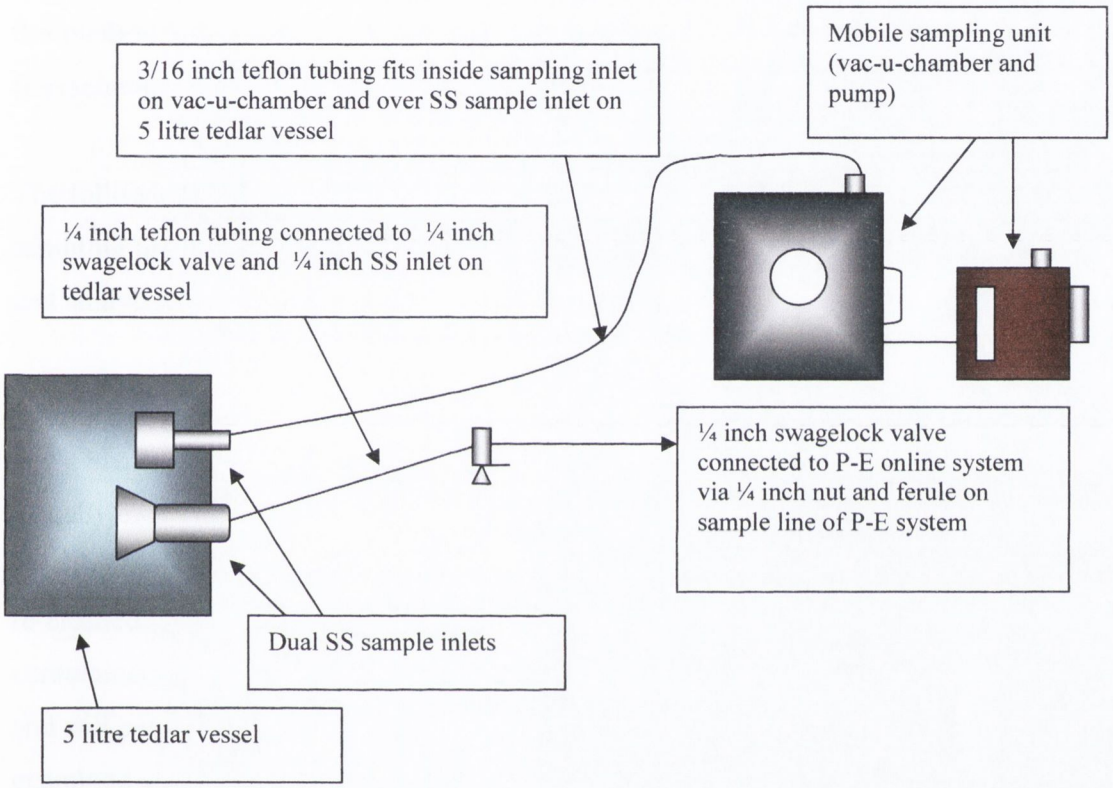

Figure I.1 setup for simultaneous sampling from 5 litre sample reservoir for mobile sampling method and online system run as standard

The above setup was used in the robustness determinations and also in showing linearity of response above determined concentration range.

APPENDIX J: Quality Control for mobile sampling method

Quality control can be defined as 'The operational techniques and activities that are used to fulfil requirements of quality.' (ISO 8402,1994) Method validation gives an idea of a method's performance capabilities and limitations which may be experienced in routine use while the method is in control. In routine use, specific controls need to be applied to the method to verify that it remains in control, *i.e.* is performing in the way expected (Eurachem, 1998).

The following procedures should be carried out when extended periods of mobile sampling are anticipated, they are carried out to ensure the mobile sampling procedure and analytical method are both operating as expected.

As often as practical but at least weekly, a Tedlar bag should be taken at random, cleaned and a blank analysis taken as per section 3.1.3. The resulting chromatogram should be visually examined for significant peaks relating to contamination in the Tedlar vessel. If significant contamination of the compounds of interest are observed the vessel should be re-cleaned and re-analyzed. In addition, a second Tedlar vessel should be examined for contamination. If contamination is observed in the second random vessel being analyzed and still persists in the initial vessel after re-cleaning, all vessels should be blank examined and any vessels where significant contamination is observed after 2 cleaning procedures should be discarded. a third vessel should be examined. It is advisable that all Tedlar vessels be replaced at most every 3 months to ensure limited difficulties in relation to vessel contamination and degradation.

A 1 point calibration using tedlar vessels should be carried out every second week as per section 3.2.5. The average response factor for six replicate analysis should be within ± 10% of the average response factor seen for a 1 point calibration using tedlar bags in table 3.7.
Alternately, a multi-point calibration can be carried out using the procedure outlined in section 3.2.5 for different tedlar vessel "valve open times". The average response factors

should be within ± 10% of the average response factors seen in table 3.7. If the 1 point calibration peak responses are greater than ± 10% of the average 1 point calibration response factors using tedlar bags, in table 3.3, a multi-point calibration must be carried out to verify linearity of response.

If the average peak areas at any calibration level for the multi-point calibration are greater than ± 10% of the average peak areas presented in table 3.3, the P-E system should be re-calibrated as standard using the 1 point calibration sampled through the dedicated calibrant line from the NIST traceable standard.

If the average response factor for this 1 point calibration of the system, calibrated as standard, is greater than ±10% of the average response factor for this form of 1 point calibration, in table 3.7,the problem is most likely the analytical system and a full investigation should be carried out into the cause of this non-linear system response.

If the average response factor is within the ±10% of the average response factor in table 3.7 for the P-E system calibrated as standard (online 1 point calibation), the problem most likely relates to the tedlar vessels or connections from the vessels to the P-E system. Sampling can not proceed until satisfactory calibration has been carried out and a linear response has been established.

Daily or weekly quality control checks can also be carried out by analyzing a single, 1 point calibration standard from the tedlar vessels. If the response factor for this "1 off" analysis is within ±10% of the mean response factor obtained for the last calibration carried out, all results analyzed between that calibration and this "1 off" analysis can be considered quality assured. An interesting point should be noted here, in that this procedure can be used to quality assure samples obtained when the P-E online system run as normal is sampling ambient air over a long period of time. Instead of having to load a dedicated calibration sequence with the associated time delays and ambient sampling "down time", one off quality assuring calibration samples can be analyzed using tedlar vessels. This effectively limits the time taken to calibrate the system as standard, and also

enables calibration on a more frequent basis, thus quality assuring results with a higher degree of confidence.

Finally, every 2 weeks to 1 month a comparison of accuracy and precision for 1 sample should be carried out as in sections 3.6 and 3.7. This ensures that the operator is carrying out the sampling and analysis procedures as per section 3.1.1 and 3.1.2 correctly and also that no problems i.e, pump flow variability, are affecting results to a significant degree.

Although not always practical to do so, the above procedures should be carried out as often as possible. Their implementation will ensure limited "down time" of the system due to early detection of potential problems and will also quality assure results obtained.

APPENDIX K: Measured and modelled values for entire campaign

n-pentane						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	0.660	0.271	0.469	0.089	0.030	0.052
17/07/03	0.126	0.198	0.019	0.059	-0.001 (0)	0.036
18/07/03	0.217	0.081	0.048	0.025	0.016	0.014
22/07/03	0.004	0.166	-0.037 (0)	0.042	-0.031 (0)	0.016
23/07/03	0.044	0.229	-0.059 (0)	0.073	-0.062 (0)	0.038
24/07/03	0.099	0.119	0.044	0.039	-0.007 (0)	0.023
25/07/03	0.126	0.185	0.057	0.060	0.016	0.035
28/07/03	0.081	0.113	0.070	0.035	0.079	0.020
29/07/03	0.398	0.124	0.000	0.039	-0.015 (0)	0.023
05/08/03	0.725	0.182	0.088	0.058	0.077	0.034
06/08/03	0.029	0.155	-0.040 (0)	0.047	-0.041 (0)	0.029
08/08/03	0.347	0.092	0.177	0.031	0.171	0.019
11/08/03	-0.045 (0)	0.162	-0.006 (0)	0.052	0.072	0.032
13/08/03	0.032	0.177	-0.037 (0)	0.051	-0.083 (0)	0.030
15/08/03	0.137	0.255	0.007	0.078	No sample	0.051
19/08/03	0.079	0.072	-0.011 (0)	0.022	0.009	0.013
21/08/03	0.068	0.087	-0.009 (0)	0.026	-0.010 (0)	0.015
25/08/06	0.088	0.166	-0.017 (0)	0.051	0.022	0.030
26/08/03	0.081	0.081	0.077	0.024	0.041	0.015
27/08/03	0.055	0.069	0.023	0.022	-0.029 (0)	0.013

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.1 Daily measured and modelled concentrations for n-pentane (ppbv)

iso-pentane						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	1.517	0.569	1.143	0.186	0.100	0.110
17/07/03	0.368	0.437	0.090	0.131	-0.048 (0)	0.080
18/07/03	0.504	0.192	0.113	0.060	0.012	0.034
22/07/03	0.062	0.349	-0.024 (0)	0.087	-0.017 (0)	0.034
23/07/03	0.087	0.520	-0.120 (0)	0.166	-0.156 (0)	0.086
24/07/03	0.342	0.280	0.141	0.092	0.019	0.054
25/07/03	-0.040 (0)	0.398	0.053	0.128	-0.017 (0)	0.076
28/07/03	0.123	0.249	0.203	0.076	0.165	0.045
29/07/03	2.589	0.281	0.000	0.089	-0.060 (0)	0.053
05/08/03	2.314	0.383	-0.098 (0)	0.121	0.129	0.072
06/08/03	-0.001 (0)	0.326	-0.124 (0)	0.099	-0.204 (0)	0.061
08/08/03	0.845	0.197	0.471	0.066	0.267	0.042
11/08/03	-0.125 (0)	0.357	0.018	0.115	0.224	0.070
13/08/03	-0.033 (0)	0.402	-0.216 (0)	0.115	-0.286 (0)	0.068
15/08/03	0.445	0.535	0.098	0.163	No sample	0.106
19/08/03	0.188	0.172	-0.050 (0)	0.052	0.005	0.031
21/08/03	0.182	0.218	-0.003 (0)	0.066	-0.018 (0)	0.038
25/08/06	0.321	0.375	-0.034 (0)	0.115	0.035	0.068
26/08/03	0.284	0.197	0.168	0.059	0.136	0.037
27/08/03	0.119	0.157	0.005	0.050	0.059	0.030

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.2 Daily measured and modelled concentrations for iso-pentane (ppbv)

ethene						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	Modelled	Measured (bkg corr.)	modelled
16/07/03	1.664	1.321	1.653	0.432	0.100	0.255
17/07/03	2.201	1.207	0.310	0.361	0.040	0.220
18/07/03	0.920	0.652	0.013	0.203	0.079	0.114
22/07/03	0.228	0.810	-0.131 (0)	0.203	-0.167 (0)	0.079
23/07/03	0.795	1.550	-0.029 (0)	0.493	-0.121 (0)	0.255
24/07/03	1.034	0.916	0.439	0.299	0.148	0.176
25/07/03	1.041	1.013	0.387	0.326	0.242	0.194
28/07/03	0.157	0.687	0.243	0.211	0.100	0.123
29/07/03	1.319	0.837	0.480	0.264	0.278	0.159
05/08/03	0.840	0.890	0.162	0.282	0.203	0.167
06/08/03	0.628	0.757	0.045	0.229	-0.214 (0)	0.141
08/08/03	1.875	0.502	0.524	0.167	0.178	0.106
11/08/03	-0.141 (0)	0.986	0.074	0.317	0.218	0.194
13/08/03	0.688	1.198	0.025	0.343	-0.240 (0)	0.203
15/08/03	0.497	1.242	0.042	0.379	No sample	0.247
19/08/03	0.591	0.581	-0.179 (0)	0.176	-0.105 (0)	0.106
21/08/03	0.483	0.819	0.209	0.247	-0.022 (0)	0.141
25/08/06	0.696	1.119	-0.257 (0)	0.343	0.048	0.203
26/08/03	0.755	0.705	0.229	0.211	-0.020 (0)	0.132
27/08/03	0.607	0.467	0.276	0.150	0.438	0.088

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.3 Daily measured and modelled concentrations for ethene (ppbv)

propene						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	0.312	0.391	0.306	0.128	0.030	0.076
17/07/03	0.968	0.357	0.124	0.107	0.006	0.065
18/07/03	0.318	0.193	0.033	0.060	0.020	0.034
22/07/03	0.128	0.240	-0.033 (0)	0.060	0.018	0.023
23/07/03	0.212	0.458	-0.020 (0)	0.146	-0.053 (0)	0.076
24/07/03	0.473	0.271	0.141	0.089	0.122	0.052
25/07/03	0.368	0.299	0.140	0.096	0.061	0.057
28/07/03	0.098	0.203	0.093	0.062	0.071	0.036
29/07/03	0.403	0.247	0.148	0.078	0.119	0.047
05/08/03	0.187	0.263	0.049	0.083	0.007	0.049
06/08/03	0.234	0.224	0.036	0.068	-0.034 (0)	0.042
08/08/03	0.558	0.148	0.155	0.049	0.071	0.031
11/08/03	-0.067 (0)	0.292	-0.009 (0)	0.094	0.041	0.057
13/08/03	0.289	0.354	-0.001 (0)	0.102	-0.042 (0)	0.060
15/08/03	0.081	0.367	-0.042 (0)	0.112	No sample	0.073
19/08/03	0.221	0.172	-0.050 (0)	0.052	-0.001 (0)	0.031
21/08/03	0.188	0.242	0.060	0.073	0.017	0.042
25/08/06	0.202	0.331	-0.083 (0)	0.102	-0.021 (0)	0.060
26/08/03	0.296	0.208	0.105	0.062	0.014	0.039
27/08/03	0.239	0.138	0.107	0.044	0.191	0.026

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.4 Daily measured and modelled concentrations for propene (ppbv)

1,3 butadiene						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	0.082	0.139	0.073	0.045	0.010	0.027
17/07/03	0.317	0.127	0.076	0.038	0.051	0.023
18/07/03	0.114	0.069	-0.004 (0)	0.021	-0.004 (0)	0.012
22/07/03	0.054	0.085	0.001	0.021	-0.003 (0)	0.008
23/07/03	0.070	0.163	-0.010 (0)	0.052	-0.026 (0)	0.027
24/07/03	0.122	0.096	0.027	0.032	0.019	0.019
25/07/03	0.092	0.107	-0.002 (0)	0.034	-0.001 (0)	0.020
28/07/03	0.024	0.072	-0.001 (0)	0.022	-0.016 (0)	0.013
29/07/03	0.301	0.088	-0.044 (0)	0.028	0.059	0.017
05/08/03	0.003	0.094	-0.036 (0)	0.030	-0.046 (0)	0.018
06/08/03	0.080	0.080	0.032	0.024	0.037	0.015
08/08/03	0.110	0.053	0.038	0.018	0.049	0.011
11/08/03	-0.039 (0)	0.104	-0.039 (0)	0.033	-0.039 (0)	0.020
13/08/03	0.106	0.126	-0.003 (0)	0.036	-0.017 (0)	0.021
15/08/03	0.061	0.131	0.020	0.040		0.026
19/08/03	0.030	0.061	-0.023 (0)	0.019	-0.002 (0)	0.011
21/08/03	0.234	0.086	0.000	0.026	0.000	0.015
25/08/06	0.070	0.118	-0.005 (0)	0.036	0.028	0.021
26/08/03	0.063	0.074	0.032	0.022	0.026	0.014
27/08/03	0.047	0.049	-0.002 (0)	0.016	0.014	0.009

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.5 Daily measured and modelled concentrations for 1,3 butadiene (ppbv)

Benzene						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	0.330	0.276	0.326	0.090	0.030	0.053
17/07/03	0.245	0.249	0.056	0.074	0.013	0.045
18/07/03	0.148	0.133	0.004	0.041	-0.012 (0)	0.023
22/07/03	0.063	0.169	0.002	0.042	-0.029 (0)	0.017
23/07/03	0.134	0.318	-0.034 (0)	0.101	-0.061 (0)	0.052
24/07/03	0.156	0.187	0.067	0.061	0.009	0.036
25/07/03	0.147	0.210	0.052	0.068	0.027	0.040
28/07/03	0.059	0.141	0.084	0.044	0.076	0.025
29/07/03	0.307	0.171	0.180	0.054	0.123	0.032
05/08/03	0.111	0.186	0.035	0.059	0.066	0.035
06/08/03	0.130	0.158	0.005	0.048	-0.015 (0)	0.029
08/08/03	0.223	0.104	0.026	0.035	0.003	0.022
11/08/03	0.024	0.203	0.055	0.065	0.088	0.040
13/08/03	0.139	0.245	0.066	0.070	-0.097 (0)	0.042
15/08/03	0.081	0.259	-0.005 (0)	0.079		0.051
19/08/03	0.175	0.118	-0.069 (0)	0.036	-0.168 (0)	0.021
21/08/03	0.055	0.166	0.007	0.050	-0.039 (0)	0.029
25/08/06	0.167	0.229	-0.021 (0)	0.070	0.033	0.042
26/08/03	0.173	0.143	0.082	0.043	0.061	0.027
27/08/03	0.153	0.096	-0.021 (0)	0.031	0.074	0.018

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.6 Daily measured and modelled concentrations for benzene (ppbv)

acetylene						
	25metres		120metres		240metres	
Date	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled	Measured (bkg corr.)	modelled
16/07/03	1.335	0.523	1.066	0.171	-0.010 (0)	0.101
17/07/03	0.943	0.478	0.321	0.143	0.162	0.087
18/07/03	0.805	0.258	-0.110 (0)	0.080	-0.082 (0)	0.045
22/07/03	0.358	0.321	0.087	0.080	0.003	0.031
23/07/03	0.292	0.614	-0.160 (0)	0.195	-0.173 (0)	0.101
24/07/03	0.838	0.363	0.380	0.119	0.127	0.070
25/07/03	0.506	0.401	0.042	0.129	0.069	0.077
28/07/03	0.532	0.272	0.329	0.084	0.176	0.049
29/07/03	0.252	0.331	-0.091 (0)	0.105	-0.218 (0)	0.063
05/08/03	0.369	0.352	0.094	0.112	0.273	0.066
06/08/03	0.137	0.300	-0.198 (0)	0.091	-0.205 (0)	0.056
08/08/03	0.593	0.199	0.344	0.066	0.252	0.042
11/08/03	-0.106 (0)	0.391	0.069	0.126	0.168	0.077
13/08/03	0.351	0.474	-0.028 (0)	0.136	0.096	0.080
15/08/03	0.444	0.492	-0.054 (0)	0.150	No sample	0.098
19/08/03	0.041	0.230	-0.095 (0)	0.070	-0.006 (0)	0.042
21/08/03	0.135	0.324	0.033	0.098	-0.082 (0)	0.056
25/08/06	0.448	0.443	-0.080 (0)	0.136	0.167	0.080
26/08/03	0.493	0.279	0.113	0.084	0.041	0.052
27/08/03	0.144	0.185	0.003	0.059	0.077	0.035

Bkg corr. = background corrected. Negative background corrected values assumed to be zero for comparisons with model.

Table K.7 Daily measured and modelled concentrations for acetylene (ppbv)