Measurement of Ambient Concentrations of Benzene, Toluene and Xylene in the vicinity of Petrol Service Stations.

By

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Abstract

Ambient air monitoring in the vicinity of three petrol service stations was undertaken to determine concentrations of three volatile organic compounds; benzene, toluene and xylene (BTX). Quantitative measurements were undertaken using both diffusive and active sampling onto a solid adsorbent material followed by thermal desorption and a gas chromatography/mass spectrometry (GC/MS) determination. Mean weekly BTX concentrations are reported for forecourt pumps, forecourt perimeter, roadside and background sampling locations over a four-week monitoring campaign.

Diffusive sampling was performed using Chromosorb 106 and Tenax, and a high degree of correlation was observed between the BTX concentrations measured using the two adsorbent materials. The Wilcoxon Signed Rank Test revealed no significant difference in the measured benzene concentrations, while the toluene and xylene levels differed significantly using the two adsorbent materials. The observed difference in the measured concentrations may be attributed to the lack of validation of the diffusive sampling rates for Tenax at environmental levels for one-week sampling periods.

The observed rank order of BTX concentrations at the sampling locations was; forecourt pumps area > forecourt perimeter > roadside > background locations where mean BTX concentrations were 7.3, 4.5, 2.2 and 0.9μg/m^3, respectively. The BTX concentrations measured at the forecourt pumps area of all three stations were approximately 5 to 15 times higher than the corresponding background levels. Concentrations measured in the forecourt pumps and perimeter areas were shown to be dependant on the scale of the service station and prevailing meteorological conditions. It is suggested that the volume of traffic is the predominant source of BTX measured at the roadside sampling locations. Mean background concentrations of BTX were approximately 1μg/m^3.

Ratios of measured BTX concentrations at forecourt pumps, forecourt perimeter and roadside sampling locations were consistent with expected values. However, the BTX ratios at the background sampling location Station A seem to be influenced by an alternative source of xylene other than petrol vapour or vehicular emissions.

BTX concentrations measured at forecourt service areas in the current study were considerably lower than previous studies where levels of up to 187, 325 and 142μg/m^3, respectively for BTX have been reported. Background concentrations were also shown to be lower than previously reported results, however, in the current study the background locations were sub-urban as opposed to the urban site selected for previous studies.

Mean benzene concentrations at the forecourt pumps area were approximately 50% higher than the proposed EU annual average limit value of 5μg/m^3. The highest weekly toluene concentration recorded for the study was 29.7μg/m^3, which is significantly lower than the WHO guideline value of 260μg/m^3.

Higher BTX concentrations were observed for the short four-hour active sampling period at Station C, the results however confirmed the rank order of sampling locations observed for the diffusive monitoring campaign.

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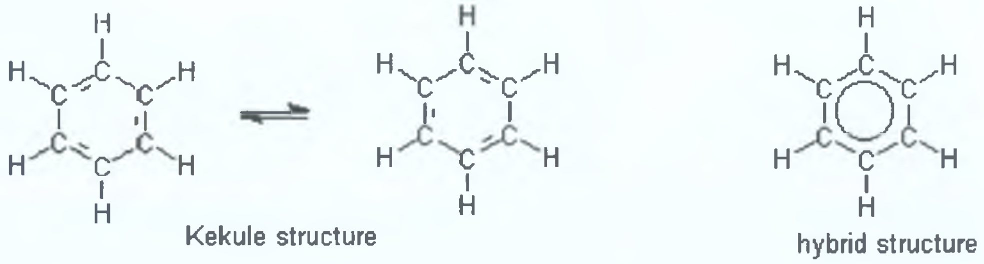
Abbreviations

VOC	Volatile Organic Compound
BTX	Benzene, toluene and xylene
PAH	Polyaromatic Hydrocarbon
EU	European Union
CEC	Commission of the European Community
EEA	European Environment Agency
ERLAP	European Reference laboratory for Air Pollution
EPA	Environmental Protection Agency, Ireland
USEPA	Environmental protection Agency, United States of America
WHO	World Health Organisation
ISO	International Standards Organisation
CEN	European Committee for Standardisation
NGO	Non-Governmental Organisation
GC/MS	Gas Chromatography/Mass Spectrometry
GC/FID	Gas Chromatography/Flame Ionisation Detector
ATD	Automated Thermal Desorption
µg	microgram (10^{-6}g)
pg	picogram (10^{-9}g)
ppb	parts per billion
m^3	cubic metre (10^3 litres)
cm	centimetre (10^{-2}m)

Chapter 1. Introduction

Benzene (C_6H_6) is an aromatic organic compound (Figure 1) and is a known carcinogen. It has a boiling point of 80°C and evaporates readily to the vapour phase, it can therefore be classed as a volatile organic compound (VOC).

Figure 1. The structure of benzene.



Benzene is present in petrol and it is also emitted in motor vehicle exhaust fumes. It has been estimated that over 80% of the benzene emitted into the air in the European Community is derived from vehicle exhaust emissions (RIVM, 1988). As a result of the universal use of petrol and automobiles benzene is now ubiquitous in ambient air. The role of VOC's in the formation of photochemical oxidants such as ozone is a well recognised environmental concern. However, the protection of human health is the primary concern arising from elevated concentrations of benzene in ambient air. Benzene is known to cause leukaemia (CONCAWE, 1995; WHO, 1996) and is classified as a class 1 carcinogen by the International Association on the Risks of Cancer (IARC, 1987).

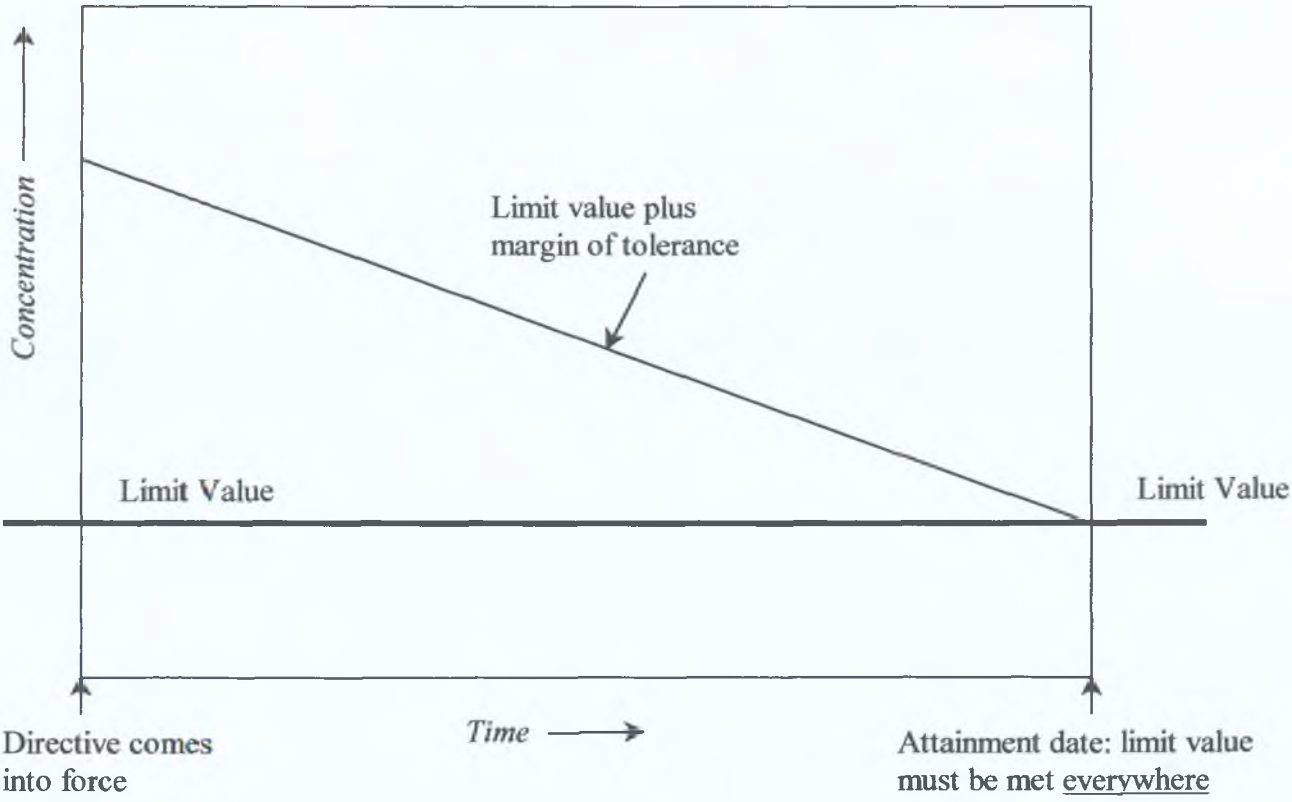
1.1 The Ambient Air Quality Framework Directive

European Council Directive 96/62/EC of 27th September 1996 on ambient air quality assessment and management (the Air Quality Framework Directive) was introduced to fulfill the fifth environment action programme on the establishment of long-term air quality objectives in Member States. The four objectives of the Directive are to :

- define and establish objectives for ambient air pollution in the Community designed to avoid, prevent and reduce harmful effects on human health and the environment as a whole
- assess ambient air quality in Member States on the basis of common methods and criteria
- obtain adequate information on ambient air quality and ensure that it is made available to the public inter alia by means of alert thresholds, and
- maintain ambient air quality where it is good and improve it in other cases.

The overall aim of the framework directive is to harmonise the approach to ambient air quality assessment and management across all European Member States. The basic principle of the European Commissions assessment and management approach is described in Figure 2. Each country will be divided into zones and the monitoring, assessment, management and reporting of air quality will be undertaken in relation to these zones and to limit values, assessment thresholds and margins of tolerance to be set for listed pollutants. Zones where concentrations are considerably in excess of the limit value ('hot spots') will be allowed to exceed the limit value by a specified percentage, this percentage is termed the 'margin of tolerance' and is reduced annually such that by the attainment date the limit value applies everywhere.

Figure 2. Diagram of the limit value and margin of tolerance under the Air Quality Framework Directive.



In such areas specific action plans are required in order to bring the concentrations below the limit value by the attainment date. Details of these action plans are part of the reporting obligations related to the Framework directive. In other areas it is assumed that the benefits accruing from existing general air pollution control measures in the period up to the atainment date will be sufficient to reduce/mainatin concentrations below the limit value by that date. The extent of monitoring and assessment in any zone will be determined mainly by population size and the air quality status when the new approach comes into effect - monitoring, dispersion modelling, objective estimation and indicative measurement are the approprite assessment techniques. Alert thresholds will also apply for some of the pollutants, these will keep the general public informed of particular pollution incidences as they occur.

Annex I of the Air Quality Framework Directive lists atmospheric pollutants to be taken into consideration in the assessment and management of ambient air quality. With the adoption of the first Daughter Directive under the Air Quality Framework Directive on 24th September 1998, European Ministers agreed a common position on limit values for sulphur dioxide (SO_2), nitrogen dioxide and oxides of nitrogen (NO_x), particulate matter and lead (Pb). The Daughter Directive sets limit values and provides guidance on the ‘reference method’ to be used for the determination of pollutant concentrations in ambient air. The ‘reference method’ for each pollutant is specified such that each Member State will report concentrations which have been determined using the same analytical method. Indicative techniques are measurements using simple methods, or carried out for a restricted time. They are less accurate than continuous high quality measurement but can be used to explore air quality as a check where pollution levels are relatively low, and to supplement high quality measurement in other areas.

The volatile aromatic hydrocarbon benzene, listed under "other air pollutants" in Annex 1 is currently the subject of a proposed Daughter Directive. The proposed Directive will mark the first time the EU will have set an air quality standard for a carcinogen.

1.2 The "benzene" directive

Benzene is a ubiquitous chemical in ambient air and it arises mainly as a result of emissions from motor vehicle exhausts and through evaporation of petrol during vehicle refuelling (Perez-Ballesta and De Saeger, 1995; Swaen and Slangen, 1995).

The protection of human health forms a prominent role in setting a limit value for this carcinogenic agent. There is at present no EC ambient air quality limit value for benzene. Agreement on a recommendation for a limit value was not reached by the working group on benzene, which was made up of representatives from the European Environment Agency (EEA), Industry and Non-Governmental Organisations (NGO's). Dispute arises over the proposed limit value because there are no agreed exposure levels for carcinogens below which they can be classified as safe. The "benzene" directive will therefore have implications on future directives dealing with carcinogenic compounds such as polyaromatic hydrocarbons (PAH's). Given that the compound is a known human genotoxic carcinogen it was agreed that the principle of "as low as it is reasonably achievable" (ALARA) should be applied and that limit values for benzene should be reconsidered in due course to determine whether further progress was then necessary and practical.

The proposal for a limit value of $5\mu g/m^3$ as an annual mean to be met by 2010 was strongly supported by experts from ten Member States and NGOs. The view is that the Auto-Oil agreement of 29th June 1998, which limits the benzene content of petrol to 1% by 1st January 2000, along with separate actions needed to meet other environmental targets will enable a high rate of compliance with the proposed limit value. It is understood that industry as well as several more industrialised Member States were in favour of a less stringent limit value of 10 or $20\mu g/m^3$. There are no provisions in the proposed Daughter Directive to set an alert threshold value for benzene. The commission is to report by 2004 on the implementation of this Directive. Since many of the measures which would reduce benzene concentrations would also reduce concentrations of other air pollutants the report is to be presented as an integral part of an air quality strategy, designed to allow the community to review and propose air quality objectives (CEC, 1998).

According to the Commission there is a great deal of uncertainty in the database of information concerning benzene concentrations across the Community (CEC, 1998). It is therefore imperative that a ‘reference method' be adopted for the determination of ambient concentrations of benzene and measurement networks using indicative methods with comparable uncertainties be established. The UK is one country which has had a BTX monitoring network comprising 13 sites for several years including one at Belfast, Northern Ireland (AEA Tecnology, Internet, 1998). Hourly concentrations are measured using continuous cycling gas chromatographs (CCGC) and each site instrument requires regular maintainence and calibration which involves a substantial capital investment. Indicative techniques should allow greater sample numbers to be processed for less cost while maintaining a high level of certainty in the concentration measured. The results must be 'fit for purpose' for any indicative measurement technique. One such technique which may be used for determination of ambient concentrations of benzene is the diffusive sampling technique.

A diffusive sampler is a device that is capable of taking samples of gas or vapour from the atmosphere at a rate controlled by a physical process, such as diffusion through a static layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler (Brown and Saunders, 1987). Diffusive samplers have considerable advantages over other techniques which ultimately result in low operating costs and their ability to be used in remote areas without the need for power. This allows their use in monitoring networks in relatively high numbers over large areas. Also diffusive samplers give long-term averages which is consistent with the proposed European limit value which is set on a yearly basis.

In the current study the diffusive sampling technique is employed to monitor ambient air in the vicinity of three Petrol Service Stations for benzene, along with the other two aromatic compounds, toluene and xylene. These three compounds are collectively referred to as BTX. The ambient air in and around the forecourt of petrol service stations has previously been identified as a potential 'hot spot' with respect to elevated concentrations of benzene (Perez-Ballesta and De Saeger, 1995; Cram and Little, 1995).

The primary aim of this thesis is to use the diffusive sampling technique to measure potentially elevated concentrations of benzene in ambient air at specific locations in the vicinity of Petrol Service Stations.

The following objectives were established in order to accomplish this aim:

- The basic principles, advantages and limitations of diffusive sampling are described. Alternative methods for the determination of benzene concentrations in ambient air are listed.
- Available published data on benzene concentrations in ambient air generated using diffusive sampling is collated and discussed.
- A sampling campaign to measure benzene, toluene and xylene (BTX) in the vicinity of three petrol service stations was designed and undertaken using diffusive and active (pumped) sampling.
- BTX concentrations are reported for forecourt, forecourt perimeter, roadside and background sampling locations in the area around the three Petrol Service Stations.
- The results of this study are compared to any relevant publications and to the proposed limit value of the forthcoming 'benzene' Directive.
- Two different adsorbent materials are evaluated for the measurement of BTX in ambient air. The suitability of the two materials is discussed and results generated using the two are compared.

CHAPTER 2. Literature Review

2.1 Benzene

Benzene (CAS Registry Number 71-43-2) is a clear, colourless, highly flammable liquid with an aromatic odour and a density of 0.87g/cm^3 at room temperature. Benzene evaporates readily having a boiling point of 80°C and a vapour pressure of 9.95 kPa at 20°C. Benzene is moderately soluble in water and miscible with most organic solvents (Merck Index, 10th ed.,1983).

Benzene was discovered in 1825 by Michael Faraday, who isolated the compound from an oily condensate deposited from a gas used at that time for illumination. August Kekulé was the first to recognise that aromatic compounds all contain a six carbon unit which is retained through most chemical transformations and degradations (Figure 1). Benzene was eventually identified as being the parent compound of the aromatic series which includes toluene and xylene. As this group of compounds proved to be distinctive in ways other than their odours, the term aromatic began to take on a purely chemical connotation.

Benzene is a raw material used extensively as a solvent in the chemical and drug industry. It is used as a starting material and intermediate in the synthesis of numerous chemicals (such as styrene, cumene and cyclohexane). Benzene is also used in the manufacture of rubbers, detergents, explosives, pharmaceuticals and dyestuffs and it is also found in coal tar, petroleum naphtha and petrol.

2.1.1 Sources of Benzene in Ambient Air

Natural sources of benzene include emissions from volcanoes and forest fires. These sources are considered minor when compared to anthropogenic sources (Canadian Environmental Protection Act, 1993). All benzene observed at ground level in the northern hemisphere is likely to have resulted from human activities, in particular the use of petrol and oil (CEC, 1999).

The benzene content of petrol in Europe is currently 2% or less (Cummins, 1999) but in the past however, this percentage was as high as 5% (RIVM, 1988). Emissions of benzene to the atmosphere occur as a result of evaporative processes during vehicle refuelling and transport, and due to incomplete combustion in the engines of petrol driven vehicles. The main types of evaporative emissions associated with petrol vapour loss from vehicles are;

(i) diurnal emissions which may occur while a vehicle is parked and its fuel tank is heated by an increase in ambient temperature

(ii) 'hot soak' emissions occur following engine shutdown due to heat being transferred from the engine and exhaust system to the fuel

(iii) 'running loss' emissions occur where engines are used under extreme conditions, such as operating at low speeds using high volatility fuel at high ambient temperatures (Patterson and Henein, 1972).

It is estimated that 35% of the anthropogenic volatile organic compound (VOC) emissions are due to vehicle exhaust and evaporative losses (Watkins, 1991), but in urban areas the contribution to the VOC emissions from traffic may reach 60 - 80% of the total emissions (Perez-Ballesta and De Saeger, 1995). Within the EC, road transport accounts for 80-85% of the benzene emissions, this contribution is seen to vary considerably (from 38 to 93%) between the Member States (CEC, 1999). The National Institute for Public Health and the Environment, Netherlands estimated that in 1981 a total of 198,000 metric tonnes of benzene was emitted to the atmosphere in the European Community (RIVM, 1988) and of this total an estimated 85% (171,000 tonnes) was emitted by cars.

Two other significant pathways by which benzene and other VOC's can enter ambient air are (i) liquid fuel from petrol pump displacing vapours in cars fuel tank and (ii) the analogous scenario when petrol is delivered to a service stations underground tanks and vapour is displaced through a pressure vent. The latter situation has been addressed by the introduction of stage 1 controls under the EPA Act, 1992 (Control of Volatile Organic Compound Emissions resulting from Petrol Storage and Distribution) Regulations, 1997 (S.I. No. 374 of 1997) which give effect to the provisions of EC Directive 94/63/EC. The pathway of VOC emission described in (i) above has been addressed in Europe to some extent by the introduction of the push through seal in the neck of the cars fuel tank. This system does not, however, form a vapour seal and vapour emissions will persist as the liquid fuel displaces the vapour unless a carbon canister is fitted to the car to further prevent the emissions. Stage II controls use specially designed petrol dispensing nozzles to collect vapour displaced during refuelling and route it to the stations underground fuel storage tanks (Lave *et al*, 1990). This technology is still under development, however, its introduction would be expected to significantly reduce airborne concentrations of petrol vapours and harmful VOC's in the areas around petrol service stations.

In California, USA there has been a 49% decrease in airborne concentrations of benzene at seventeen monitoring stations across the state over the period 1990 to 1995. The reductions are attributed to fuel regulations that the California Air Resources Board (ARB) have put in place aimed specifically at reducing benzene and VOC emissions (Hammond, 1998). Regulations included limiting the volatility of petrol, increasing the amount of oxygenated compounds in the fuel (this has the effect of reducing the carbon monoxide emissions, however, it has the secondary effect of reducing VOC emissions) and specifically limiting the benzene content of petrol (Hammond, 1998).

In Europe a similar approach to cleaner-burning fuels is being taken through the Auto Oil Programme. As a result of the Auto-Oil conciliation agreement reached on the 29th June 1998, the European Council and the European Parliament have decided to limit the percentage of benzene in petrol to 1% in the year 2000 (CEC, 1998). This reduction would be expected to have a marked effect on benzene concentrations in ambient air. However, according to Swaen and Slangen, 1994 most of the benzene emitted from the automobile originates from combustion processes and is independent of the benzene content of fuel. Section 4.3 of the explanatory memorandum for the proposed 'benzene' directive also suggests that the major part of benzene emitted is produced by chemical reactions occurring during combustion of petrol in the engine.

2.1.4 Exposure to Benzene

The primary routes of potential human exposure to benzene are through inhalation and dermal contact (ATSDR, 1991). The potential for dermal contact with benzene for the majority of the population is small and therefore inhalation is the most significant route of entry of benzene into the human body, with approximately 50% of inhaled benzene being absorbed (WHO, 1996). The environmental levels of benzene in urban air normally range between 2 to 10μg/m^3 (Plant & Wright, 1996). In the World Health Organisation (WHO, 1996) guideline on benzene, an estimate of the daily adult intake of benzene was calculated as 100μg based on a 24-hour respiratory volume of 20m^3 at rest.

Tobacco smoke also contains benzene and a typical smoker inhales approximately 30μg of benzene per cigarette (WHO, 1996). Tobacco smoke may therefore account for a large proportion of the public's exposure to benzene. Elevated benzene concentrations of 22.2 and 10.8μg/m^3 have been reported in smokers ambient air and breath, respectively by Keith and Winegar (1993). Cigarette smoke may therefore represent a significant source of airborne benzene for a large proportion of the population.

There is no threshold below which effects can be assumed not to occur, however a precise estimate of the risks of benzene is difficult to establish. WHO in 1996 adopted as a guideline a unit risk of 6 x 10^{-6}, this means that 6 people in every million are at risk of contracting leukaemia when continually exposed to benzene at a concentration of 1μg/m^3 for a lifetime. It is derived by extrapolating data on worker exposure in the 1940's. Experts including representatives of WHO and the United States Environmental Protection Agency (USEPA) have since examined benzene and assigned a lowest plausible risk estimate as 5 x 10^{-8} (two orders of magnitude lower), however, they were unable to determine where in this range the "correct" risk estimate is. Translating the range of unit risks given above into an annual average concentration which equates to a lifetime risk of one in a million gives a range of concentrations of 0.2 to 20μg/m^3. WHO provide no recommendations as to what level of risk is tolerable (CEC, 1999).

The USEPA estimates that, if an individual were to breathe air containing benzene at a concentration of 0.1μg/m^3 over his or her entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical.

2.1.3 Benzene Toxicity

Benzene is a known human genotoxic carcinogen, classified by the International Association on the Risks of Cancer (IARC, 1987) as a class 1 carcinogen. The USEPA has classified benzene as a Group A compound which is defined as, '*known human carcinogen of medium carcinogenic hazard'*.

Acute (short-term) inhalation exposure to benzene may cause drowsiness, dizziness, headaches and unconsciousness in humans. Exposure to benzene liquid and vapour may irritate the skin, eyes and upper respiratory tract. Death may result from exposure to very high levels of benzene (CONCAWE, 1995).

Chronic (long-term) inhalation exposure has caused various disorders in the blood, including reduced numbers of red blood cells and aplastic anaemia in occupational environments. Toxicity to the humoral and cellular immune systems has also been recorded (WHO, 1996).

Menstrual disorders and a decreased size of ovaries have been observed in women occupationally exposed to high levels of benzene (ATSDR, 1991). Several occupational studies suggest that benzene may impair fertility in women exposed to high levels. Adverse effects on the foetus, including low birth weight, delayed bone formation and bone marrow damage have been observed where pregnant animals were exposed to benzene by inhalation (CONCAWE, 1995).

Increased incidence of leukaemia (cancer of the tissues that form white blood cells) has been observed in humans occupationally exposed to benzene (ATSDR, 1991).

Due to its carcinogenic effect on humans, benzene concentration levels in workplace air are strictly regulated, and its use as a solvent has therefore diminished in recent years. A limit value for benzene in workplace air was set in EC Directive 97/42/EC adopted on 27th June 1997 (CEC, 1997). In Ireland the National Authority for Occupational Safety and Health has set an Occupational Exposure Limit (OEL) of 16mg/m^3 (5 ppm) over an 8-hour reference period.

It is generally accepted that exposure to high concentrations of benzene induces leukaemia, what is not clear however is whether or not there is a threshold below which the agent will not be able to express its carcinogenic potential.

2.1.4 Fate of Benzene in the Atmosphere

The main environmental concern associated with elevated concentrations of VOC's in ambient air is the phenomenon of photochemical oxidant formation. Photochemical oxidants are compounds such as ozone, hydrogen peroxide and peroxyacyl nitrate (PAN) which are formed as a result of a complex series of reactions involving VOC's , NO_x and sunlight. The three aromatic compounds benzene, toluene and xylene have significant photochemical oxidant formation potential (EPA, 1997).

Benzene is moderately water soluble and is removed from the air by precipitation. Because of its short persistence in the atmosphere, its nonhalogenated nature, and its low absorption of infrared radiation of critical wavelengths, benzene is not associated with depletion of stratospheric ozone or with global warming (Canadian Environmental Protection Act, 1993)

2.2 Monitoring Benzene in Ambient Air

There are at present many approaches used to monitor levels of VOC's, including benzene, in ambient air. The conventional method of analysing ambient air for volatile organic compounds involves the collection of a representative sample using pumps to draw a known volume of air through liquid reagent impingers or an adsorbent bed, followed by determination by an analytical technique. The analytical instrumentation used in analysis of air samples for organic pollutants includes; gas chromatography/flame ionisation detector (GC/FID), Gas Chromatography/Mass Spectrometry (GC/MS), High Pressure Liquid Chromatography (HPLC), Fourier Transform Infra-Red Spectrophotometry (FTIR), UV/Vis Spectrophotometry (Perez-Ballesta *et al*, 1998*b* and 1998*c*).

There are some in-situ monitoring techniques which measure the concentration directly and in real time. These include the innovative techniques of Differential Optical Absorption Spectrometry (DOAS), Differential Absorption Light Detection and Ranging (LIDAR), Direct Mass Spectrum Analysis and the Open Path Spectrophotometer (OPSIS) system (Perez-Ballesta *et al*, 1998*b* and 1998*c*). These systems are expensive to purchase and to operate as they require routine maintenance and calibration to primary standards. This involves highly qualified personnel on a regular basis and cylinders of prepared standard (calibrant) and blank gases. Such gas standards are also very costly and may be valid for periods of 3 to 12 months only. These techniques also require power and a secure shelter in which the instrumentation is housed. Given the high costs involved, the potential for use of these direct measuring instruments in monitoring networks appears to be limited.

Diffusive (or Passive) sampling is another technique which can be used for monitoring ambient air concentrations of benzene and other VOC's. Having been introduced initially for the determination of air contaminants in occupational situations (Palmes and Gunnison, 1973), diffusive sampling of ambient air has gained great impetus over the past decade. Due to their similar chemical and physical properties, benzene is usually monitored in conjunction with two other aromatic hydrocarbons, toluene and xylene, and collectively referred to as BTX.

2.3 Diffusive Sampling

Palmes and Gunnison (1973) described a tube-type sampler for sulphur dioxide which based on molecular diffusion was capable of quantitative measurements of this gaseous pollutant. Though initially applied to SO_2 the potential of applying the sampling principle to any gaseous airborne contaminant was recognised. A diffusive sampler is a device that is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process, such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler (Brown & Saunders, 1987; CEN, 1998*a*). The development and use of diffusive samplers for the measurement of gas and vapour concentrations in air represents a major advance in environmental sampling. The elimination of the sampling pump removes sampler responsibilities as well as costly pump requirements including maintenance and calibration. Also as the pump represents a significant source of both random and systematic error, freedom from dependance on a sampling pump provides an opportunity to improve the overall uncertainty of the measured concentration (Harper & Purnell, 1987).

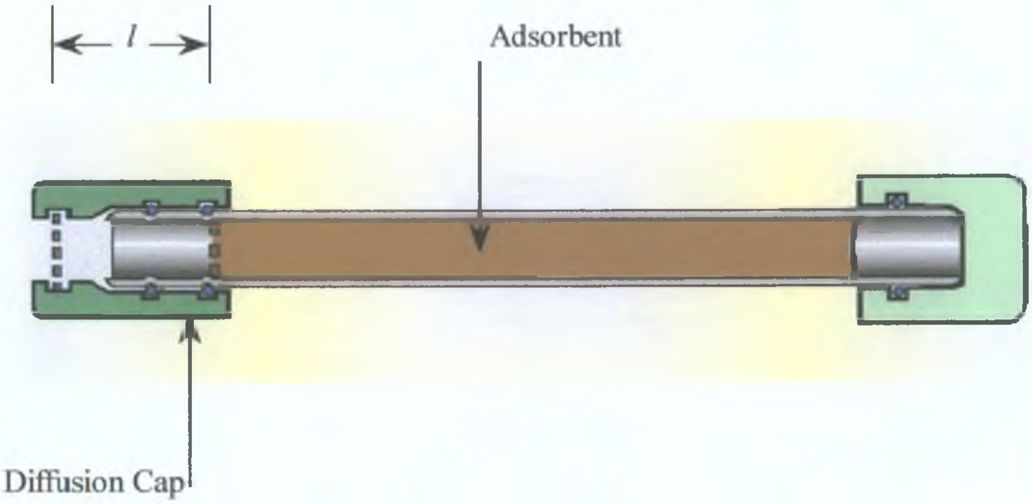
Diffusive sampling has been used for over twenty years in occupational hygiene to monitor personal exposure to harmful compounds in workplace air. The application of the technique to ambient air measurements is a more recent development (Brown, 1993). The advantages over the traditional methods are:

(i) involvement of unobtrusive equipment,
(ii) no consumable items are needed,
(iii) unattended operation during prolonged sampling periods,
(iv) no power requirements therefore suited to remote sampling locations, and
(v) no requirement for highly skilled operators.

As a result, low operating costs apply, allowing the use of diffusive samplers in monitoring networks in relatively high numbers. Moreover, they give long-term averages which will be consistent with the proposed European limit value which is to be set on a yearly basis.

In operating diffusive samplers molecules diffuse because of a concentration gradient through an intake opening with the cross sectional area, A, along a diffusion path length, l, to a sampling medium at the surface of which they are adsorbed (Figure 3).

Figure 3. Diagram of Perkin-Elmer tube-type diffusive sampler showing diffusion path length (l).



This process of diffusion is described by Fick's first law of diffusion:

$$\frac{dm_i}{dt} = D_i.\frac{A}{l}.dc_i \qquad (1a)$$

or

$$m_i = \frac{A.D_i.(c_{i1} - c_{i2}).t}{l} \qquad (1b)$$

where m_i = amount of substance in pg

t = exposure time in minutes

A = cross-sectional area of the sampler in cm^2

l = length of the diffusion path in cm

D_i = diffusion coefficient of the substance i in cm^2/min

c_i = concentration of the substance i in air in $\mu g/m^3$

c_{i1} = concentration of the substance i in ambient air being sampled in $\mu g/m^3$

c_{i2} = concentration of the substance i in air at sorbent surface in $\mu g/m^3$

The diffusive uptake rate is the rate at which the diffusive sampler collects a particular gas or vapour from the atmosphere, expressed in picograms per parts per billion per minute ($pg\ ppb^{-1}\ min^{-1}$) or cubic centimetres per minute ($cm^3\ min^{-1}$).

The uptake rate of the sampler with regard to the substance *i* is given by:

$$U_i = D_i.\frac{A}{l} \qquad (2a)$$

or

$$U_i = \frac{m_i}{c_i.t} \qquad (2b)$$

Although the uptake rate, U_i, has units of cubic centimetres per minute this is really a reduction of picograms per micrograms per cubic metre per minute, (pg (μg m^{-3})$^{-1}$ min^{-1}), and does not indicate a real volumetric flow of (analyte in) air (CEN, 1998*b*). Computer models and practical experiments on uptake rates in exposure chambers provide much of the current information on uptake rates (Brown, 1993).

The performance of a diffusive sampler depends critically on the selection and use of a sorbent or collection medium. The medium must have a high sorption efficiency for the pollutant of interest, i.e. the collection medium used must have physical characteristics to be capable of quantitatively trapping the analyte of interest. It is therefore desirable to select an adsorbent material with high sorption capacity and which results in a low vapour pressure of the analyte when adsorbed on the adsorbent material (CEN 1998*c*). The residual vapour pressure of the sampled compound at the sorbent surface will then approach zero, and the concentration of analyte *i*, at the sorbent surface (c_{i2}) will be negligible in comparison to the ambient concentration (c_{i1}), this is referred to as 'zero sink' condition. Under these conditions the observed uptake rate will be close to its ideal steady-state value, which can be calculated from the geometry of the sampler and the diffusion coefficient of the analyte in air. Assuming the concentration at the intake opening is equal to analyte (i) concentration in the ambient air outside the diffusive sampler (c_i), and the concentration at the surface of the sampling medium is zero ("zero sink" - condition), then the adsorbed amount of substance is proportional to the substance dose (product of concentration c_i and exposure time t).

$$m_i = D_i.\frac{A}{l}.c_i.t \qquad (3a)$$

or

$$m_i = \frac{A.D_i.c_i.t}{l} \qquad (3b)$$

The German publication LUA-Materialien No. 46, Essen (1998) and Brown (1998) state that both laboratory experiments and empirically determined uptake rates were found to depend on the dose, and the substance mass adsorbed by the sampler in relation to the dose is well described by power functions.

The issue of sampler response time was addressed by Bartley *et al* (1983) who observed that the sampling of fluctuating concentrations could be associated with an error increasing without limit, approaching infinity in the case of dimensionless peaks. In practice though the error averages around zero if the sampling period is long enough. These observations were based on occupational hygiene use of diffusive samplers where

Short Term Exposure Level (STEL) measurements are made and large fluctuations in pollutant concentrations can occur. In the case of environmental use of diffusive samplers the error can be assumed to be zero as exposure time / sampling period is generally one to four weeks and the ambient air concentrations of the pollutants of interest would not be expected to vary to the same extent as the occupational situation. (Brown, 1993).

2.3.1 Environmental Factors Affecting Diffusive Sampler Performance

Several environmental factors can affect the performance of the diffusive sampler, these include ambient temperature and pressure, humidity, precipitation and air velocity (wind speed). Of these perhaps the most significant are wind speed and temperature.

Ambient air velocity may influence the effective diffusion path length of a tube-type diffusive sampler by causing turbulence in the static air layer within the tube. The reduction of the effective diffusive path length has the effect of increasing the effective uptake rate. The relationship between the reduction in diffusive path length (and effect on sampler uptake rate) and wind speed has been found to be highly variable (Gair and Penkett, 1995). Tube-type samplers require a minimum face velocity of 0.001m/sec, enabling their use in almost any conceivable situation (Brown *et al*, 1981). In practice, diffusive samplers have been used successfully in wind speeds of up to 5 m/sec (Perez-Ballesta and De Saeger, 1995). The draft ISO method ISO/CD 16017-2 (1998) states that Perkin-Elmer tube-type diffusive samplers may be used in situations where average wind speeds of up to 10m/sec prevail.

The temperature of the ambient air also affects the uptake rate as the diffusion coefficient of the analyte of interest is temperature dependent. This effect is most pronounced for the most volatile analyte for example in the case of benzene on chromosorb 106 in the temperature range -4 to +22°C this amounts to -2.5% per degree, toluene exhibits a dependence of -1.4% per degree and xylene approximately -1.0% per degree (LUA-Materialien No. 46, 1998). The lowering of the uptake rate is a manifestation of a phenomenon known as 'back diffusion'. 'Back diffusion' is the loss of analyte from the adsorbent material to the air above the surface and is a result of a system in equilibrium. The extent of 'back diffusion' will depend on the vapour pressure of the analyte concerned and the sorption efficiency of the adsorbent material used (CEN, 1998*c*).

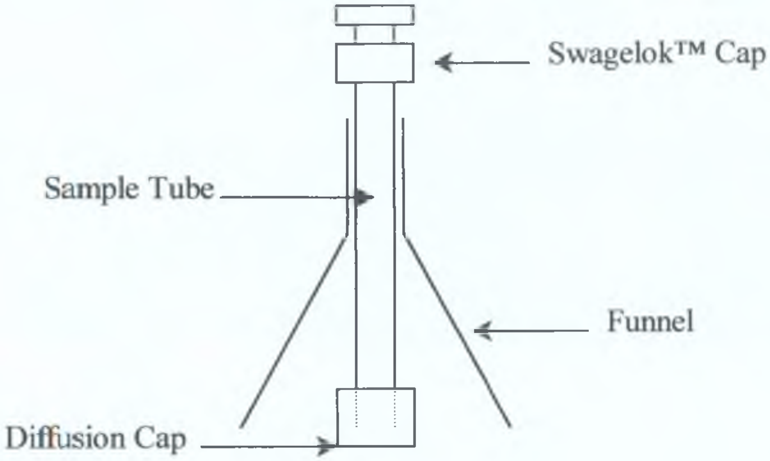
The use of diffusive samplers using a relatively weak adsorbent material such as chromosorb 106 in a tube-type sampler to monitor for benzene in ambient air has essentially been limited to ambient temperatures in the range 0°C (Hafkenscheid & Mowrer, 1996) to 30°C (Perez-Perez-Ballestaand De Saeger, 1995). The technique can be applied at temperatures outside this range but account must be taken of the dependence of the uptake rate on ambient temperatures.

At high temperatures the back diffusion effect is more pronounced than at lower temperatures so that the uptake rate seemingly drops at higher temperatures. For diffusive sampling of benzene on chromosorb 106 the loss of analyte due to back diffusion has been estimated at approximately 20%, however, for higher boiling compounds the effect is less significant (about 8% in the case of toluene and 2% in the case of xylene) (LUA-Materialien No. 46, Essen, 1998).

The issue of loss of analyte through 'back diffusion' was addressed by Hafkenscheid (1998) in a study of the feasibility of applying bi-layer diffusive samplers for ambient air measurements. In the study the effective uptake rates for a range of VOC's (including benzene) were measured for four different Perkin-Elmer type samplers packed with (i) Tenax GR, (ii) bi-layer 20mg Tenax GR followed by 180mg Carbopack B, (iii) bi-layer 30mg Tenax GR followed by 170mg Carbopack B and (iv) 250mg Carbopack B. Carbopack B is a stronger adsorbent material i.e. has a higher sorption capacity. The effect observed was an effective increase in the uptake rates for the bi-layer samplers. The increase indicates that the effect of back diffusion is compensated for by the migration of analyte into the stronger adsorbent.

Diffusive samplers must be protected from precipitation as rain or melted snow can block the sampling surfaces, particularly, of tube samplers oriented downwards (which is the usual position to avoid the ingress of particulate matter) (CEN, 1998). Provision of shelter for the Perkin-Elmer tube-type sampler is often achieved by the use of an adapted funnel inverted to provide protection while maintaining ambient air movement past the diffusion cap (Figure 4).

Figure 4. Perkin-Elmer ATD sampling tube fitted with protective weather hood.



2.4 Methods of Analysing Diffusive Samples for VOC's

Analysis of the collected sample is usually performed by one of two desorption techniques followed by separation and detection in a chromatographic system. The two methods of desorption are

(i) solvent desorption, and

(ii) thermal desorption.

The analytical technique of thermal desorption as the name implies uses heat to desorb the analyte from the adsorbent material, before being cryofocused and introduced to the gas chromatograph. Solvent desorption uses a strong solvent (such as carbon disulphide, CS_2) or a cocktail of solvents to extract the analyte from the adsorbent. Solvent desorption/gas chromatography is the technique on which the bulk of U.S. National Institute for

Occupational Safety and Health (NIOSH) methods for VOC measurements in workplace air is based (NIOSH, 1994). The extraction of analyte from the adsorbent material is sometimes aided by the use of an ultrasonic bath for a specified period. This type of desorption is essentially solvent extraction of the adsorbent material and represents quite severe or aggressive desorption conditions. As a consequence very strong adsorbent materials to which the analyte is strongly held can be used for solvent desorption.

In thermal desorption, adsorption must be readily reversible by merely heating the sorbent in a flow of heated carrier gas this is a relatively moderate approach to desorption when compared to the broadly applied solvent desorption. If the sorbent used has a high sorption efficiency (i.e. a strong adsorbent) the desorption may not be quantitative. Therefore, adsorbent materials used for thermal desorption tend to be relatively weak for example Chromosorb 106 and carbograph for the compounds benzene, toluene and xylene. Where a weak sorbent is used the phenomenon of "back diffusion" is sometimes observed and c_{i2} (in equation 1b) becomes non-zero, thus the uptake rate will decrease with exposure time.

The sensitivity of the thermal desorption technique will be better than solvent desorption as the introduction of a solvent represents a dilution of sample. In thermal desorption the analyte is swept off the sample tube into a cold trap where the analyte is cryofocused to improve chromatography and sensitivity, no dilution takes place. The total contents of the sample tube if required may be introduced to the chromatographic system. However, instrumental sensitivity is such that a split is generally introduced to allow only a representative percentage (e.g. 1%) of the contents of the sample tube reach the analytical column (ISO, 1998). Large volume injectors fitted to GC systems allow volumes of up to 1 ml to be injected into the GC, these have the effect of lowering the detection limits and enables solvent desorption to match the performance of thermal desorption for detection limits. The main disadvantage of thermal desorption is that only one analysis of the sample is possible whereas in solvent desorption multiple injections of the desorbed solution are possible.

The Perkin-Elmer ATD-400 is the most commonly used instrument for thermal desorption, it is superior to its predecessor the ATD-50 in many respects. Perkin-Elmer have had a patent on automated thermal desorption instruments since the development of the first instrument some 20 years ago.

2.5 Diffusive Sampling of BTX in Ambient Air – Previous Studies

The diffusive sampling technique has been used in a number of studies to assess ambient air concentrations of benzene and other VOC's (Perez-Ballesta *et al*, 1998*a*; Hafkenscheid and Mowrer, 1996; Mowrer *et al*, 1996; Plant and Wright, 1996, 1997 and 1998 and EPA, 1997). Two studies have used diffusive sampling to determine the concentrations of VOC's in ambient air at locations around Petrol Service Stations (Perez-Ballesta and De Saeger, 1995 and Cram and Little, 1995). Several other studies have compared the diffusive sampling technique with other more widely accepted techniques (Boyle and Bullen, 1998; Perez-Ballesta *et al*, 1998*b*).

Background urban ambient air concentrations of BTX in the agglomeration of Bologna were determined using Perkin-Elmer diffusive sampling tubes packed with Carbopack-B (Perez-Ballesta *et al*, 1998*a*). Sampling was confined to urban background areas away from any VOC sources such as traffic. Average concentrations of 2.3, 6.8 and 3.7µg/m^3, for BTX respectively were reported for the spring-summer period and 3.8, 13.3 and 8.2µg/m^3, respectively for the winter-spring period.

In 1997 a report which included the results of a ten month survey on baseline concentrations of VOC's in Dublin city was published by the Irish Environmental Protection Agency (EPA). Benzene, toluene and xylene (BTX) were monitored using tube-type diffusive samplers packed with Tenax. Sampling was carried out over 13 measurement periods of 2 - 3 weeks at 20 sites in the Dublin city area, most of which were located in areas where the high concentrations of pollutants were expected. The results of the measurement campaign (thirteen 2 - 3 week periods) give average benzene, toluene, p-xylene and o & m-xylene concentrations of 4.97, 11.70, 11.84 and 14.88µg/m^3, respectively. The ratio of toluene to benzene concentrations over the entire survey was reported as 2.35 which is consistent with expected results (Plant and Wright, 1998). Diffusive sampling tubes used in the monitoring campaign were similar in design to the commercially available Perkin-Elmer ATD tube for which there exists a wealth of data. The samplers differed fundamentally, however, in their size and hence geometry from the widely used PE ATD tubes.

Ambient air concentrations of benzene and other traffic related VOC's were determined using diffusive sampling tubes packed with a range of different adsorbent materials at urban and rural locations in Sweden (Hafkenscheid and Mowrer, 1996). Mean background BTX concentrations reported for the ambient urban air was 4.3, 9.6 and 9.1µg/m^3, respectively.

Mowrer *et al* (1996) reported ambient air concentrations of benzene in 30 Swedish cities measured using diffusive sampling tubes packed with Tenax. The results reported over the period of October 1994 to March 1995 ranged from 2.4 to 6.2µg/m^3.

The Health and Safety Laboratory (HSL), Sheffield, UK have co-ordinated local, national and worldwide diffusive monitoring surveys for BTX (Plant and Wright, 1996, 1997 & 1998). In the world survey Perkin-Elmer tube type diffusive samplers packed with

Chromosorb 106 and Carbograph TD-1 were sent by post to volunteers in 17 countries along with instructions on the operation of the device. Benzene concentrations in the range 1 to 3 µg/m^3 were reported along with toluene and m-xylene concentrations of 1 to 23 µg/m^3 and 1 to 9 respectively. The ratios of B:T:X were recorded as an approximate average ranging from 1 : 2 : 1.5 to 1 : 8 : 3. This survey concludes that diffusive samplers can be transported and used by personnel unfamiliar with the operating procedure.

BTX concentrations were measured in the vicinity of Petrol Service Stations in Brussels and Murcia using diffusive Perkin-Elmer tubes packed with Chromosorb 106 (Perez-Ballesta and De Saeger, 1995). Elevated BTX concentrations up to fifteen times higher than the background levels measured were recorded for the stations studied.

In a similar study conducted in Middlesborough, Cram and Little (1995) used Perkin-Elmer tube-type samplers packed with Tenax to measured the levels of benzene at locations around two Petrol Service Stations. Measured benzene concentrations were found to be in the rank order expected, with highest mean levels at the forecourt pumps (12.9ppb - 42.1µg/m^3) and the lowest at background locations (1.6ppb - 5.2µg/m^3) with roadside and forecourt perimeter levels midway between (6.8ppb - 22.2µg/m^3 and 7.8ppb - 25.4µg/m^3, respectively).

Background atmospheric benzene measurements using diffusive samplers and an Automatic Urban Network (AUN) pumped GC analyser have been compared over a ten month period by Boyle and Bullen, (1998). Benzene was monitored simultaneously using a pumped GC analyser and Perkin-Elmer diffusive sampling tube packed with Chromosorb 106. A pumped GC analyser typically preconcentrates sample air for 10 to 60 minutes before analysing by chromatographic techniques, output data would usually consist of hourly average values. The diffusive samplers were exposed for consecutive 14 day periods. No information is provided on the protection of samplers from precipitation or the height at which samplers were exposed.

The results show good agreement between the annual averages and the standard deviations for both sets of data. The average benzene concentrations measured over the ten months were 0.61 ppb (2.0 $\mu g/m^3$) for the AUN and 0.55 ppb (1.8 $\mu g/m^3$) for the diffusive samplers. The percentage relative standard deviation (%RSD) for both sets of measurements was 40%, however data from the AUN provided 82% time coverage as compared with 100% for the diffusive samplers.

A study comparing different measurement techniques for the measurement of VOC's in ambient air (Perez-Ballesta *et al*, 1998*b*) included an assessment of diffusive samplers packed with Chromosorb 106, Carbopack-B and Tenax. The results generated using the diffusive samplers packed with Chromosorb 106 and Carbopack-B were comparable to the Continuous Cycling Gas Chromatograph (CCGC). The results of the diffusive sampers packed with Tenax showed 'an erratic behaviour'.

CHAPTER 3. Materials and Methods

Ambient air in and around three Petrol Service Stations was monitored diffusively for the three aromatic hydrocarbons; benzene, toluene and xylene (BTX). Sampling was performed using Perkin-Elmer tube-type diffusive samplers packed with Chromosorb 106 and Tenax. Active (pumped) sampling was also performed at one station using air sampling pumps and Perkin-Elmer tubes packed with Chromosorb 106. Analysis of samples was carried out by thermal desorption followed by gas chromatography/mass spectrometry (GC/MS). Diffusive uptake rates used for the three volatile aromatic hydrocarbons on Chromosorb 106 and Tenax were taken from the literature and are given in Table 3.

3.1 Characteristics of the Petrol Stations Monitored

Three Petrol Stations (A, B and C, Appendix 1) were considered for the purpose of this study. Petrol station A, located 750m north-east of Naas town centre on a moderately busy road close to several large residential housing estates, was characterised by little open space comprising tall trees opposite (west), a tall wall to the north and residential housing to the east and west. Petrol station B, located 500m south-west of the town centre on a quiet road close to a small residential housing estate. This site is bordered by residential housing to the south, a small car-park to the north and open spaces east and west of the site. At Station B no suitable locations were available for forecourt perimeter monitoring, also the forecourt perimeter was not clearly defined. Petrol station C is located 200m east of the town centre immediately adjacent to a heavily trafficked road. This site is surrounded by commercial properties to the north and west, a large supermarket car park immediately south and a busy road junction to the east.

Petrol Service Station A recently renovated its underground storage tanks and a petrol vapour recovery system was installed in order to comply with the sixth schedule of Statutory Instrument No. 374 of 1997 on the control of VOC emissions from petrol storage and distribution. Stations B and C were not fitted with such a recovery system. However, vent tubes were used to discharge the petrol vapours above the forecourt canopy at a height of approximately 6m. The numbers and types of fuel pumps at each station are presented in Table 1.

Table 1. Types of fuel and number of pumps.

	Petrol		**Diesel**
Petrol Station	**Unleaded**	**Leaded**	
A	8	4	2
B	1	1	2
C	8	4	4

3.2. Instrumentation and Apparatus

Diffusive sampling tubes used were purchased commercially, prepacked, conditioned and uniquely numbered from Supelco Ltd (catalogue number 2-5056 for Chromosorb 106 tubes and catalogue number 2-5055 for Tenax). Brass Swagelok™ end caps with Teflon™ ferrules were used to seal tubes prior to and after sampling. The sample tubes have the dimensions of 6.4mm Outer Diameter (O.D.) and 89mm length, the Internal Diameter (I.D.) is 5mm. For diffusive sampling a diffusion cap is used, the cap is a mesh which ensures the sampling tube does not become blocked and the diffusive path length is 15mm with the diffusion cap in place (Figure 3).

Chromosorb 106 is a synthetic cross-linked porous polymer based on polystyrene-divinylbenzene. It is non-polar and suitable for trapping VOC's in the approximate boiling range 50 to 200°C (ISO, 1998 DIS 16017-1). Chromosorb™ is a trademark of Manville Corp., USA. Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide. It is used both as a packing material for chromatography columns and for trapping VOC's with boiling points of 100°C and higher (ISO, 1998 DIS 16017-1). Tenax™ is a trademark of Enka Research Institute, NV, NL.

Sample tubes were desorbed using a Perkin-Elmer Automated Thermal Desorption System (ATD-400) into a Varian Saturn 4D Gas chromatography/mass spectrometry (GC/MS) system. The analytical column used was a special 'low bleed' capillary column, Chrompack CP-Sil 5 CB-MS 50m x 0.32mm ID 1.2μm phase.

3.3 Sampling Strategy

Ambient air concentrations of BTX were measured around three Petrol Service Stations using diffusive sampling tubes packed with Chromosorb 106. At one station (Station B) two different adsorbent materials were used and compared for diffusive sampling. Active (pumped) air sampling was performed at Station C using adsorbent tubes and sampling pumps. This allows a grab sample for a period of elevated BTX concentrations to be quantified and compared to the mean weekly values obtained by diffusive sampling.

3.3.1 Diffusive Sampling

Unleaded petrol contains between 35 - 40% aromatic hydrocarbons (Perez-Ballesta and De Saeger, 1995), and the composition of fuel vapour is directly related to the fuel’s liquid composition. Due to their toxic properties and their presence in fuels at significant levels, BTX measurements are a useful tracer of total VOC's emitted from petrol stations.

BTX measurements were performed at four sampling locations :

(i) sub-urban background
(ii) roadside
(iii) forecourt perimeter
(iv) forecourt

Sample tubes were conditioned at 250°C for 30 minutes prior to use. Diffusive sampling tubes were exposed with one Swagelok™ fitting in place and a diffusion cap in place on the appropriate end of the sampling tube (marked with two grooves). The diffusion cap is essentially a mesh cover which allows diffusion to occur while preventing insects etc. entering and thus blocking the sample tube. Diffusive samplers were fixed at a height of approximately 2 to 3 metres above ground and were protected from precipitation by means of an adapted funnel inverted and fitted over the sampler allowing free movement of air over the sampler inlet. Four consecutive sampling periods of one week were established for each Petrol Service Station (Table 2). A control/blank sample tube was transported with each weeks samples and exposed for the duration of the sampling period with both Swagelok™ fittings in place.

Table 2 . Sampling periods during the monitoring campaign.

Petrol Station	Season / Period	From	To
A	Autumn - Week 1	18/11/98	25/11/98
A	Autumn - Week 2	25/11/98	2/12/98
A	Autumn - Week 3	2/12/98	11/12/98
A	Autumn - Week 4	11/12/98	21/12/98
B & C	Winter - Week 1	20/1/99	27/1/99
B & C	Winter - Week 2	27/1/99	3/2/99
B & C	Winter - Week 3	3/2/99	10/2/99
B & C	Winter - Week 4	10/2/99	22/2/99

Diffusive samplers were collected at the end of each sampling period, recapped with the brass Swagelok™ end caps and stored until analysis. Samples were analysed in two batches station A and then stations B and C together. Once collected this type of sample tube sealed with brass Swagelok™ end caps fitted with Teflon™ ferrules has been found to be stable for over two years (Verkoelen and Nielen, 1988).

Diffusive sampling uptake rates for BTX on Perkin-Elmer tubes packed with Chromosorb 106 are taken from ISO (1998) where uptake rates were validated at environmental levels over different exposure periods. Uptake rates for Tenax packed Perkin-Elmer tubes are taken from the Method for the Determination of Hazardous Substances No. 80 (Health and Safety Executive, 1995).

Table 3. Diffusive uptake rates for BTX for the Perkin-Elmer diffusive sampler.

	Chromosorb 106	**Tenax**
benzene	0.48 cm^3 min^{-1}	0.41 cm^3 min^{-1}
toluene	0.54 cm^3 min^{-1}	0.44 cm^3 min^{-1}
xylene	0.55 cm^3 min^{-1}	0.42 cm^3 min^{-1}

3.3.2 Active (Pumped) Sampling

In addition to diffusive sampling, active (pumped) samples were taken at petrol station C at various positions in and around the forecourt area on one afternoon during 'normal' operation. Pumped samples were collected using intrinsically safe calibrated SKC sampling pumps to draw a known volume of sample air through a Perkin-Elmer ATD tube packed with Chromosorb 106 (Table 4). Tubes used for active sampling were conditioned and sealed in the same manner as for diffusive sampling.

Table 4. Volumes of air sampled during active sampling of petrol station C.

Sampling Location	Sample Volume (l)
Forecourt Pumps A	12.2
Forecourt Pumps B	12.6
Forecourt at Shop Door	9.9
Forecourt 10m Downwind of Pumps	10.2
Roadside	11.1
Perimeter of Forecourt Downwind	11.3
Perimeter of Forecourt Upwind	11.1

In both active and diffusive sampling the analytes are adsorbed on the adsorbent, then desorbed and quantified by gas chromatography/mass spectrometry. In active sampling, the air sample is drawn through the adsorbent by means of a pump while in diffusive sampling, the analytes reach the adsorbent by molecular diffusion in accordance with Fick's first law of diffusion.

3.4 Calibration of Analytical System

Calibration standards for each of the three analytes were prepared by spiking conditioned ATD tubes with gravimetric standards of the three compounds in methanol. A conventional gas chromatographic injection port with the back modified to fit the ATD tube was used (Appendix 2). Injection of standards onto tubes was performed using a calibrated syringe to deliver 3µl of standard into the system with a tube packed with Chromosorb 106 in place. After injecting, the tube was purged with zero grade nitrogen (N_2) for 3 minutes at a flow rate 100ml/min. This permits the volatile methanol which is unretained to be swept through the tube leaving the compounds of interest trapped on the adsorbent material. Calibration curves (Appendix 4) were prepared to cover the range of 1 to 100ng/tube for benzene and 1 to 300ng/tube for toluene and xylene. Total xylene (sum of meta, ortho and para isomers) was quantified relative to the meta isomer. These weights correspond to airborne concentration ranges of 0.2 to 19µg/m^3 (benzene) and 0.2 to 60µg/m^3 (toluene and xylene) in sample air based on a seven day exposure period.

The GC/MS system was 'tuned' using United States Environmental Protection Agency (USEPA) recommended criteria for tune compound 4-bromofluorobenzene (BFB) each day the system was in use (Appendix 5).

3.4.1 Method Sensitivity

The Method Detection Limit (MDL) using the analytical conditions detailed above is 1ng/sample tube for each of the three aromatic hydrocarbons. This equates to 0.2μg/m^3 for a one week sampling period for each analyte in ambient air.

3.5 Sample Analysis

Sample tubes were desorbed using a Perkin-Elmer Automated Thermal Desorption System (ATD-400) using the following conditions. Sorbent tubes were desorbed for 5 minutes at a temperature of 220°C to a Tenax cold trap at a temperature of –30°C. Once desorption was complete the cold trap temperature was raised rapidly to 250°C. Analysis of samples (separation and detection of analytes) was performed using a Varian Saturn 4D Gas chromatography/mass spectrometry (GC/MS) system.

The analytical column used was a special ‘low bleed’ capillary column, Chrompack CP-Sil 5 CB-MS 50m x 0.32mm ID 1.2μm phase. This capillary column was specifically designed for low level determinations using GC / MS. The stationary phase of the capillary column is chemically bonded and non-polar. The column was run at an initial temperature of 50°C for 4 min then the temperature was ramped up to 260°C and held there for 2 minutes. Examples of standard and sample chromatograms are given in Appendix 3.

CHAPTER 4 Experimental Results

4.1 Diffusive Sampling Results

4.1.1 Petrol Service Station A

The airborne concentrations of benzene, toluene and xylene (BTX) measured during the various diffusive sampling periods of the campaign for Petrol Service Station A are shown in Tables 4 - 7. The lowest airborne concentrations of the three aromatic compounds were detected at the background sampling location and roadside with the highest concentrations occurring at forecourt pumps 1 (pumps closest to shop). The levels measured at the forecourt perimeters were approximately midway between the background and forecourt pumps concentrations.

Benzene concentrations were typically 4 to 14 times higher in the forecourt area of the petrol station than at background and roadside sampling locations. The highest benzene concentration measured was 16.6μg/m^3 at forecourt pumps 1 during the second sampling period. Toluene and xylene concentrations were found to be 10 to 30 times higher in the forecourt area of the petrol station than at background and roadside sampling locations. Mean forecourt concentrations for BTX over the measurement campaign were 8.4, 17.0 and 14.5μg/m^3, respectively. The ratios of BTX concentrations in the vicinity of petrol station A ranged between 1 : 2 : 1.5 to 1 : 3 : 5.

Table 5. Weekly BTX concentrations measured at Petrol Service Station A during the sampling period 18/11/98 to 25/11/98.

Sampling Location	Concentration $\mu g/m^3$		
	benzene	**toluene**	**xylene**
Baseline/Background	1.3	2.2	3.5
Forecourt Boundary 1	1.8	4.1	5.7
Forecourt Pumps 1	7.5	18.3	16.2
Forecourt Pumps 2	4.7	12.3	12.5
Forecourt Boundary 2	4.4	9.1	7.2

Table 6. Weekly BTX concentrations measured at Petrol Service Station A during the sampling period 25/11/98 to 2/12/98.

Sampling Location	Concentration $\mu g/m^3$		
	benzene	**toluene**	**xylene**
Baseline/Background	0.5	0.7	2.6
Forecourt Boundary 1	3.8	7.9	8.5
Forecourt Pumps 1	16.6	29.7	21.6
Forecourt Pumps 2	10.0	19.2	17.0
Forecourt Boundary 2	1.3	4.1	5.9
Roadside	1.1	3.2	5.4

Table 7. Weekly BTX concentrations measured at Petrol Service Station A during the sampling period 2/12/98 to 11/12/98.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	0.3	0.6	2.1
Forecourt Boundary 1	1.2	3.4	4.9
Forecourt Pumps 1	6.7	16.1	14.0
Forecourt Pumps 2	6.4	13.7	12.6
Forecourt Boundary 2	5.0	8.8	6.4
Roadside	1.4	4.0	5.7

Table 8. Weekly BTX concentrations measured at Petrol Service Station A during the sampling period 11/12/98 to 21/12/98.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	0.6	1.0	2.3
Forecourt Boundary 1	3.0	5.3	5.4
Forecourt Pumps 1	10.6	19.3	14.8
Forecourt Pumps 2	4.4	9.7	9.4
Forecourt Boundary 2	1.4	3.2	3.8
Roadside	1.4	3.4	4.7

4.1.2 Petrol Service Station B

Concentrations of BTX measured during the different sampling periods of the campaign for Petrol Service Station B are shown in Tables 8 - 11. Perkin-Elmer ATD tube-type samplers packed with two different adsorbent materials, Chromosorb 106 and Tenax, were employed in the monitoring campaign for Station B. Chromosorb 106 is recommended over Tenax as an adsorbent material for monitoring benzene in air (Brown, 1995 and ISO, 1998) and results are presented for both adsorbent materials in Tables 8 - 11. The lowest airborne concentrations for the three aromatic compounds were detected at the background sampling location with the highest concentrations measured at forecourt pumps. The levels measured at roadside locations were found to be about midway between the background and forecourt pumps concentrations. No monitoring was performed at forecourt perimeter locations due to the fact that the forecourt area was not clearly defined and due to the absence of suitable sampling locations.

Benzene concentrations are generally 4 to 10 times higher in the forecourt area of the petrol station than the background sampling location. The highest benzene concentration of 10.0µg/m^3 was measured at forecourt pumps using Tenax during the second sampling period. Toluene and xylene concentrations were 5 to 20 times higher in the forecourt area of the petrol station than the background sampling location. Mean forecourt concentrations of BTX at station B over the campaign were 6.1, 11.1 and 8.5µg/m^3, respectively. Ratios of BTX concentrations were found to be approximately 1 : 2 : 2 to 1 : 3 : 3.

Table 9. Weekly BTX concentrations measured at Petrol Service Station B during the sampling period 20/1/99 to 27/1/99.

Sampling Location	**Concentration μg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background C106	1.3	0.3	0.4
Baseline/Background Tenax	0.6	2.9	1.7
Forecourt Pumps C106	5.4	8.0	6.2
Forecourt Pumps Tenax	5.3	10.5	8.7
Roadside Upwind C106	1.1	0.3	0.3
Roadside Upwind Tenax	0.8	0.7	1.0
Roadside Downwind C106	1.8	1.1	1.0
Roadside Downwind Tenax	1.5	2.0	2.2

Table 10. Weekly BTX concentrations measured at Petrol Service Station B during the sampling period 27/1/99 to 3/2/99.

Sampling Location	**Concentration μg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background C106	0.8	0.2	0.5
Baseline/Background Tenax	0.7	0.9	1.2
Forecourt Pumps C106	9.2	17.2	11.9
Forecourt Pumps Tenax	10.0	23.3	17.9
Roadside Upwind C106	S*	S*	S*
Roadside Upwind Tenax	S*	S*	S*
Roadside Downwind C106	2.8	3.4	2.6
Roadside Downwind Tenax	2.5	4.6	3.9

S* = Samples stolen/vandalised.

Table 11. Weekly BTX concentrations measured at Petrol Service Station B during the sampling period 3/2/99 to 10/2/99.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background C106	1.4	0.8	0.8
Baseline/Background Tenax	0.9	1.0	1.0
Forecourt Pumps C106	4.4	5.5	3.7
Forecourt Pumps Tenax	5.1	5.3	5.6
Roadside Upwind C106	3.1	4.8	4.8
Roadside Upwind Tenax	S*	S*	S*
Roadside Downwind C106	2.0	1.7	1.5
Roadside Downwind Tenax	2.0	2.8	2.6

S* = Samples stolen/vandalised.

Table 12. Weekly BTX concentrations measured at Petrol Service Station B during the sampling period 10/2/99 to 22/2/99.

Sampling Location	**Concentration µg/m³**		
	benzene	**toluene**	**xylene**
Baseline/Background C106	1.0	1.2	0.9
Baseline/Background Tenax	0.7	1.0	1.2
Forecourt Pumps C106	4.9	8.3	6.0
Forecourt Pumps Tenax	4.7	11.1	8.2
Roadside Upwind C106	1.9	3.5	4.0
Roadside Upwind Tenax	1.7	3.9	5.5
Roadside Downwind C106	1.5	2.0	2.0
Roadside Downwind Tenax	1.4	2.6	2.7

4.1.3 Petrol Service Station C

Tables 12 to 15 present the airborne concentrations of BTX - in $\mu g/m^3$ - measured during the different sampling periods of the campaign for Petrol Service Station C. The rank order of BTX concentrations observed showed that the lowest airborne concentrations for the three aromatic compounds were detected at the background sampling location with the highest concentrations occurring at forecourt pumps. The levels measured at forecourt perimeter and roadside locations were found to be midway between the background and forecourt pumps concentrations.

Benzene concentrations were typically 5 to 9 times higher in the forecourt area of the petrol station than the background sampling location. The highest benzene concentration measured was $10.4\mu g/m^3$ at forecourt pumps during the second sampling period. Toluene and xylene concentrations were found to be 10 to 20 times higher in the forecourt area of the petrol station than the background sampling location. Mean forecourt concentrations of BTX at station C over the measurement campaign were 7.4, 12.7 and $9.2\mu g/m^3$, respectively. BTX ratios were calculated as approximately 1 : 2 : 1.8.

Table 13. Weekly BTX concentrations measured at Petrol Service Station C during the sampling period 20/1/99 to 27/1/99.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	1.3	0.3	0.4
Forecourt Pumps 1	6.7	9.9	7.0
Forecourt Boundary 1	5.8	9.1	7.2
Roadside	3.2	4.9	4.4

Table 14. Weekly BTX concentrations measured at Petrol Service Station C during the sampling period 27/1/99 to 3/2/99.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	0.8	0.2	0.5
Forecourt Pumps 1	10.4	20.0	13.7
Forecourt Pumps 2	7.9	16.1	11.2
Forecourt Boundary 1	7.0	13.2	9.8
Roadside	3.5	7.9	6.3

Table 15. Weekly BTX concentrations measured at Petrol Service Station C during the sampling period 3/2/99 to 10/2/99.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	1.4	0.8	0.8
Forecourt Pumps 1	7.1	10.6	7.5
Forecourt Pumps 2	5.4	8.3	6.7
Forecourt Boundary 1	5.4	8.7	7.2
Roadside	3.8	6.2	5.7

Table 16. Weekly BTX concentrations measured at Petrol Service Station C during the sampling period 10/2/99 to 22/2/99.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	1.0	1.2	0.9
Forecourt Pumps 1	8.7	15.9	11.6
Forecourt Pumps 2	5.4	9.9	7.7
Forecourt Boundary 1	6.4	11.3	8.8
Roadside	3.3	6.8	5.8

4.2 Active (pumped) Sampling Results Petrol Service Station C

Active (pumped) sampling was performed at station C on a ‘normal’ mid-week afternoon for a period of four hours. Results of the analysis of these samples are presented in Table 16. Concentrations of benzene in the forecourt area of the petrol station ranged from 4.2 to 22.6$\mu g/m^3$. Elevated concentrations of toluene and xylene were also measured at forecourt sampling locations and lowest levels were recorded for the background sampling location. Roadside and forecourt perimeter concentrations were found to be approximately midway between background and forecourt levels.

Table 17. Petrol Service Station C, active sampling 25/2/99.

Sampling Location	**Concentration $\mu g/m^3$**		
	benzene	**toluene**	**xylene**
Baseline/Background	< 1	< 1	< 1
Forecourt Pumps 1	22.6	36.8	27.5
Forecourt Pumps 2	21.4	37.5	28.0
Forecourt Shop Door	4.2	9.0	6.6
Forecourt 10m Pumps	10.7	14.7	11.0
Roadside	5.6	9.9	9.9
Forecourt Perimeter 1	6.8	10.3	8.8
Forecourt Perimeter 2	1.6	2.5	2.3

4.3 Meteorological Conditions

Meteorological conditions prevailing during the monitoring campaign are taken from the Met Eireann meteorological station at Casement Aerodrome, Baldonnel, County Dublin.

Sampling at petrol station A was carried out during the period 18th November to 21st December 1998. Meteorological conditions for the period were cold and overcast with frequent occurrences of rain. Mean daily temperatures ranged between 0 to 12°C and mean daily wind speeds ranged between approximately 1.4 to 12m/sec.

Table 18. Prevailing meteorological conditions during the sampling campaign at station A.

Sampling Period	Dates	Temperature (°C)			Average Wind Speed (m/sec)
		Min.	**Max.**	**Mean**	
1	18 – 25/11/98	-0.3	13.0	8.0	5.4
2	25/11 – 2/12/98	2.3	13.2	7.4	5.1
3	2 – 11/12/98	-1.5	13.6	7.1	5.2
4	11 – 21/12/98	-3.5	11.5	7.3	7.9

Sampling at stations B and C was performed over the period from 20th January to 22nd February 1998. Meteorological conditions for the period were cold and overcast with occasional occurrences of rain. Mean daily temperatures ranged between -1 to 12°C and mean daily wind speeds ranged between approximately 1.5 to 9.5m/sec.

Table 19. Prevailing meteorological conditions during the sampling campaign at stations B and C.

Sampling Period	**Dates**	**Temperature (°C)**			**Average Wind Speed (m/sec)**
		Min.	**Max.**	**Mean**	
1	20 – 27/1/99	0.6	11.9	5.4	7.9
2	27/1 – 3/2/99	3.0	11.7	8.6	4.8
3	3 – 10/2/99	-4.8	11.4	3.9	6.2
4	10 – 22/2/99	0.8	11.4	6.3	7.0

Figure 5 . Flow vector for the four sampling periods for station A, 18/11/98 to 21/12/98. The chart shows the wind speed and direction to which the wind was blowing over the course of sampling.

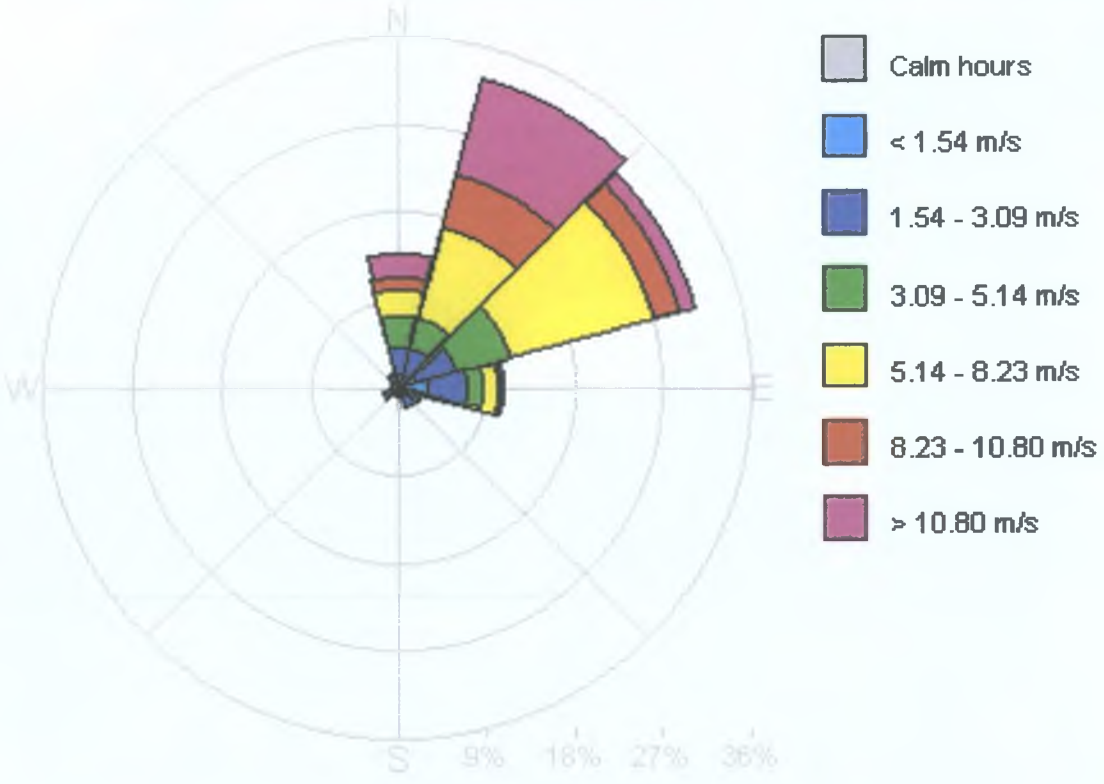
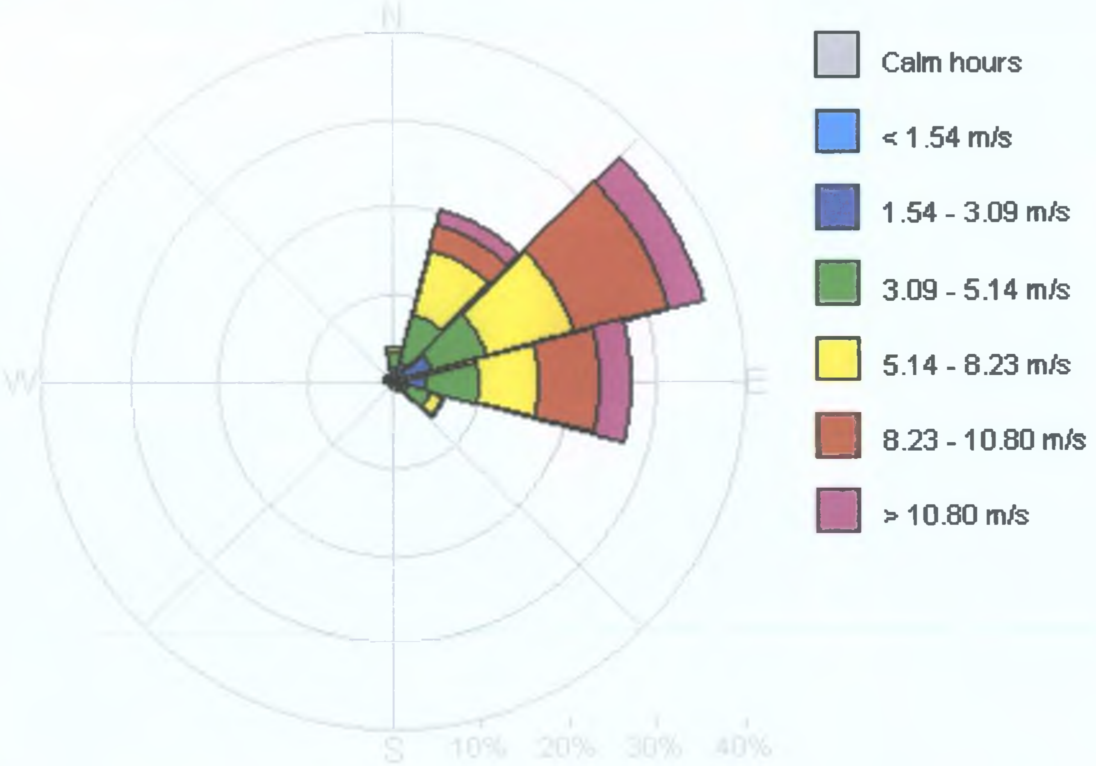


Figure 6 . – Flow vector for the four sampling periods for stations B and C, 20/1/99 to 22/2/99. The chart shows the wind speed and direction to which the wind was blowing over the course of sampling.



CHAPTER 5 Discussion

5.1 Comparison of BTX Results measured using Chromosorb 106 and Tenax Adsorbent Materials

Ambient air concentrations of BTX were determined at Petrol Station B using Perkin-Elmer diffusive tubes packed with both Chromosorb 106 and Tenax. These measurements were undertaken to enable comparisons to be carried out on the performance of the two materials for diffusive monitoring of BTX in ambient air. Paired weekly concentrations of BTX measured using Chromosorb 106 and Tenax at sampling locations around Service Station B are shown in Table 20. The data includes sample pairs from forecourt pump areas, roadside and background sampling locations.

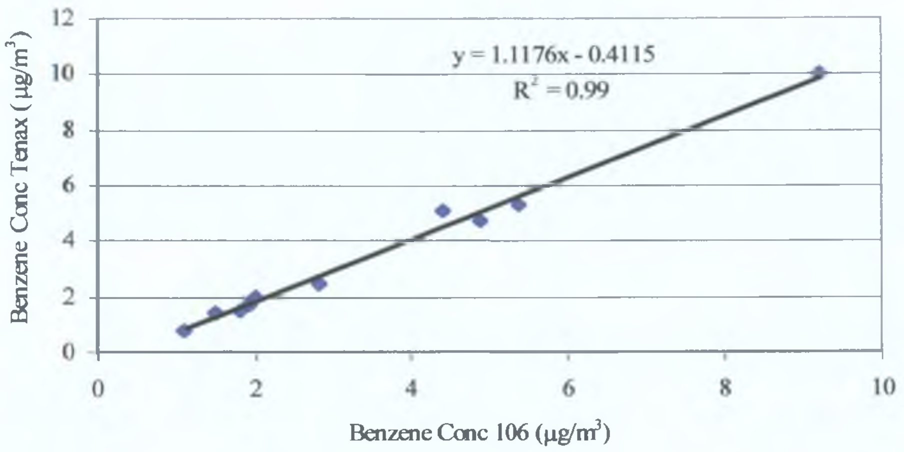
The data was plotted using Excel™ software to check for correlation between the results generated using the two different materials. The charts shown in Figure 7 show the degree of correlation between the BTX results using the two adsorbent materials.

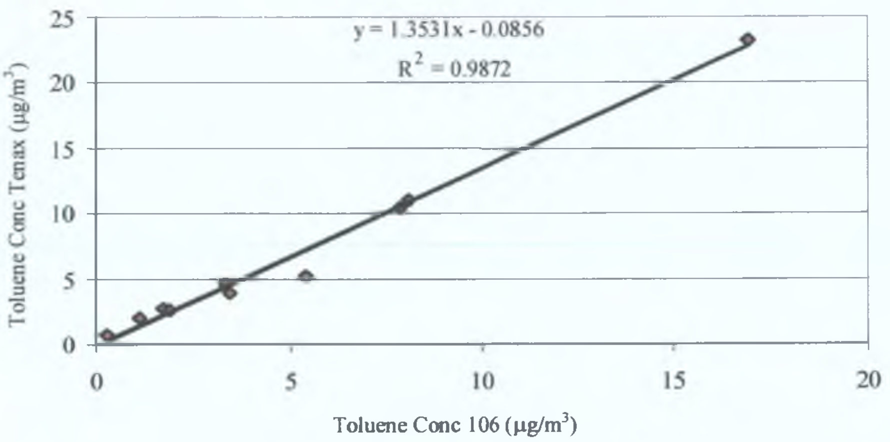
Table 20. Concentrations of BTX measured at Station B using diffusive samplers packed with Chromosorb 106 and Tenax.

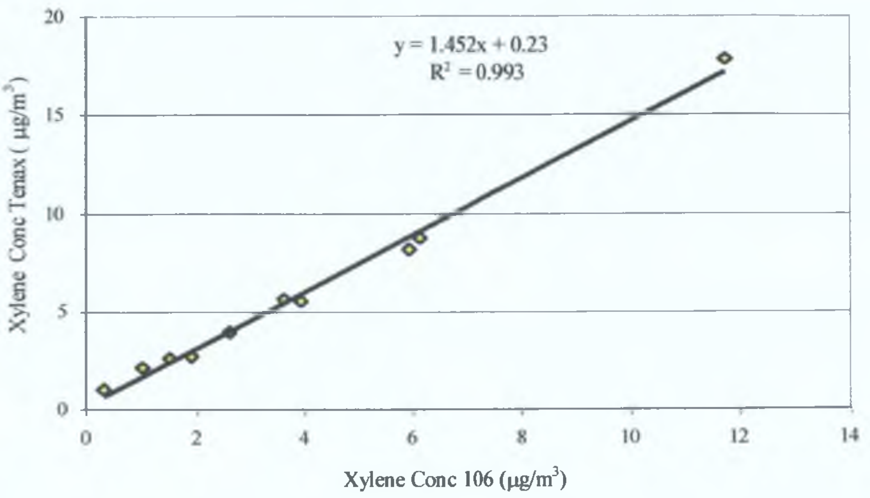
Sample	**Concentration µg/m³**					
	benzene		**toluene**		**xylene**	
	C 106	Tenax	C 106	Tenax	C 106	Tenax
1	5.4	5.3	7.9	10.5	6.1	8.7
2	1.1	0.8	0.3	0.7	0.3	1.0
3	1.8	1.5	1.1	2.0	1.0	2.2
4	9.2	10.0	16.9	23.3	11.7	17.8
5	2.8	2.5	3.3	4.6	2.6	3.9
6	4.4	5.1	5.4	5.3	3.6	5.6
7	2.0	2.0	1.7	2.8	1.5	2.6
8	4.9	4.7	8.1	11.1	5.9	8.2
9	1.9	1.7	3.4	3.9	3.9	5.5
10	1.5	1.4	1.9	2.6	1.9	2.7

The charts show the linear regression line of best fit for the BTX concentrations measured using Chromosorb 106 and Tenax. Each chart shows a high degree of agreement between the two sets of data (Chromosorb 106 and Tenax). Correlation analysis of the data confirms a high degree of correlation between results for the two adsorbent materials. R^2 values (correlation coefficients) of approximately 0.99 were obtained for each of the three compounds. Although a high degree of correlation exists between the BTX concentrations measured using the two adsorbent materials it does not necessarily follow that the numeral results are the same or similar. Therefore, statistical analysis of the data generated was required in order to evaluate whether or not the measured concentrations of BTX for the two adsorbent materials are from populations with the same median (i.e. are the measured concentrations the same using Chromosorb 106 and Tenax?).

Figure 7. Correlation of BTX measurements made between diffusive samplers packed with Chromosorb 106 and Tenax.


Correlation of Benzene Measurements


Correlation of Toluene Measurements


Correlation of Xylene Measurements

The Wilcoxon Signed Rank Test was recommended for the statistical analysis of the data (Boland, Personal Communication). This test compares the medians by looking at the differences in pairs of data (Chromosorb 106 – Tenax). The Wilcoxon test is a non-parametric test and therefore does not assume that the data are sampled from a Gaussian distribution. If the resultant p-value generated from the test is less than 0.05, the hypothesis that the difference in medians is a coincidence is rejected. If the p-value is greater than 0.05, the data does not give any reason to conclude that the medians of the differ i.e. the results generated using the two adsorbent materials do not differ statistically.

Table 21. Results of statistical analysis of measured concentrations using Chromosorb 106 and Tenax.

Compound	p-value for Wilcoxon Signed Rank Test	Reason to conclude significant difference
benzene	0.15	No
toluene	0.003	Yes
xylene	0.001	Yes

In a study of sorbing agents for the sampling of VOC's from air (Brown, 1995), the sorbent that best satisfied the acceptance criteria for a range of VOC's (including benzene) was Chromosorb 106. Tenax was reported to be suitable for a more limited range of higher molecular weight organic vapours. Chromosorb 106 is the recommended adsorbent material for hydrocarbons ranging from C_6 (hexane) to C_{10}

(decane) and substances in a similar boiling range, 67 to 174°C (ISO, 1998), which includes benzene (80°C), toluene (111°C) and xylene (137-140°C). Therefore, Chromosorb 106 is the recommended adsorbent material for sampling BTX in ambient air. Tenax is reported to have a sorption capacity some four times lower than Chromosorb 106 for benzene and is therefore not generally recommended for benzene determinations in air, however the two adsorbents are recommended for toluene and xylene (ISO, 1998).

The predicted outcome of this comparison of the two adsorbent materials is that xylene is expected to show a higher degree of correlation than toluene with the more volatile benzene having the lowest correlation of the three compounds. The predicted lack of correlation for benzene is based on the volatility of the compound and the difference in sorption capacity between Tenax and Chromosorb 106 for benzene.

Contrary to the findings of Brown (1995) the Wilcoxon Signed Rank Test detected no significant difference in the data obtained for benzene using the two different adsorbent materials. This unexpected result may be explained by the fact that sampling at Station B was carried out over the one month period from 20/1/99 to 22/2/99 during which the highest ambient temperature recorded was 11.9°C. The mean temperature for the period was 6.5°C and at these low temperatures the evaporation rate of benzene will be significantly reduced. Therefore, 'back diffusion' of the analyte from Tenax will be retarded and the analyte will remain adsorbed on the porous polymer. This observation is supported by the fact that the sorption capacity of the diffusive sampler will not be approached at the concentrations measured and therefore, no significant losses of the analyte should occur. Also, since the ambient temperature over the survey was low (mean 6.5°C), the vapour pressure of benzene will have been significantly reduced. In short, the net effect of the sampling conditions (low temperatures and relatively low substance dose) is a reduction in 'back diffusion' of benzene from the adsorbent material (LUA-Materialen No. 46, 1998).

For toluene and xylene however the Wilcoxon test revealed there is a significant difference in the data generated using Chromosorb 106 and Tenax. The agreement in benzene results using the two adsorbent materials which is explained above in terms of the relatively low ambient temperatures for the period of sampling would be expected to extend to measured concentrations of toluene and xylene. At the relatively low temperatures reported the 'back diffusion' effect for these two compounds will also be significantly reduced. Toluene and xylene have lower vapour pressures than benzene (Merck Index, 10th ed., 1983). Agreement in the measured concentrations between the two adsorbent materials however, is not observed for toluene and xylene. The p-value for the Wilcoxon test indicates best agreement for benzene and most significant difference for xylene. This suggests that the level of agreement between the two adsorbent materials may be related to the volatility and/or molecular weight of the analyte. The p-value for the Wilcoxon test is in rank order of the boiling points and molecular weight of the compounds (Table 22).

Table 22. Boiling points and molecular weight of benzene, toluene and xylene.

Compound	Boiling Point (°C)	Molecular weight
benzene	80	78
toluene	110	92
xylene	140	106

Another factor in the discrepant results for toluene and xylene using the two adsorbent materials may be the manner in which the diffusive uptake rates have been determined. Diffusive sampling uptake rates for BTX using Perkin-Elmer ATD tubes packed with Chromosorb 106 are taken from a 1998 draft ISO standard. The sampling rates have been determined experimentally at environmental levels over a one-week sampling period. The uptake rates have therefore been validated for the exact conditions under which they have been employed. The diffusive sampling rates for BTX on Tenax packed tubes have not been validated at environmental levels over a one-week period. Generally uptake rates for BTX on Tenax have been determined either theoretically or from laboratory experiments at higher concentrations over shorter time frames (Goelen et al, 1997). These uptake rates were intended for use in the area of occupational/workplace air sampling at levels which differ by several orders of magnitude from environmental levels. Validation of the uptake rates for BTX on Tenax at environmental levels over longer sampling periods would be required before gaining acceptance as a reliable quantitative tool. However, once the limitations and errors associated with the use of Tenax for BTX measurements are understood and quantifiable its use in diffusive sampling of ambient air for BTX may gain acceptance.

5.2 Diffusive Sampling

5.2.1 Comparison of Measured BTX Concentrations at Service Station A Sampling Locations

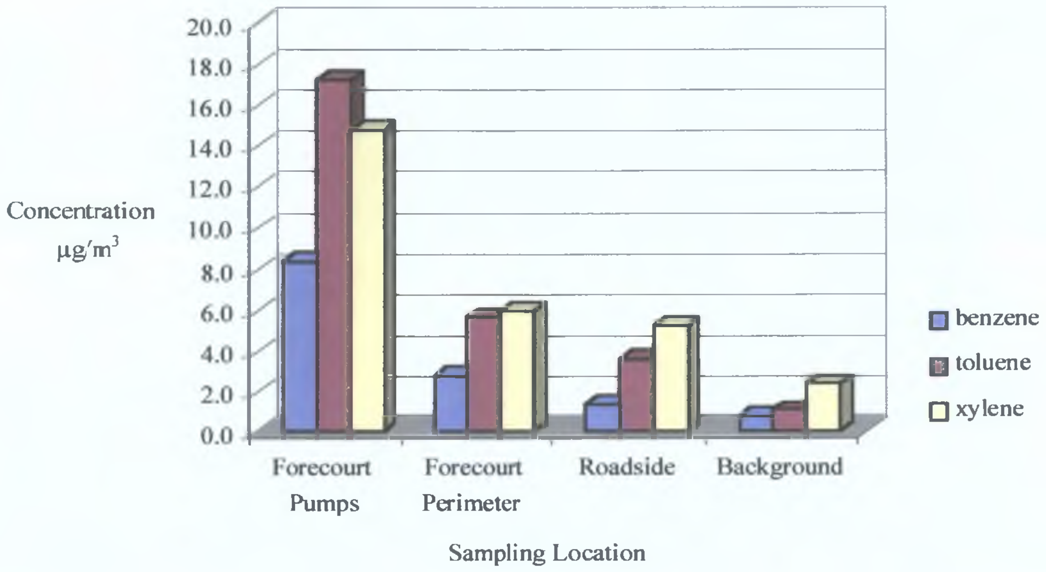
Ambient air concentrations of BTX were measured around petrol service Station A over a four week period from 25/11/98 to 21/12/98 using diffusive sampling tubes packed with Chromosorb 106. Weekly BTX concentrations at petrol service Station A are summarised in Tables 5 – 8 in the results section.

The mean concentrations of BTX at each sampling location over the four sampling periods are given in Table 23 and Figure 8.

Table 23. Mean concentrations of BTX at four sampling locations over sampling campaign at Station A.

Compound	Forecourt Pumps	Forecourt Perimeter	Roadside	Background
benzene	8.4	2.7	1.3	0.7
toluene	17.3	5.6	3.5	1
xylene	14.8	5.9	5.2	2.3

Figure 8. Histogram showing the mean concentrations of BTX at four sampling locations over sampling campaign at Station A.



From Figure 8, two trends are apparent. Measured concentrations for all three compounds occur in a rank order, with the forecourt pumps showing the highest levels of BTX and background concentrations being lowest. Also the ratios of B : T : X are inconsistent over the four sampling locations.

The highest concentrations of BTX are observed in the area of the forecourt pumps at service Station A. Mean concentrations of benzene, toluene and xylene measured at the forecourt pumps over four sampling periods were 8.4, 17.3 and 14.8µg/m^3, respectively. Mean BTX concentrations of 2.7, 5.6 and 5.9µg/m^3, respectively were measured at forecourt perimeter locations. These concentrations were some three times lower than levels found at the forecourt pumps. Mean roadside BTX concentrations, measured 100 metres from forecourt area, were 1.3, 3.5 and 5.2µg/m^3

respectively. With the exception of xylene these are approximately half the airborne levels measured at the forecourt perimeter. Mean background concentrations measured for the duration of the sampling campaign were approximately 1μg/m^3 for benzene and toluene and 2.3μg/m^3 for xylene.

The observed rank order of measured concentrations suggests that the most significant source of airborne BTX in the immediate environment is the area of the forecourt pumps (Cram and Little, 1995). Measured concentrations do not differentiate between BTX that originates from the evaporation/spillage of petrol and those emitted from vehicle exhausts. The forecourt canopy and shop building provide some shelter to the pumps area from the effects of the wind and rain, this may enable higher concentrations of BTX to develop in this area. Sampling of the forecourt pumps area was carried out at two locations, 1 and 2. Forecourt pump site 1 is located approximately 5m from the shop building. Therefore, it is anticipated that the building will generate a wake effect on this sampling location, resulting in eddy's and turbulent mixing both horizontally and vertically. The result of this is that petrol vapours may be retained longer due to this mixing area, before eventually being dispersed. As a consequence, higher concentrations of BTX are expected. The second forecourt sampling location (forecourt pumps 2) is 5m further from the effects of the buildings and closer to the free moving air at the roadside. The road runs south-west to north-east in the same direction of the prevailing winds and is bordered by tall trees on either side leading to possible channelling of winds. Petrol vapours at sampling location 2 are therefore expected to disperse more rapidly, and measured BTX concentrations are expected to be lower than at forecourt location 1. The highest benzene concentration of 16.6μg/m^3 was measured during the second sampling period at forecourt pumps 1. Forecourt concentrations of toluene and xylene for this period were also the highest measured (29.7 and 21.6μg/m^3, respectively). During this period the average wind speed was 5.1m/sec, however, the final 72 hours of this sampling period were typified by wind speeds of calm to 3m/sec. Wind speeds for this three-day period were the lowest for the entire sampling campaign at Station A. It is thought that the elevated BTX concentrations measured during this sampling period may be attributed to the calm meteorological conditions observed (Figure 9). It is speculated that the calm conditions retarded the dispersion of the evaporated petrol vapours from the area of the forecourt pumps. Concentrations of BTX for at forecourt pumps 2 measured over the same period were 10.0, 19.2 and 17.0μg/m^3 also above the mean forecourt levels over the campaign. Highest average wind speeds of 7.9m/sec were measured during the fourth sampling period at Station A (Figure 9). BTX concentrations measured at forecourt pumps 1 for the period were 10.6, 19.3 and 14.8μg/m^3, respectively. These are significantly above the mean BTX forecourt concentrations for the study. Levels measured at the second forecourt sampling location (forecourt pumps 2) for this period of high wind speed were 4.4, 9.7 and 9.4μg/m^3 for BTX respectively some 36 to 58% lower. The effect of high wind speeds on tube-type diffusive samplers is to increase their effective uptake rates as a result of turbulence in the static air layer within the tube. The relationship between the reduction in diffusive path length (and effect on sampler uptake rate) and wind speed has been found to be highly variable (Gair and Penkett, 1995). It is suggested that due to possible building wake effects the diffusive samplers at the two forecourt pump sampling locations (1 and 2) may have experienced different wind speeds which ultimately may have caused different uptake rates for the three aromatic compounds to be observed at the two sampling locations.

A wake effect is where a low-pressure region is generated by an obstruction resulting in a disruption to the 'normal' wind flow pattern.

The difference in measured concentrations at the two forecourt pump locations may be due to the building wake effects mentioned above causing one or more of a number of effects including variable uptake rates and delayed dispersion of the VOC's from the area of the pumps. However, the pumps closest to the shop may simply be used more frequently than those at forecourt pump location 2. Unfortunately volumes of fuels sold was not made available to the present study so this can not be confirmed. Also no account has been taken of the different users of the pumps as this may also be a factor.

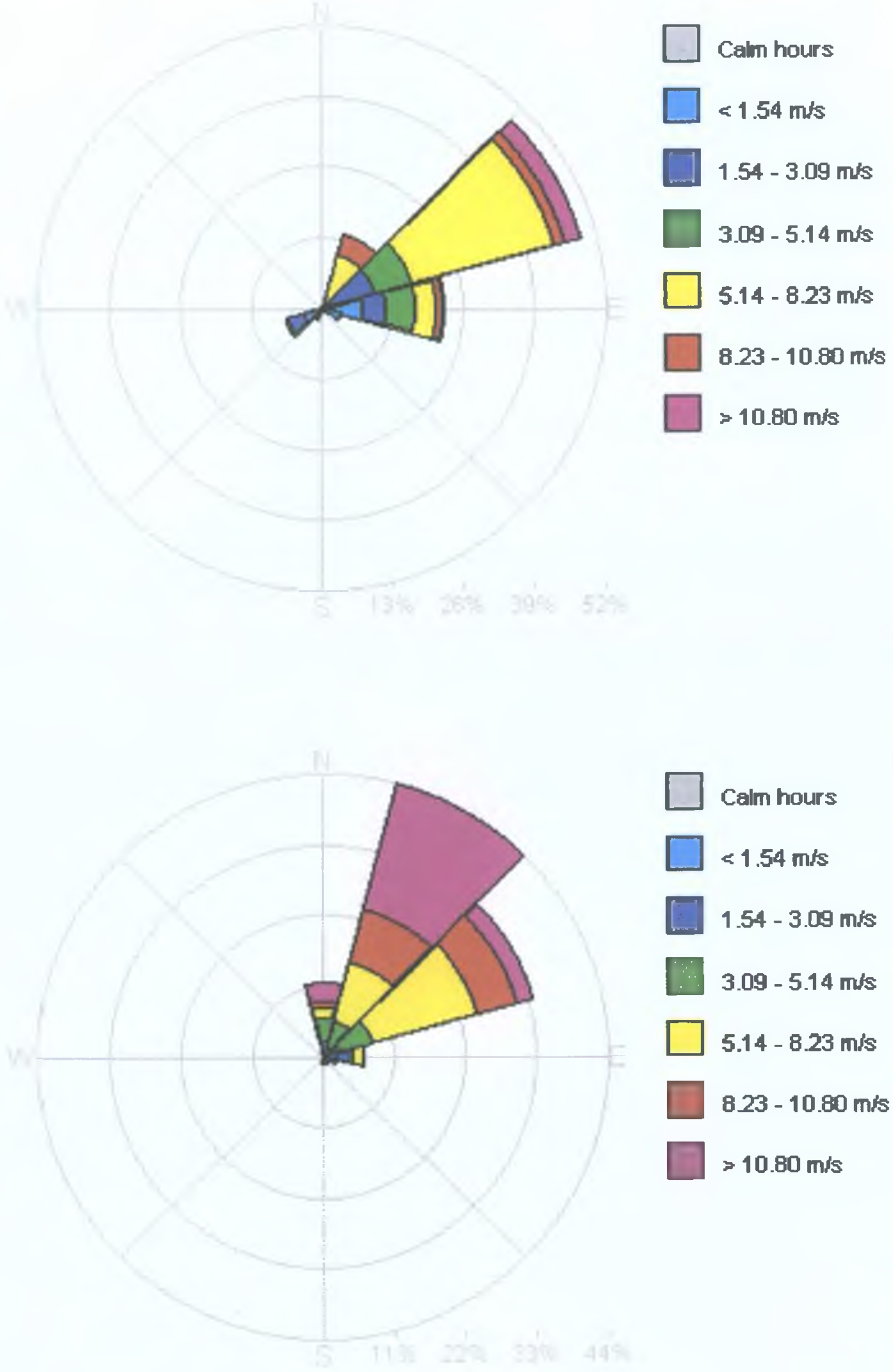
The next sampling location in the rank order was the forecourt perimeter, here the valves and vents for filling the underground storage tanks are located, and cars are parked for the forecourt convenience store and car wash. The vent pipes from the underground tanks were fitted with VOC adsorption traps in accordance with the sixth schedule of Statutory Instrument No. 374 of 1997. It is anticipated that the principal source of BTX at the forecourt perimeter will be evaporation from liquid fuel at the pumps during refuelling and exhaust emissions from cars. More rapid dispersion of VOC's from the perimeter locations than the forecourt pumps is expected as less shelter from the elements is provided. These factors (distance from source and exposure to wind) may lead to lower measured concentrations of BTX at the perimeter sampling locations. This is supported by the fact that measured concentrations of BTX at the forecourt perimeter were approximately 60% lower than those measured at the forecourt pumps.

The roadside sampling location, approximately 100m from the forecourt service Station, was next in the rank order of BTX concentrations measured. Exhaust emissions from passing traffic would be the major source of BTX at this sampling location. BTX from the forecourt area of the Station would be expected to make a negligible contribution to the levels measured at this distance due to the extent of atmospheric dispersion and dilution. The road runs south-west to north-east in the same direction as the prevailing winds and is bordered by tall trees on either side leading to possible channelling of winds. The background concentrations measured for Station A are the lowest in the rank order observed. The sampling location for background measurements was located in a residential estate typical of this sub-urban area, situated over 1km from the service Station and 250m from the nearest road. There are no other petrol service Stations in the locality of the background sampling location.

In summary, the rank order of BTX concentrations measured at petrol service Station A was as previously reported (Cram and Little, 1995), forecourt pumps > forecourt perimeter > roadside > background and highest BTX concentrations were observed during periods of low wind speeds.

Figure 9 shows the flow vectors for the periods of lowest and highest wind speeds, week 2 and week 4 respectively. The prevailing winds were from the south-west for both periods, however, wind speeds reported during sampling period 4 were significantly higher with speeds of over 8.23 m/sec for approximately 40% of the sampling period.

Figure 9 – Flow vectors for the second (top) and fourth sampling periods at Station A.



5.2.2 Comparison of Measured BTX Concentrations at Service Station B Sampling Locations

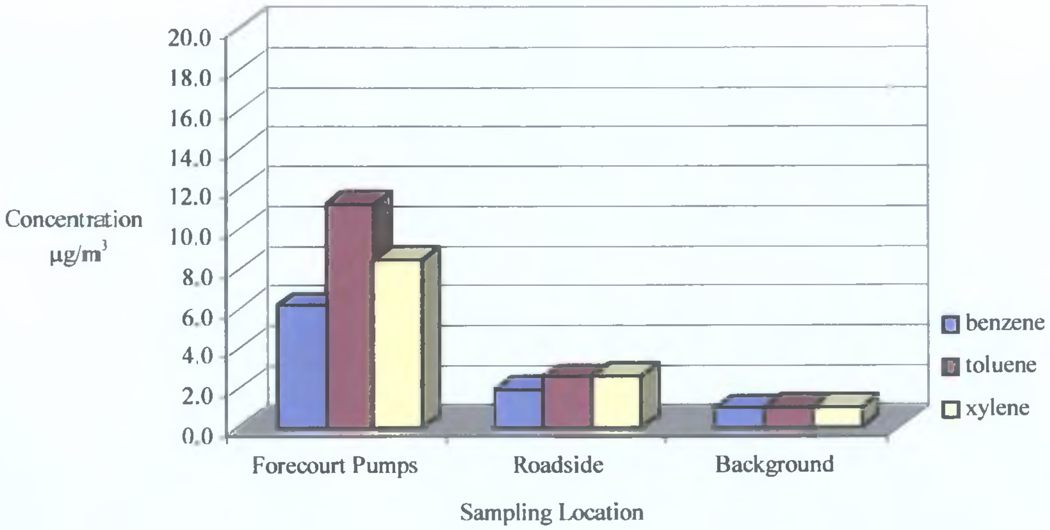
Ambient air concentrations of BTX were measured around petrol service Station B over the four week period from 20/1/99 to 2/2/99 using diffusive sampling tubes packed with Chromosorb 106 and Tenax. Measured concentrations of BTX at petrol service Station B are summarised in Tables 8 – 11 of the results section.

The mean concentrations of BTX (using results generated using both adsorbent materials) at each sampling location over the four sampling periods are given in Table 24 and Figure 10.

Table 24. Mean concentrations of BTX at four sampling locations over sampling campaign at Station B.

Compound	Forecourt Pumps	Roadside	Background
benzene	6.1	1.9	0.9
toluene	11.2	2.5	1.0
xylene	8.5	2.6	1.0

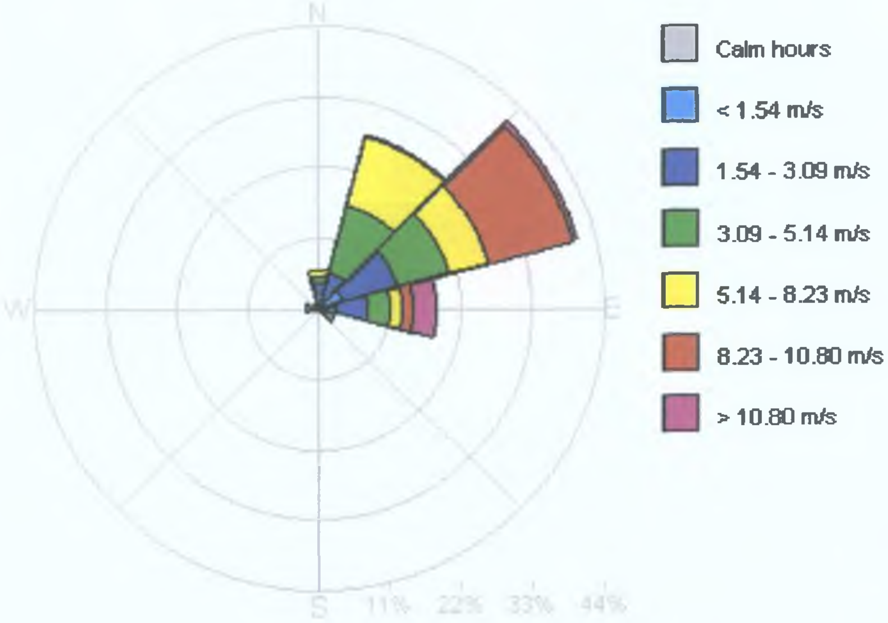
Figure 10. Histogram showing the mean concentrations of BTX at three sampling locations over sampling campaign at Station B.



The mean BTX concentrations for the three sampling locations monitored at Station B follow the rank order expected (Cram and Little, 1995) i.e. forecourt > roadside > background. The roadside sampling locations for Station B are located between 50 – 70 metres from the forecourt area of the Station. No measurements were made at a forecourt perimeter location for Station B as no suitable clearly defined boundary existed. The levels measured in the forecourt pumps area were generally 3 to 5 times higher than the nearby roadside.

Highest levels of BTX (10.0, 23.3 and 17.9μg/m^3, respectively) were detected at the forecourt pumps during the second sampling period, 27/1 to 3/2/99, at Station B. During this week a mean wind speed of 4.8m/sec and a mean ambient temperature of 8.6°C were recorded (Figure 11). This wind speed was the lowest over the four sampling periods at Station B and the ambient temperature for the period was the highest for the study. The elevated BTX concentrations detected during this sampling period may be attributed to the meteorological conditions. An increased evaporation rate of petrol vapours may have resulted from the relatively high ambient temperatures, and with relatively calm winds being observed for the period, the rate of dispersion of the VOC's evolved may have been reduced.

Figure 11. Flow vector for the second sampling period at Station B (27/1 to 3/2/99).



5.2.3 Comparison of Measured BTX Concentrations at Service Station C Sampling Locations

Ambient air concentrations of BTX were measured in the vicinity of petrol service Station C over the same four week period as Station B, from 20/1/99 to 22/2/99, using diffusive sampling tubes packed with Chromosorb 106. Weekly concentrations of BTX at petrol service Station C are given in Tables 12 – 15 of the results section.

The mean concentrations for BTX at each sampling location over the four sampling periods are given in Table 25 and Figure 12.

Table 25. Mean concentrations of BTX at four sampling locations over sampling campaign at Station C.

Compound	**Forecourt Pumps**	**Forecourt Perimeter**	**Roadside**	**Background**
benzene	7.4	6.2	3.5	1.1
toluene	13.0	10.6	6.5	0.6
xylene	9.3	8.2	5.5	0.6

Figure 12. Histogram showing the mean concentrations of BTX at four sampling locations over the sampling campaign at Station C.

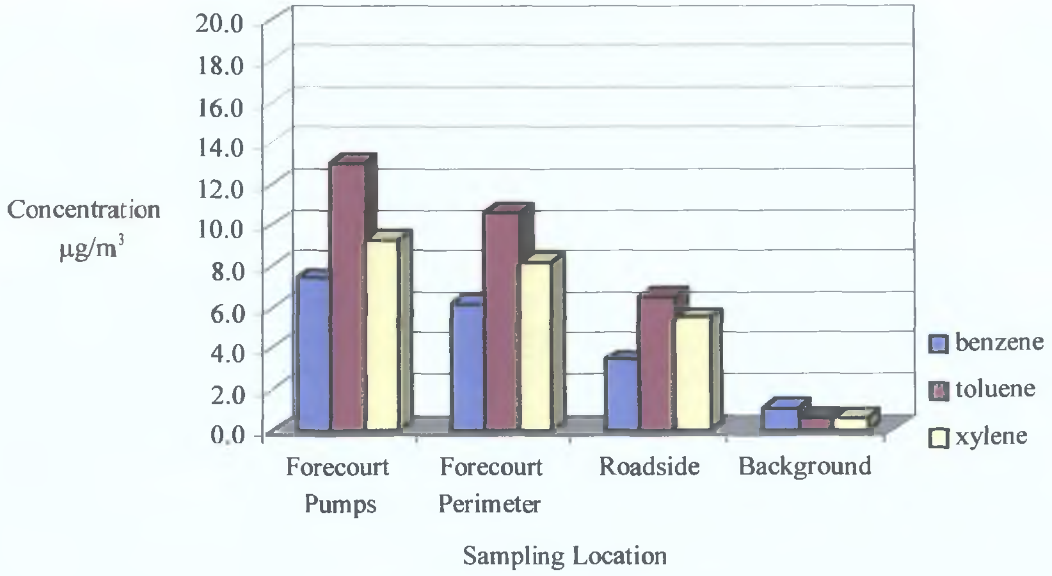
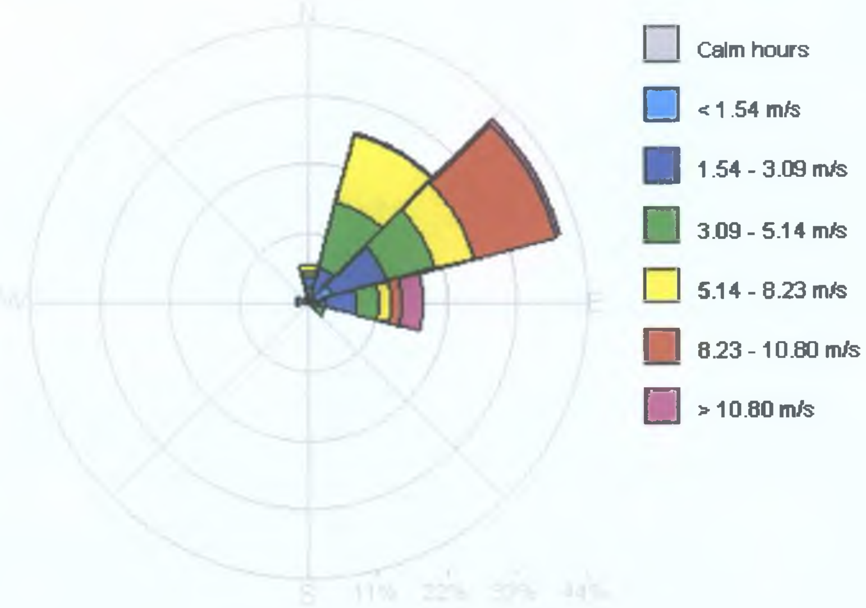


Figure 12 above clearly illustrates the rank order of BTX concentrations observed at Station C i.e. forecourt pumps > forecourt perimeter > roadside > background. This rank order is consistent with those previously reported by Cram and Little in 1995. The rank order at Station C confirms the forecourt pumps area as the region of highest BTX concentrations. Mean BTX concentrations in the forecourt pumps area of Station C over the study were 7.4, 13.0 and 9.3µg/m^3, respectively. Sampling was performed at two locations in the forecourt pumps area, 1 and 2. Location 1 is the pump island closest to the forecourt shop and 2 is closest to the roadside. The levels measured were consistently higher at location 1, and as previously discussed it is suggested that this is due to the building wake effects of the forecourt shop building. BTX Concentrations measured at the forecourt boundary location were found to be approximately 15 to 25% lower than those in the forecourt area. Mean airborne BTX levels detected at the forecourt perimeter were 6.2, 10.6 and 8.2 μg/m^3, respectively. Mean BTX concentrations measured at the roadside were 3.5, 6.5 and 5.5μg/m^3, respectively, a further 40 to 50% lower than mean forecourt perimeter levels measured. Background levels for Station C averaged 1.1, 0.6 and 0.6μg/m^3, respectively.

Highest forecourt benzene concentration observed at Station C was 10.4μg/m^3, recorded for the second sampling period (27/1 to 3/2/99) when lowest wind speeds and highest temperatures occurred. Toluene and xylene concentrations for this period were 20.0 and 13.7μg/m^3, respectively. Figure 13 shows the flow vector for this sampling period. Conversely, the lowest observed BTX concentrations occurred for the first period (6.7, 9.9 and 7.0μg/m^3, respectively) during which the highest wind speeds were reported.

Figure 13. Flow vector for the second sampling period at Station C (27/1 to 3/2/99).



Mean BTX concentrations of 6.2, 10.6 and 8.2μg/m^3, respectively were measured at the forecourt perimeter sampling location of Station C. The forecourt perimeter sampling location was approximately 20m north-east of the forecourt pumps where mean BTX concentrations of 7.4, 13.0 and 9.3μg/m^3, respectively were recorded. Prevailing winds for the sampling campaign at Station C were from the south-west, (Figure 6). The elevated concentrations of BTX measured at the forecourt pumps and the prevailing wind direction suggest that petrol vapours from the pump area may be a significant source of BTX measured at the perimeter location. The forecourt perimeter sampling location was also situated within 10m of the roadside, where traffic lights control a major junction. The road is heavily trafficked, particularly at peak commuter hours and queues are not uncommon. The proximity of the road junction with heavy peak hour traffic is thought to be a significant factor in the elevated levels of BTX measured at the forecourt perimeter. This is supported by the elevated BTX concentrations measured at the roadside opposite Station C and adjacent to the junction (3.5, 6.5 and 5.5$\mu g/m^3$, respectively). Exhaust emissions from vehicles using the pumps and forecourt shop are another potential source of BTX for this sampling location. The underground fuel storage tanks are vented at a height of approximately 6 – 7 metres, and may, depending on meteorological conditions, contribute to BTX concentrations measured in the vicinity of the forecourt.

In summary, elevated BTX concentrations measured at the forecourt perimeter of Station C are thought to be a consequence of the nearby fuel pumps and the direction of prevailing winds. The proximity of a heavily trafficked road and exhaust emissions from vehicles on the forecourt area are also believed to contribute to the elevated BTX concentrations.

Mean roadside concentrations for Station C were 3.5, 6.5 and 5.5$\mu g/m^3$, respectively for BTX. This is mainly due to the busy junction adjacent to the service Station. The junction is controlled by traffic lights where queuing is not uncommon, particularly during peak hour traffic. These factors have the potential to increase the BTX levels in the roadside ambient air adjacent to Station C.

5.3 Active (Pumped) Sampling

5.3.1 Comparison of Measured BTX Concentrations at Service Station C Sampling Locations

Ambient air concentrations of BTX were measured at petrol service Station C during ‘normal’ operating conditions over four hours using active (pumped) sampling onto ATD tubes packed with Chromosorb 106. Active sampling involves the active movement of air through the sample collection device by means of an air sampling pump. The sampling pumps used were calibrated SKC personal air sampling pumps which are intrinsically safe for use in explosive or flammable environments.

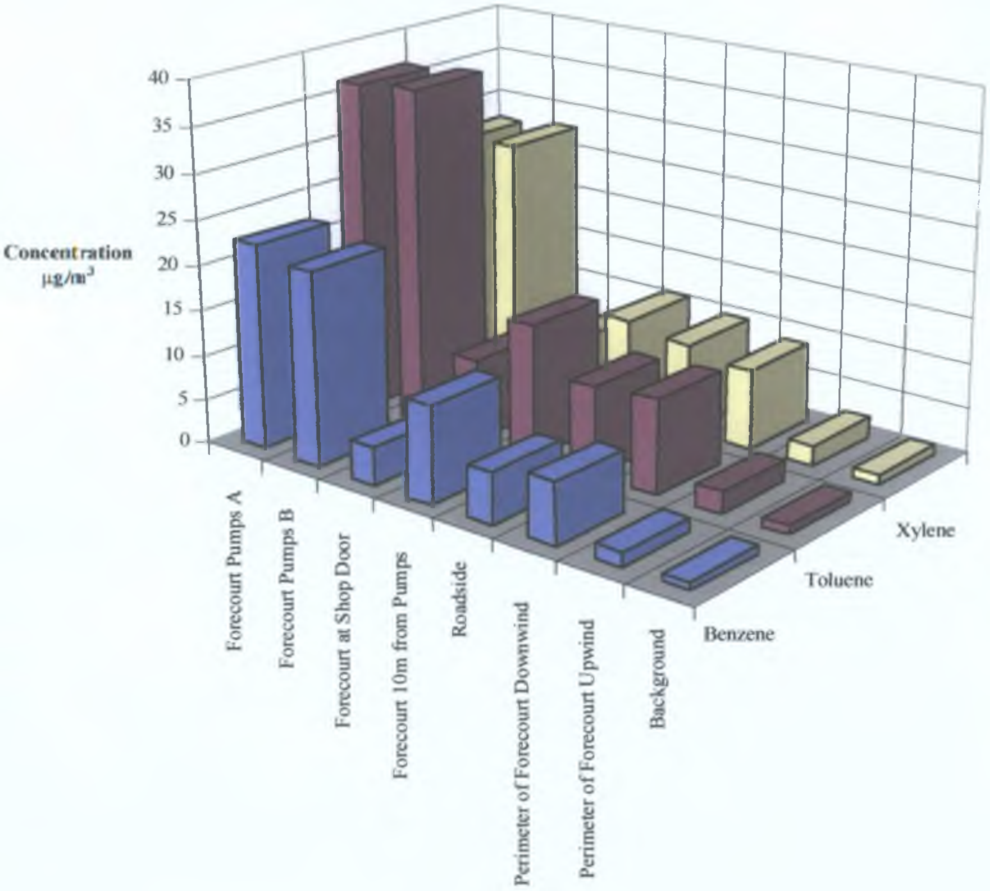
Sampling was conducted at eight sampling locations around the petrol service Station over a four-hour period on the afternoon of 25th February 1999. Analysis of the samples was carried out along with the diffusive samples collected. The results are presented in Table 26 and Figure 14.

Table 26. Concentrations of BTX measured at Station C using active sampling 25th February 1999.

Sampling Location	**Concentration µg/m^3**		
	benzene	**toluene**	**xylene**
Baseline/Background	0.9	1.0	1.0
Forecourt Pumps 1	22.6	36.8	27.5
Forecourt Pumps 2	21.4	37.5	28.0
Forecourt Shop Door	4.2	9.0	6.6
Forecourt 10m Pumps	10.7	14.7	11.0
Roadside	5.6	9.9	9.9
Forecourt Perimeter 1	6.8	10.3	8.8
Forecourt Perimeter 2	1.6	2.5	2.3

The highest BTX concentrations were measured in the forecourt pumps area using active sampling. BTX concentrations measured were approximately 22, 37 and 28µg/m^3, respectively at the forecourt pumps. The lowest levels of BTX were recorded for the background sampling location, measured concentrations were 0.9, 1.0 and 1.0µg/m^3 for BTX, respectively. Other sampling locations including roadside and forecourt perimeters were in the range between background and forecourt pumps levels measured. This is the same as the rank order previously observed for the diffusive samples analysed i.e. forecourt pumps > forecourt perimeter > roadside > background.

Figure 14. Histogram showing the concentrations of BTX measured at Station C using active sampling 25th February 1999.



5.3.2 Comparison of BTX Concentrations at Service Station C measured using Active and Diffusive Sampling

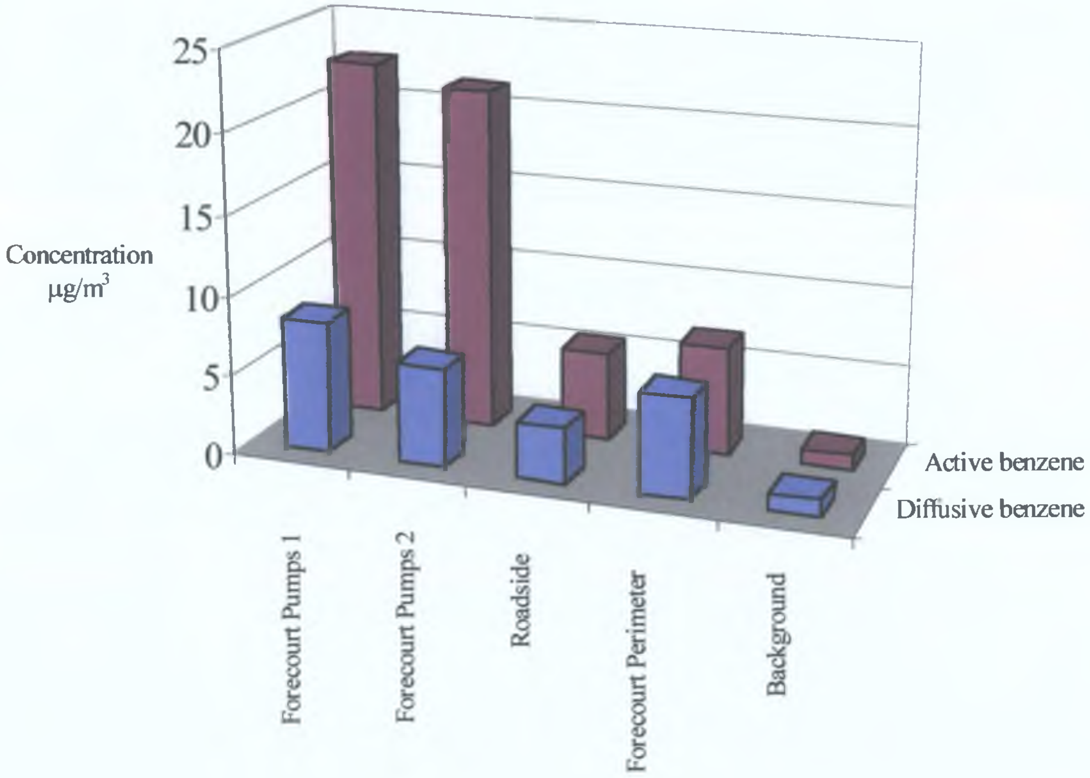
The measured concentrations of BTX for the active sampling of Station C differ considerably from the levels determined by diffusive sampling. Table 27 and Figure 15 shows the results of both diffusive and active monitoring at the same locations for BTX at Station C.

Table 27. Comparison of concentrations of BTX measured at sampling locations at Station C using both diffusive and active sampling.

Sampling Location	Concentration µg/m^3 Diffusive Sampling			Concentration µg/m^3 Active Sampling		
	benzene	**toluene**	**xylene**	**benzene**	**toluene**	**xylene**
Background	1.1	0.6	0.7	0.9	1.0	1.0
Forecourt Pumps 1	8.2	14.1	10.0	22.6	36.8	27.5
Forecourt Pumps 2	6.2	11.4	8.5	21.4	37.5	28.0
Roadside	3.5	6.5	5.6	5.6	9.9	9.9
Forecourt Perimeter	6.2	10.6	8.3	6.8	10.6	8.8

Measured concentrations of BTX were higher for the samples collected using sampling pumps than the samples collected diffusively. This is due to the fact that the diffusive samplers were exposed for a one-week period which includes periods during which no emissions are likely to occur, while the active (pumped) samples were collected during a four-hour period of continuous emissions. The service Stations studied were in operation for 16 hours each day (7am – 11pm), the diffusive samplers average the concentration over a 168 hour period so the Station was only in operation for 112 hours, 67%, of the period. The pumped samples were collected while the Station was operating between 2pm and 6pm.

Figure 15. Histogram comparing concentrations of benzene measured at sampling locations at Station C using both diffusive and active sampling.



The measured concentrations of BTX at roadside, forecourt perimeter and background sampling locations were very similar for both sampling techniques, this suggests good agreement between the methods (Figure 15). At the forecourt pumps locations, however, the pumped samples collected show considerably higher concentrations than the samples collected diffusively. This is explained by the fact that the active samples were collected during the afternoon and evening period which is anticipated to be a relatively busy period on the forecourt. Therefore, the 'grab' sample concentrations measured may not be representative of the prevalent concentrations at that location over a longer period of time.

5.4 Ratios of Measured BTX Concentrations

5.4.1 Station A

Ratios of benzene, toluene and xylene concentrations are inconsistent across the range of sampling locations and concentrations. The ratio toluene : benzene concentrations ranged from 1.8 at highest measured concentrations to 3.2 for low concentrations, and averaged 2.3 (18% Relative Standard Deviation). Xylene : benzene ratios ranged from 1.3 at higher concentration levels to 4.9 for low concentrations, and averaged 2.6 (43.5% RSD). Mean BTX ratios over the study for Station A were calculated as 1 : 2.3 : 2.6. The benzene : toluene and the benzene : xylene ratios are in the expected ranges, however, the toluene : xylene ratio is greater than previously reported values (Plant and Wright, 1996, 1997 and 1998).

At lower concentration sampling locations i.e. forecourt perimeter, roadside and background the measured xylene concentrations did not agree with predicted ratios or ratios found at the forecourt pumps location. The measured concentrations of xylene are disproportionately high giving a ratio of xylene : toluene concentrations of > 1 where the expected or 'normal' ratio is 0.5 to 0.8 (Plant and Wright, 1998). The slightly elevated xylene concentrations measured suggests there may be another source of xylene other than petrol / vehicular in the sampling locality. At sampling locations where BTX concentrations are low (background and roadside) the introduction of an alternative source of xylene at 1-2 could significantly alter the ratios of BTX concentrations. The effect will not be as marked at sampling locations where relatively elevated concentrations of BTX are measured e.g. forecourt pumps.

Another potential source of xylene in the area may be an industrial facility located approximately 1km north-east of the service Station. However, the prevailing wind direction measured during the study was from the south-east. It should be noted that the wind does blow from the north-east for short periods of the study (Figure 5 - flow vector Station A) which may have contributed to the slightly elevated xylene concentrations observed at this Station.

5.4.2 Station B

Mean BTX ratios for measured concentrations at Station B were in the range 1 : 1.3 : 1.2 to 1 : 2 : 1.7. Ratios of measured BTX concentrations at background and forecourt sampling locations are in keeping with those previously observed by Plant and Wright (1998). However, mean roadside BTX concentrations measured over the sampling campaign at Station B show a mean xylene concentration of 2.6μg/m^3 which results in a B : T : X ratio of 1 : 1.3 : 1.4 for mean results at this sampling location. This suggests a possible source of xylene other than the petrol service Station and vehicle exhaust emissions may contribute to the xylene concentrations at roadside sampling locations.

However, there are no obvious xylene sources in the locality of Station B and BTX ratios at the background sampling location for Station B were in the 'normal' range. The roadside results with the most pronounced deviation from the predicted BTX ratios were measured using Tenax, perhaps the lack of field validation for such environmental monitoring could explain the unusual xylene results.

5.4.3 Station C

Ratios of BTX concentrations at Station C were in the range 1 : 1.5 : 1.3 to 1: 2.2 :1.8 across all sampling locations. Mean BTX ratios over the four sampling periods were 1 : 1.8 : 1.3. These ratios are consistent with those suggested by Plant and Wright (1998).

5.5 Comparison of the Mean BTX Concentrations Measured at the Sampling Locations at all Three Service Stations

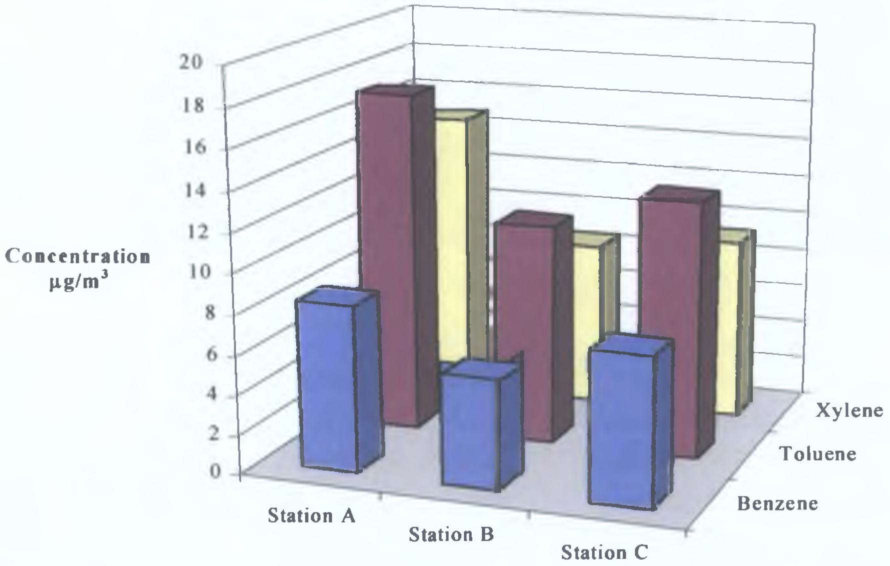
5.5.1 Forecourt Pumps Area

The mean BTX concentrations measured at the Forecourt pumps sampling locations for the three service Stations are shown in Table 28 and Figure 16.

Table 28. Mean forecourt pump area concentrations of BTX at Stations A, B and C.

Compound	**Mean Forecourt Pumps BTX Concentrations (µg/m^3)**		
	Station A	**Station B**	**Station C**
Benzene	8.4	6.1	7.4
Toluene	17.3	11.2	13.0
Xylene	14.8	8.5	9.3

Figure 16. Histogram of mean concentrations of BTX for the three Petrol Service Stations surveyed at forecourt pump sampling locations.



From figure 16 it can be seen that highest mean BTX concentrations were measured in the forecourt pumps area of Station A. Mean BTX concentrations in the forecourt pumps area of Station B were on average 27 to 40% lower. Station C forecourt pumps sampling locations show mean BTX concentrations of between 12 and 37% lower than those measured at Station A, and 10 to 20% higher than at Station B.

It is suggested that the differences observed in the concentrations at the three petrol Stations may be a reflection on the petrol throughput of for each station. This is dependant on the where the service Station is located and the ancillary services offered at the site. Another factor affecting the measured forecourt BTX concentrations may be the topography of the surrounding area, proximity of building structures and possibly the height and extent of the forecourt canopy.

Service Station A is located on a moderately busy road close to several large residential housing estates, approximately 750m north-east of Naas town centre. Traffic lights control a junction within 50m of the forecourt where cars frequently queue. The Station is positioned along a road with tall trees and a tall wall along two boundary lines and little open space. The Station forecourt houses a mini-supermarket, a car sales showroom and a car wash. Two islands house 8 unleaded, 4 leaded and 2 diesel fuel pumps on the forecourt. It is expected that the throughput of fuel and the number of users could be the highest of the three stations studied.

Service Station B is situated on a minor road route, 500m south-west of Naas, for which an alternative by-pass has been introduced in the past 5 – 10 years, the road is considerably less trafficked than those at Station A or Station C. The number of fuel pumps at Station B is 1 unleaded, 1 leaded and 2 diesel, all of which are located on one central forecourt island. The Station is on elevated ground and apart from the small shop there are no buildings to cause any significant wake effects. It is therefore anticipated that the fuel throughput and number of users of the Station is considerably less than for Station A and C.

Petrol Station C is located 200m east of Naas town centre immediately adjacent to a heavily trafficked road. This site is surrounded by commercial properties to the north and west, a large supermarket car park immediately south and a busy road junction 50m to the east. The road junction is controlled by traffic lights and forms part of the main commuter road to Dublin where queuing during peak hour traffic is not uncommon. A medium sized shop is located on the forecourt and the and the Station operates a busy car-wash within 15m of the fuel pumps.

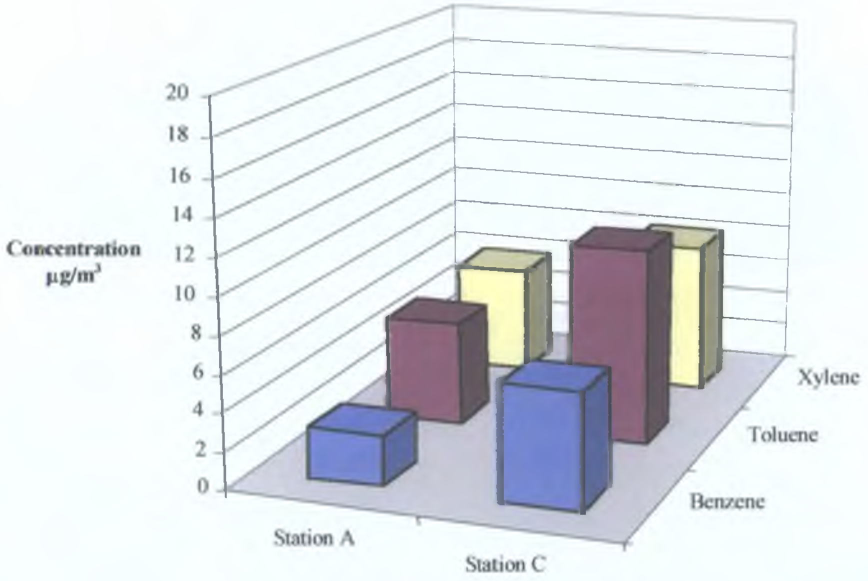
5.5.2 Forecourt Perimeter

The mean BTX concentrations for the forecourt perimeter areas of Stations A and C are presented in Table 29 and Figure 17. No forecourt perimeter results were measured for Station B due to the fact that the forecourt area was not clearly defined, and the absence of suitable sampling locations.

Table 29. Mean forecourt perimeter concentrations of BTX at Stations A and C.

Compound	**Mean Forecourt Perimeter BTX concentrations ($\mu g/m^3$)**	
	Station A	**Station C**
benzene	2.7	6.2
toluene	5.6	10.6
xylene	5.9	8.2

Figure 17. Histogram of mean concentrations of BTX for Stations A and C at forecourt perimeter sampling locations.



Highest mean BTX concentrations were measured at the forecourt perimeter of Station C. These are up to 50% higher than the BTX concentrations measured at Station A. It is suggested that the elevated BTX concentrations measured at Station C may be due to the road junction located in close proximity to the sampling location, in addition to this the sampling location was north-east of the forecourt pumps. The two forecourt perimeter sampling positions at Station A were south-west (upwind) and south east of the fuel pumps at distances of 20 and 30 metres respectively. The prevailing wind direction for the period of the sampling campaign at both stations was from the south-west.

It is therefore suggested that forecourt perimeter concentrations of BTX reported for Station C are higher than those measured for Station A as a direct result of the choice of sampling locations and the characteristics of adjacent roads.

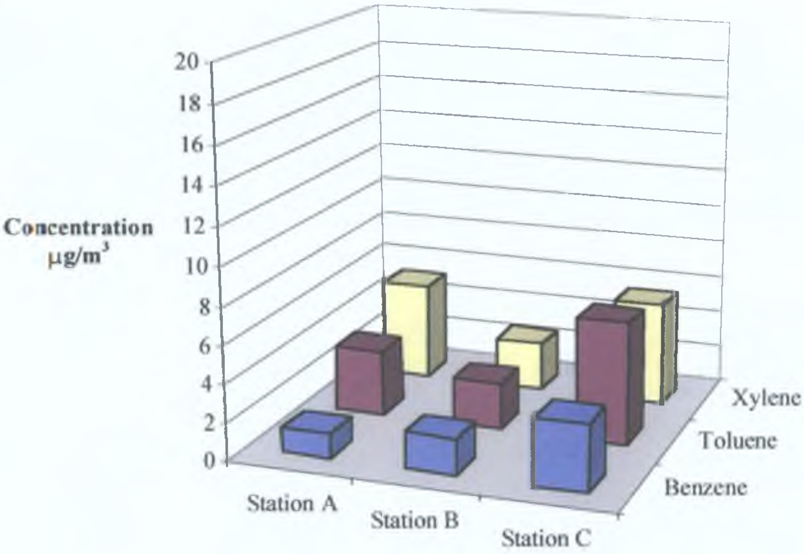
5.5.3 Roadside

The mean concentrations of BTX at roadside sampling locations for the three petrol service Stations are given in Table 30 and Figure 18.

Table 30. Mean roadside concentrations of BTX at Stations A, B and C.

Compound	**Mean Roadside BTX Concentrations (µg/m^3)**		
	Station A	**Station B**	**Station C**
benzene	1.3	1.9	3.5
toluene	3.5	2.5	6.5
xylene	5.2	2.6	5.5

Figure 18. Histogram of mean concentrations of BTX for the three petrol service Stations surveyed at forecourt pump sampling locations.



The roadside sampling locations for all three Stations were approximately 3 to 5 metres from the roadside. Sample tubes were fixed at heights of approximately 3 metres for security purposes. Mean roadside BTX concentrations measured were highest at Station C which is probably due to the traffic patterns for each of the respective roads as previously described. Station C is located close to a large road junction on a heavy commuter route and Stations B and C are located adjacent to more minor routes. At Station A and B the levels measured for benzene and toluene were similar, however, xylene levels at Station A were significantly higher. As previously discussed this is thought to be attributed to another potential source of xylene in the area.

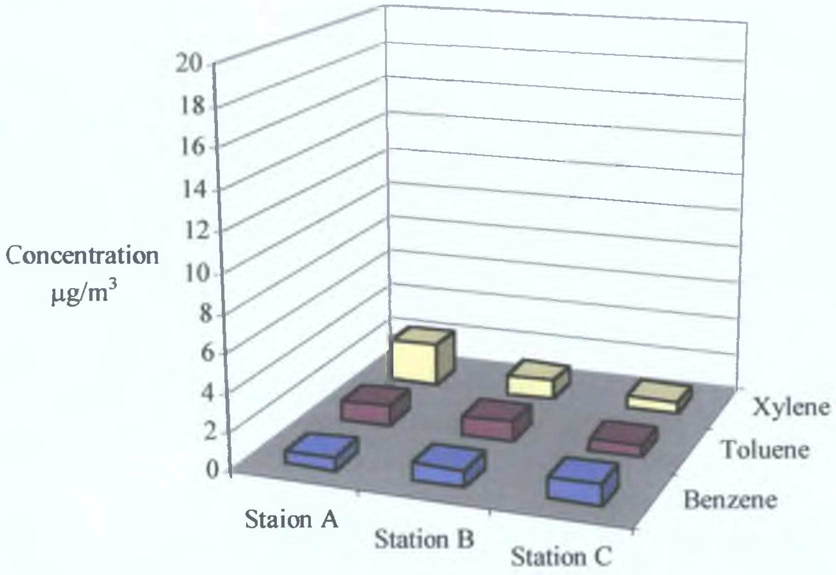
5.5.4 Background

The mean background BTX concentrations measured for the three stations are given in Table 31 and Figure 19.

Table 31. Mean background concentrations of BTX at Stations A, B and C.

Compound	**Mean Background BTX Concentrations ($\mu g/m^3$)**		
	Station A	**Station B**	**Station C**
benzene	0.7	0.9	1.1
toluene	1.0	1.0	0.6
xylene	2.3	1.0	0.6

Figure 19. Histogram of mean background BTX concentrations at Petrol Service Stations A, B and C.



The mean background concentrations of benzene and toluene were approximately 1µg/m^3 for all three stations monitored. The xylene concentrations measured at Stations B and C were also approximately 1µg/m^3, at Station A, however, the mean background xylene concentration measured was 2.3µg/m^3. As discussed previously the suggested reason for the elevated xylene levels is an alternative source of xylene from a nearby industrial installation.

5.6 Comparison of Measured BTX Concentrations with the results of Previous Studies

As outlined in the Literature Review, very few studies currently exist where BTX concentrations have been measured using diffusive sampling in the areas of petrol service stations. Diffusive sampling of ambient air is still developing as a measurement tool, however the data that does exist is very useful when attempting to draw conclusions from the current study. Measured concentrations of BTX are compared to relevant reports of BTX and VOC's in ambient air, and where possible in the vicinity of Petrol Service Stations. Studies carried out by the European Reference Laboratory for Air Pollution (ERLAP) (Perez-Ballesta and De Saeger, 1995; Perez-Ballesta *et al*, 1998*a*; Perez-Ballesta *et al*, 1998*b*; Perez-Ballesta *et al*, 1998*c* provide some of the most useful and comprehensive data published on measurement of BTX in ambient air using diffusive sampling.

Table 32, shows the mean concentrations measured during the current study at petrol Service Stations A, B and C. The results show varying levels of contamination due to sampler location, meteorological conditions and the scale of the Service Station and associated facilities. The average temperature and wind speed over the survey were 6.8°C and 6m/sec respectively, moderately cold with high wind speeds.

Table 32. Mean concentrations of BTX in service areas and background locations for Stations A, B and C.

Compound	**Concentration µg/m^3**	
	background	**service areas of petrol Stations**
benzene	0.3 – 1.4	4.4 - 16.6
toluene	0.2 – 2.9	5.3 – 29.7
xylene	0.4 - 3.5	3.7 – 21.6

As can be seen from Table 32 the mean BTX concentrations in the service areas of the petrol service stations are approximately 5 to 15 times higher than mean levels measured at background locations. These measured BTX concentrations are compared to data obtained from previous similar studies.

5.6.1 Comparison of BTX Concentrations Measured at Petrol Service Stations

Table 33, compares the current study with findings of a study carried out by the European Reference Laboratory for Air pollution (ERLAP) at the Joint Research Centre (JRC), Ispra. The study employed diffusive sampling for the monitoring of BTX in the vicinity of petrol service Stations in two cities (Murcia, Spain and Brussels, Belgium) in 1994. Diffusive sampling was carried out using PE ATD tubes packed with Chromosorb 106, sampling periods were of two weeks duration. Sample periods were therefore significantly longer than those for the current study, this may be significant as the uptake rates have been found to deviate with substance dose. However, the uptake rates used had been determined experimentally at environmental levels for a two-week exposure period. Sample analysis was carried out using thermal desorption followed by a gas-chromatographic determination. Analytical conditions used in both studies were very similar.

Table 33. Average concentrations ($\mu g/m^3$) measured for one-month sampling period in the vicinity of the petrol service Stations and background areas.

	Naas		**Murcia**		**Brussels**	
Compound	**background**	**service area**	**background**	**service area**	**background**	**service area**
benzene	0.9	4.4 - 16.6	12	33 - 187	9	21 - 71
toluene	1.0	5.3 – 29.7	34	78 - 325	13	30 - 113
xylene	1.3	3.7 – 21.6	19	44 - 142	5	14 - 33

The average temperature and wind speed recorded in Murcia were 20°C and 1.7m/sec, respectively and 12°C and 3.5m/sec in Brussels. These temperatures are significantly higher and the wind speeds are significantly lower than those recorded during the current study. A change in temperature from 5 to 35°C leads to an increase in the concentration of benzene in the gas phase by a factor of three (Owen, 1990). Conditions at Murcia and Brussels therefore favoured higher evaporative emission rates and slower dispersion of the vapours than at Naas, and may help explain the higher measured BTX concentrations. Also petrol Stations in Murcia and Brussels were studied in 1994 when the fuel composition would have differed from that currently in use in Ireland. The average benzene content of petrol sold in the EU in

1996 was over 2.5%. The benzene content of petrol has been systematically reduced over the past number of years and is to be less than 1% by 1st January 2000 (CEC, 1998).

Background BTX measurements at Murcia and Brussels were significantly higher than those measured in Naas, this may be due to the size of the towns/cities studied and the selection of background sampling locations. Naas is a relatively small town with large sub-urban housing estates, whereas Brussels and Murcia are large cities. Elevated background concentrations in Murcia and Brussels are due to the size of the conurbation and background levels were measured on busy streets. However, airborne concentrations of aromatic compounds BTX in the forecourt service area of petrol Stations studied in Murcia, Brussels and Naas were all found to be approximately 5 to 15 times higher than respective background levels measured.

The ratios of BTX concentrations measured in the two studies were also comparable with a benzene : toluene ratio ranging between 1 : 1.6 to 1 : 5 for the ERLAP study and 1 : 1.3 to 1 : 3.2 for the current study.

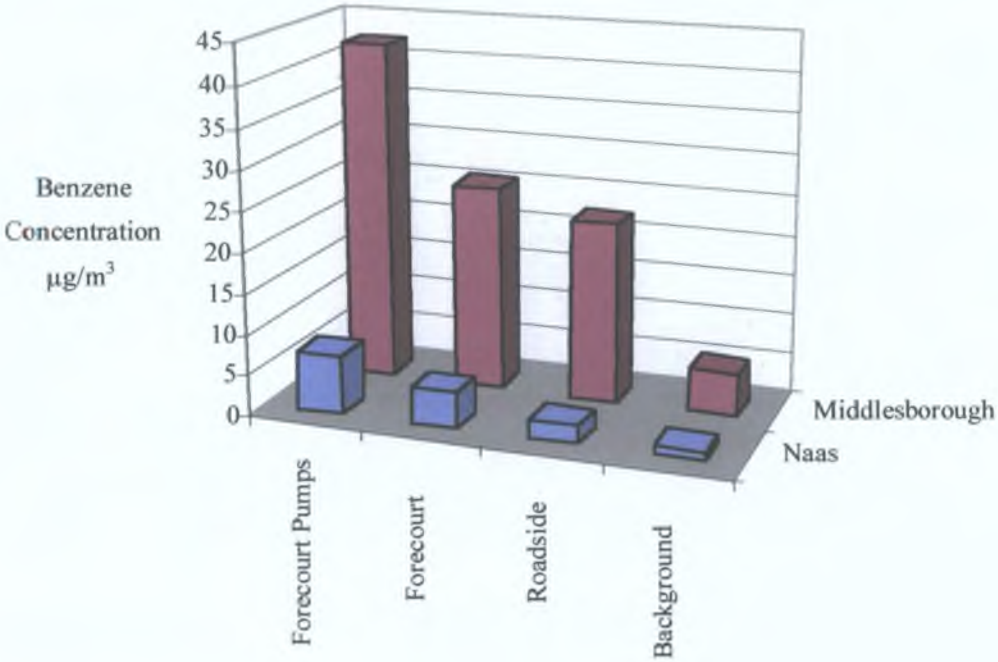
A study carried out in Middlesborough, England (Cram and Little, 1995) used diffusive samplers to measure benzene concentrations around two petrol service Stations. The survey used diffusive samplers used were PE ATD tubes packed with Tenax exposed for periods of 48 hours.

The mean benzene concentrations measured in the current study are compared to those from Middlesborough over the range of sampling locations in Table 34 and Figure 20.

Table 34. Mean airborne benzene concentrations (μg/m^3) near petrol Stations in Middlesborough and Naas.

Sampling Location	Naas	Middlesborough
Forecourt Pumps	7.3	42.1
Forecourt Perimeter	4.5	25.4
Roadside	2.2	22.2
Background	0.9	5.2

Figure 20. – Histogram showing mean benzene concentrations at petrol service Stations in Middlesborough and Naas.



Benzene levels were in the same rank order for both studies with the highest mean levels recorded at the forecourt pumps and the lowest at the background locations. The airborne benzene concentrations measured in the Middlesborough study were significantly higher than those found for the Stations in Naas. The mean concentration of benzene measured at the forecourt pumps of the Middlesborough Stations was 42.1µg/m^3, over 5 times higher than the current study in Naas, 7.3µg/m^3. The mean roadside benzene concentration measured in Naas was approximately 10 times lower than the Middlesborough roadside levels reported. Cram and Little do not provide details of the sampling locations in relation to their height above ground, distance from roadside and protection from precipitation. No meteorological data is supplied for the monitoring period and no account is taken of the scale of the Stations monitored, their operating hours or quantities of fuel sold.

A number of factors may contribute to the different concentrations measured in the two studies such as the adsorbent material used, exposure time of samplers and compositional differences in fuel composition. The benzene content of the fuel sold in 1994 was higher than that currently sold in Ireland (CEC, 1998).

5.6.2 Comparison of BTX Concentrations Measured at Background Sampling Locations

The overall mean background BTX concentrations measured in the current study are 0.9, 1.0 and 1.3μg/m^3, respectively. These concentrations were recorded at sites which would be classified as sub-urban. These are compared to background urban concentrations reported in previous studies (Table 35 and Figure 21). All studies used diffusive sampling, using various adsorbent materials and thermal desorption with a gas chromatographic determination. The different adsorbent materials used in the studies were; Dublin (EPA, 1997) – Tenax; Gothenburg (Hafkenscheid and Mowrer, 1996) selection of adsorbent materials, but primarily Tenax; Bologna (Perez-Ballesta *et al*, 1998*c*) – Carbopack-B; United Kingdom (Plant and Wright, 1997) – Chromosorb 106 and Carbograph TD-1; Brussels and Murcia (Perez-Ballesta and De Saeger, 1995 – Chromosorb 106.

The sampling and analysis for each study was similar, the fundamental differences were in the selection of adsorbent materials. Perkin-Elmer tube-type diffusive samplers were used for each study with the exception of the monitoring programme at Dublin (EPA, 1997), for this study a purge and trap apparatus was adapted to perform thermal desorption and the size of the tube for diffusive sampling was therefore different. This geometrical difference has implications on the diffusive uptake rates for this sampler for BTX.

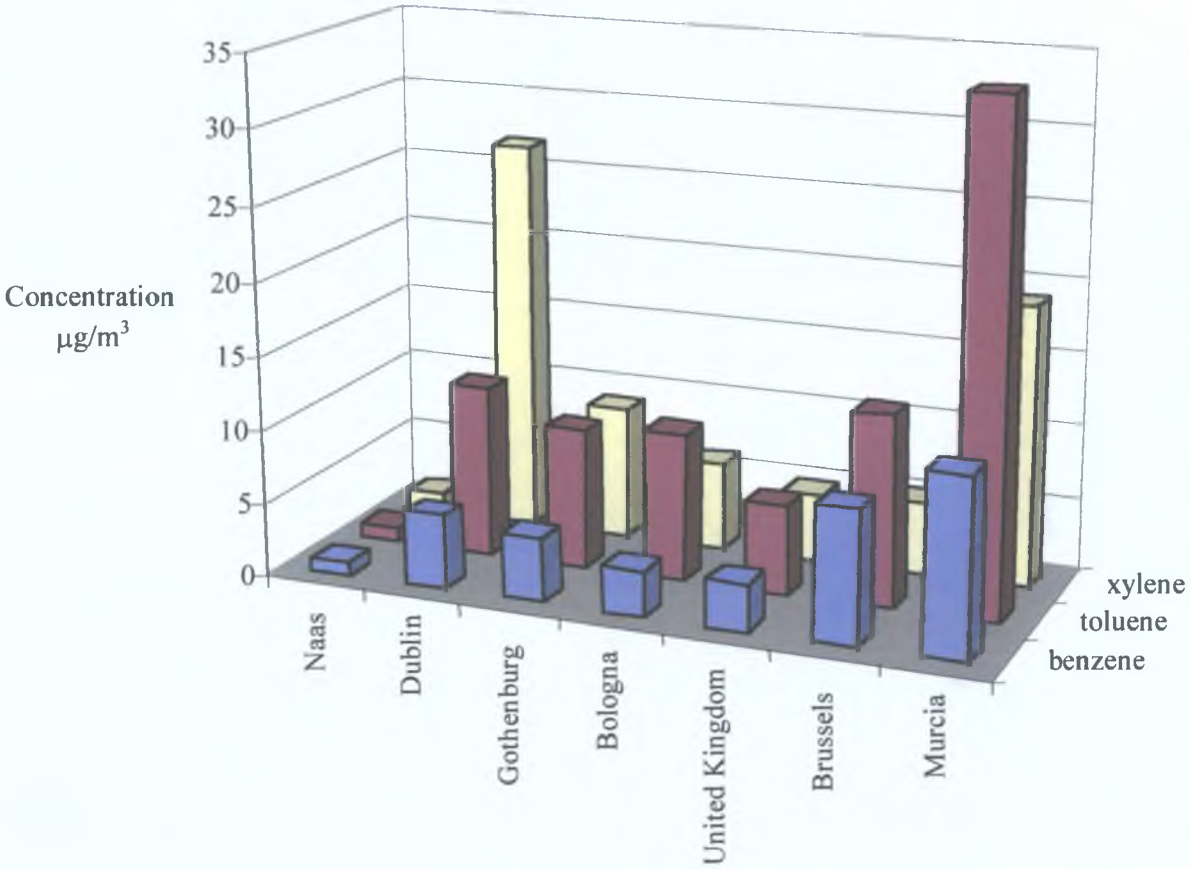
Table 35. Background concentrations of BTX measured using diffusive samplers at various locations across Europe.

	benzene	toluene	xylene
Naas	0.9	1.0	1.3
Dublin	5.0	11.7	26.7
Gothenburg	4.3	9.6	9.1
Bologna	3.1	10.1	6.0[1]
United Kingdom (Nation-wide)	3.2	6.1	4.6[2]
Brussels	9	13	5[2]
Murcia	12	34	19[2]

[1] m+p-xylene

[2] m-xylene

Figure 21. Background concentrations of BTX measured using diffusive samplers at various locations across Europe.



The highest background benzene and toluene concentrations were recorded in the city of Murcia, Spain in 1995 (Perez-Ballesta and De Saeger, 1995) and the highest reported xylene concentrations were for Dublin, Ireland (EPA, 1997). This may be due to the fact that the baseline VOC survey of Dublin measured all three isomers of xylene. In addition to this, the twenty sampling sites selected for Dublin were focused on heavily trafficked locations. The BTX concentrations measured at background sub-urban locations in the town of Naas were the lowest of the background BTX concentrations recorded of all the studies discussed.

5.6.3 Comparison of Active Sampling Results with Concawe Report

The BTX concentrations measured around the forecourt of Station C over a four hour period are presented in Table 16, in the results section. The highest benzene concentrations (22.6 and 21.4μg/m^3) were detected at the forecourt pumps locations and the lowest levels were detected at the background sampling location (< 1μg/m^3). Concawe (the oil companies European organisation for environment, health and safety) carried out a study of concentrations of benzene around service Stations and distribution terminals in nine countries in Europe in 1994. The monitoring was carried out by pumping a known volume of sample air through ATD tubes packed with Chromosorb 106 with subsequent analysis by thermal desorption and gas chromatography. The active sampling exercise in the current study was carried out in an identical manner. The results of the Concawe report are summarised in Table 36.

Table 36. Summary of benzene concentrations measured over 24 hours around a Petrol Service Station (Concawe, 1994).

Sample Position	Range of Results (μg/m^3)	Mean Result (μg/m^3)
Background	1.6 – 38.1	8.2
Traffic Only (roadside)	2.6 – 52.7	14.2
Downwind Boundary (Traffic plus forecourt)	7.3 – 91.1	20.6
Boundary	1.8 – 119.0	15.4

The results of the Concawe report are not readily compared with the current study as the sampling locations were changed as the wind direction changed for the Concawe study. In addition to this, the sampling was performed over a twenty-four hour period, whereas at Station C sampling duration was four hours. The Concawe study measured benzene concentrations of up to 119μg/m^3 at boundary locations, approximately 10 times higher than any boundary concentration measured during the current study. This may be attributed to the sampling methodology employed whereby samples were relocated to remain downwind as the wind directions changed and the fact that the study was conducted in 1994 when the benzene content of petrol being used in the EC was considerably higher than current levels.

5.7 Comparison of Measured Concentrations with Limit and Guideline Values

5.7.1 Diffusive Monitoring

The three model study sites selected for this measurement campaign were sampled using four consecutive one-week sampling periods. The proposed limit value for benzene is set as 5μg/m^3 as an annual average. Whilst the weekly data obtained in this study cannot be compared directly to any Air Quality Standard that is based on an annual average concentration, they are anticipated to be indicative of the weekly mean concentrations that can occur.

The mean ambient air benzene concentration measured in the forecourt pumps areas over all three Stations studied was 7.3μg/m^3, approximately 50% higher than the proposed annual limit value for the compound. Several of the values measured at the forecourt pumps areas of the three stations were more than double the proposed limit value. A benzene concentration over three times the proposed limit value (16.6μg/m^3) was detected in the forecourt area of Station A during the second sampling period of the study. These concentrations were made over two periods for which average wind speeds were in excess of 5m/sec. Benzene concentrations in excess of the limit value may therefore be expected to develop in the forecourt pumps area during periods of suitable meteorological conditions. However, the introduction of petrol containing less than 1% benzene in the year 2000 should lead to a reduction in forecourt concentrations of benzene.

At the forecourt perimeter the mean benzene concentration measured was 4.5µg/m^3, approximately 90% of the proposed limit value. The highest forecourt perimeter concentration of benzene measured was 7.0µg/m^3 at Station B, a concentration 40% higher than the proposed limit value. This suggests that under favourable conditions the benzene in air concentrations at forecourt perimeter locations may exceed the proposed limit value of 5µg/m^3. However, it is anticipated that for the three sites studied the annual average would be below 5µg/m^3 and any observed exceedances would be of short duration. A number of factors will assist in lowering the levels measured at the forecourt pumps and perimeter locations:

(i) the introduction of petrol containing less than 1% benzene, and

(ii) the implementation of S.I. 374 of 1997

Mean roadside benzene concentrations were 2.2µg/m^3, a value approximately 50% lower than the proposed limit value. These values are expected to remain relatively constant depending on the prevailing meteorological conditions. Roadside concentrations of benzene would therefore not be expected to exceed the proposed limit value. Background concentrations of benzene were approximately 1µg/m^3, and it is thought unlikely that these locations would experience benzene concentrations in excess of the proposed limit value. Therefore, the areas where benzene concentrations are most likely to exceed the proposed limit value are at the forecourt pumps and perimeter areas.

The highest toluene concentration measured for the diffusive monitoring campaign at the three study sites was 29.7µg/m^3 at the forecourt pumps of Station A during the second sampling period. The WHO guideline value for toluene is 260µg/m^3, and is set over a one-week averaging time. The highest value measured is therefore approximately 11% of the WHO guideline value. This suggests that the petrol service stations monitored during this study are unlikely to exceed the guideline value under 'normal' conditions.

5.7.2 Active (Pumped) Sampling

It is difficult to relate benzene concentrations measured during a four-hour sampling period to the proposed limit value, which is set as an annual average. The four-hour grab sample can not be taken as representative of the annual mean for a number of reasons. Sampling was carried out over a four-hour period during which the Station was in continuous operation and petrol vapour emissions were on going. Therefore, this grab sample has taken no account of periods during which there are no emission occurring. As the station is closed for business for approximately 33% of the 24 hour period the grab sample is readily identified as being unrepresentative of the annual average. The grab samples analysed do provide some useful data e.g. when used to determine daily maximum and minimum concentrations and study diurnal variations in measured concentrations.

Active (pumped) sampling was carried out at Station C at forecourt pumps, forecourt perimeter, roadside and background sampling locations. The observed rank order of measured benzene concentrations was forecourt pumps > forecourt perimeter > roadside > background as previously discussed. The benzene concentration measured at the forecourt pumps was 22μg/m^3 (mean of two measurements). The associated toluene concentration measured was 37.2μg/m^3 (mean of two measurements).

Chapter 6. Conclusions

The main aim of this work was to use diffusive sampling to measure ambient air concentrations of benzene in the vicinity of petrol service stations. An ambient air sampling campaign was designed and undertaken during winter 1998-1999 at various locations around three petrol service stations; forecourt pumps; forecourt perimeter; roadside and background. The diffusive sampling tubes used were Perkin-Elmer ATD tubes packed with Chromosorb 106. At one station (B) tubes packed with Tenax were sampled along side the Chromosorb 106 tubes, this enabled the results generated by the two adsorbent materials to be considered and compared.

- Mean weekly BTX concentrations measured using diffusive sampling occur in a rank order; forecourt pumps > forecourt perimeter > roadside > background.
- Concentrations of BTX measured in the ambient air in the forecourt services areas of the petrol service stations studied were 5 to 15 times higher than background levels measured.
- The forecourt concentrations of BTX measured may be related to the size of the station, the number of fuel pumps, the throughput of fuel, the vapour recovery control measures in place at the station and the prevailing meteorological conditions. The BTX concentrations measured at forecourt perimeter locations may be dependent on the sampling position relative to the forecourt pumps and the wind direction.

- The ratios of measured BTX concentrations, in the approximate range 1 : 1.3 : 1.2 to 1 : 2.2 : 2.0, were consistent with previous studies of urban ambient air. BTX ratios observed at one background sampling location were not as previously observed and this may be due to a potential elevated local source of xylene.
- BTX concentrations determined over a four-hour active sampling period were higher than those recorded for the diffusive sampling over a one-week period, due to the fact that the station was in continuous use throughout sampling. The rank order of sampling locations observed was the same as for diffusive sampling.
- The mean benzene concentrations in the forecourt pumps area of the three petrol service stations monitored was 7.3μg/m^3, approximately 50% higher than the proposed EU limit value (5μg/m^3) which is set as an annual average. Mean benzene concentrations at all other sampling locations were below this value. Mean weekly toluene concentrations measured at all sampling locations were significantly less than the WHO weekly guideline value of 260μg/m^3.
- No significant difference was detected in benzene concentrations measured using Chromosorb 106 and Tenax while toluene and xylene concentrations differed significantly.
- The diffusive sampling technique can provide high quality quantitative measurements of BTX in ambient air down to sub μg/m^3 (sub ppb) levels at a fraction of the costs of other pumped sampling or in-situ instrumental techniques. Diffusive samplers can therefore, be used in high numbers to provide coverage at a larger number of sampling locations. In addition, they give long-term averages, which are more consistent with the proposed EU limit value which is set on an yearly basis.

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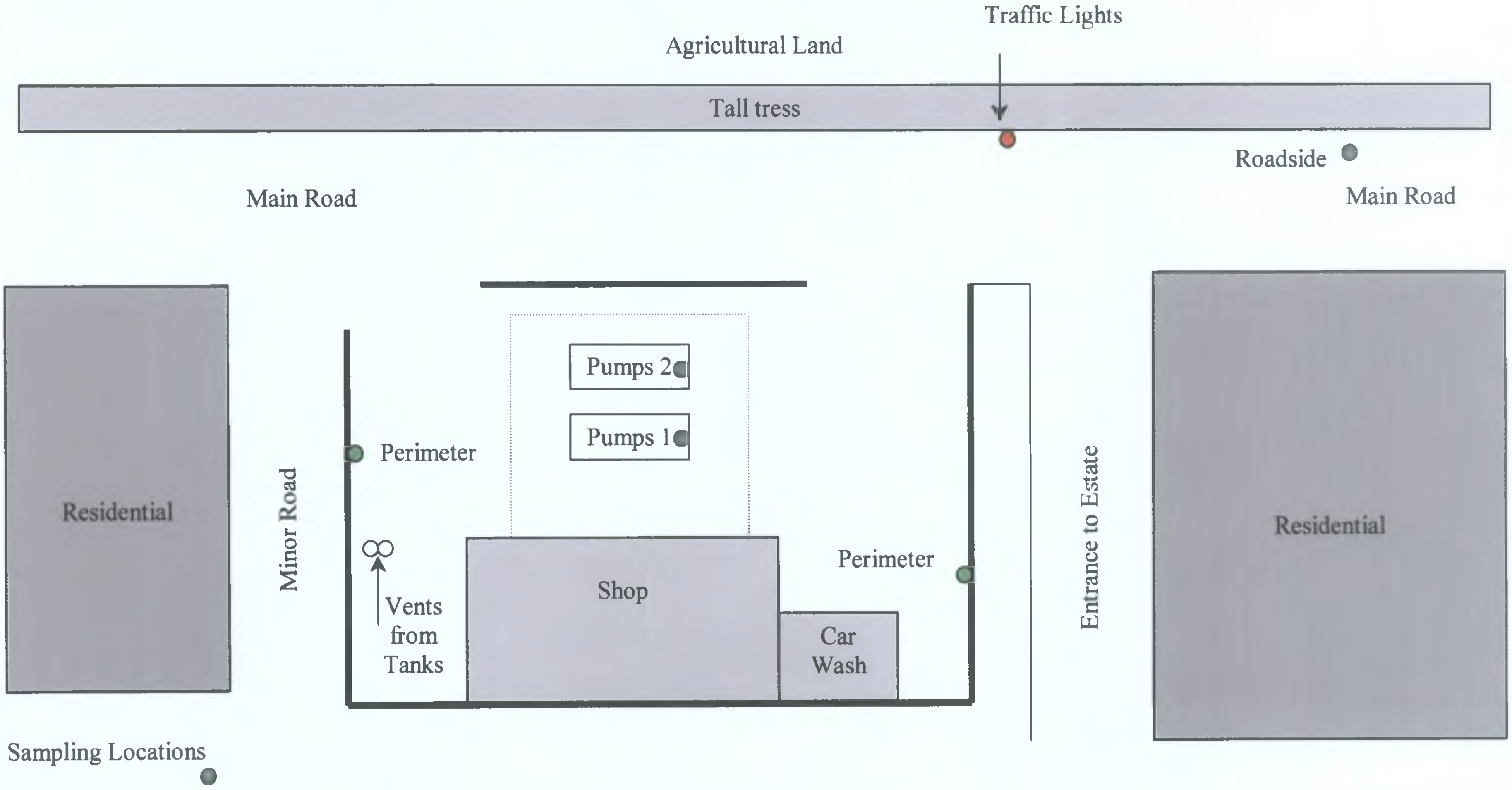
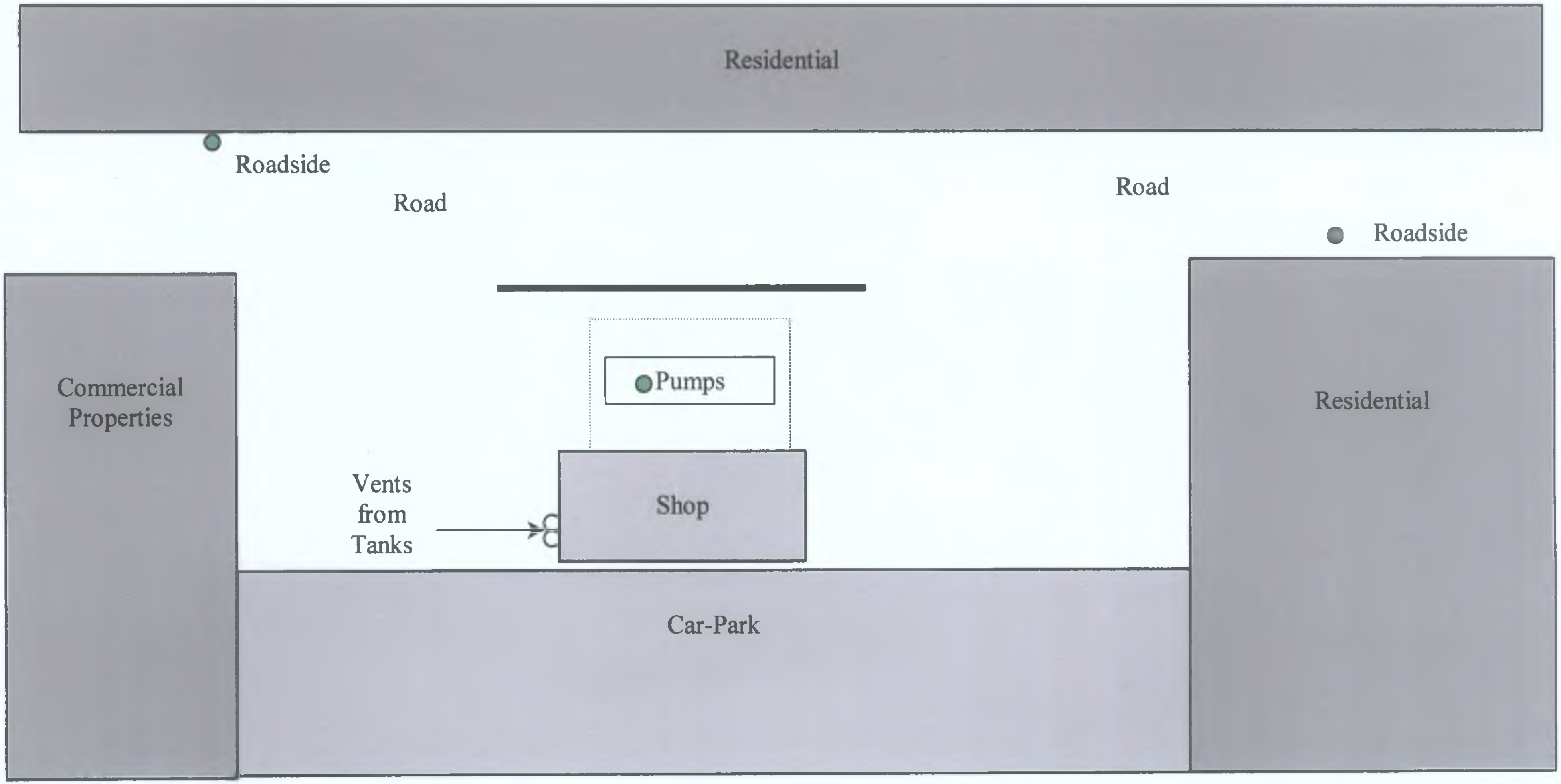
Appendices

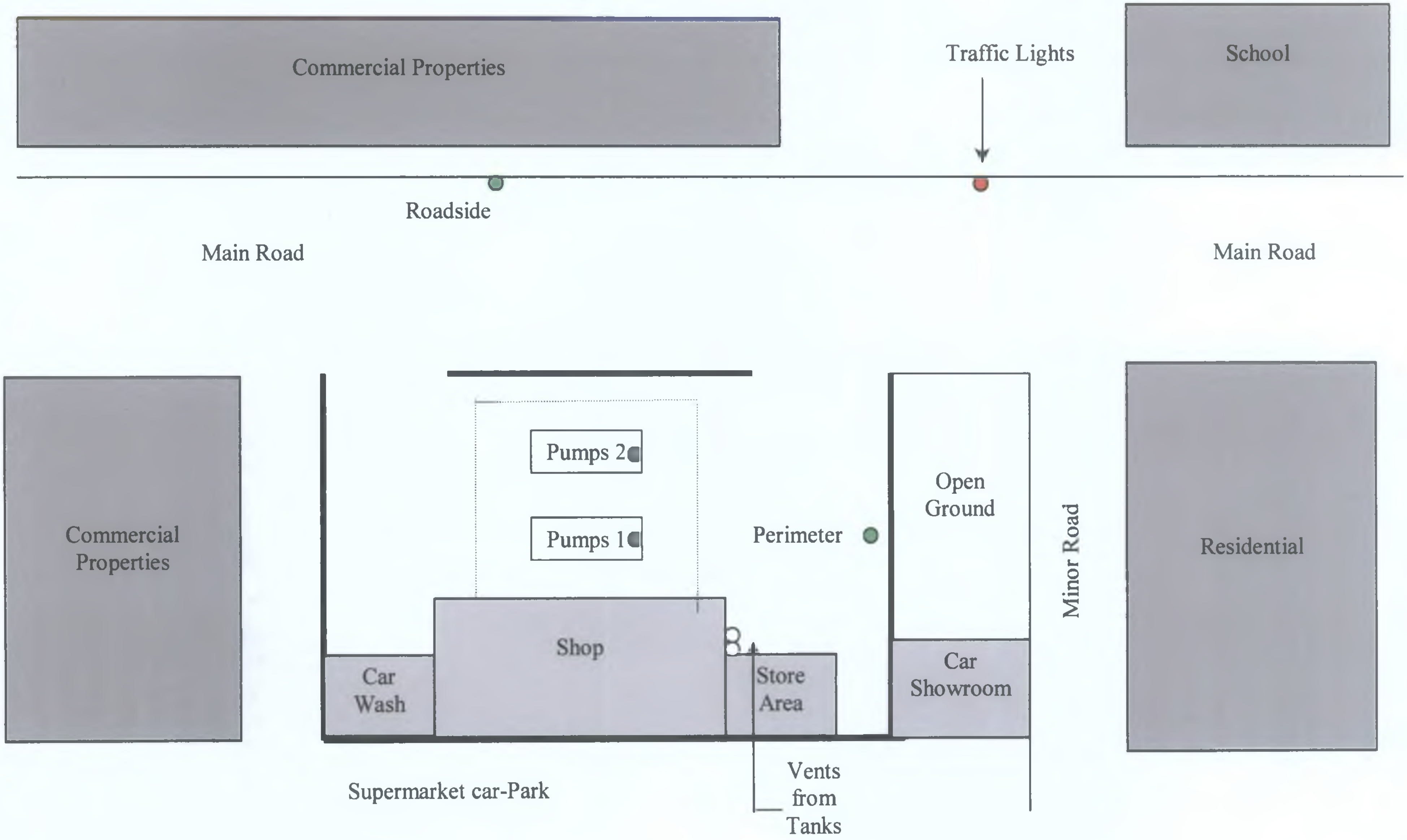
Appendix 1a. Layout of Petrol Service Station A and Sampling Locations (not to scale).



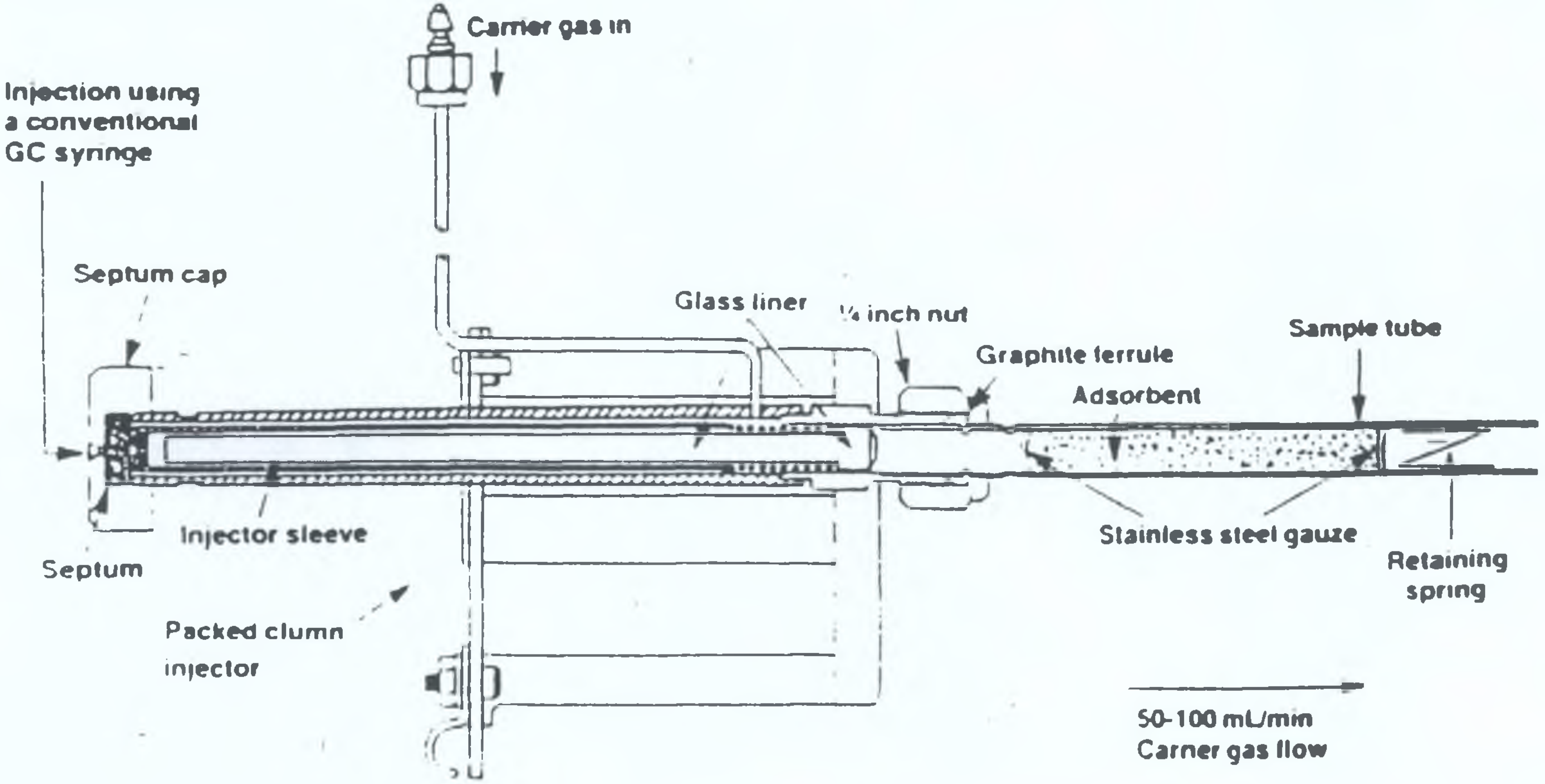
Appendix 1b. Layout of Petrol Service Station B and Sampling Locations (not to scale).



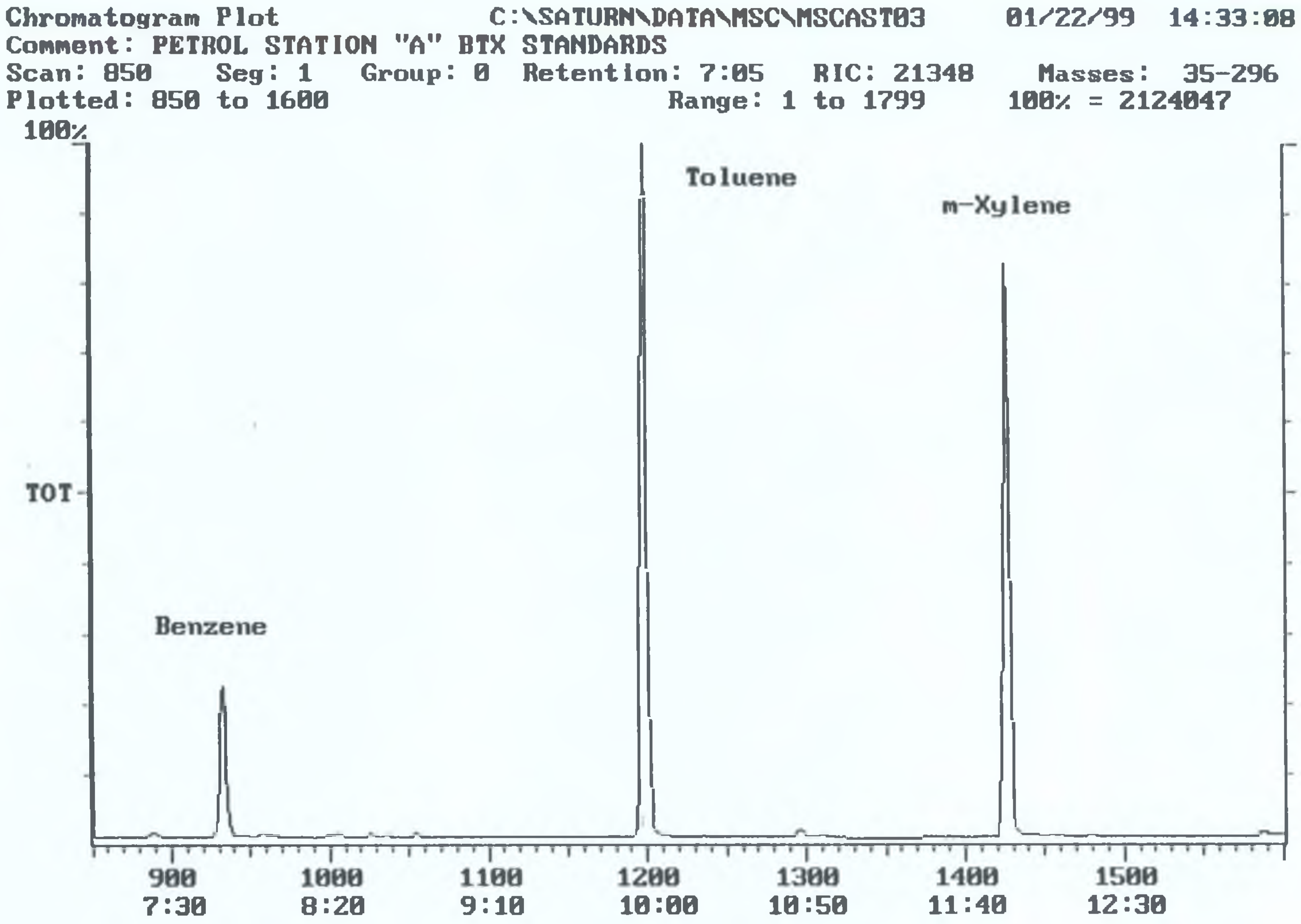
Appendix 1c. Layout of Petrol Service Station C and Sampling Locations (not to scale).



Appendix 2. System for the introduction of calibration standard onto adsorbent tube via modified packed column gas chromatograph injector.

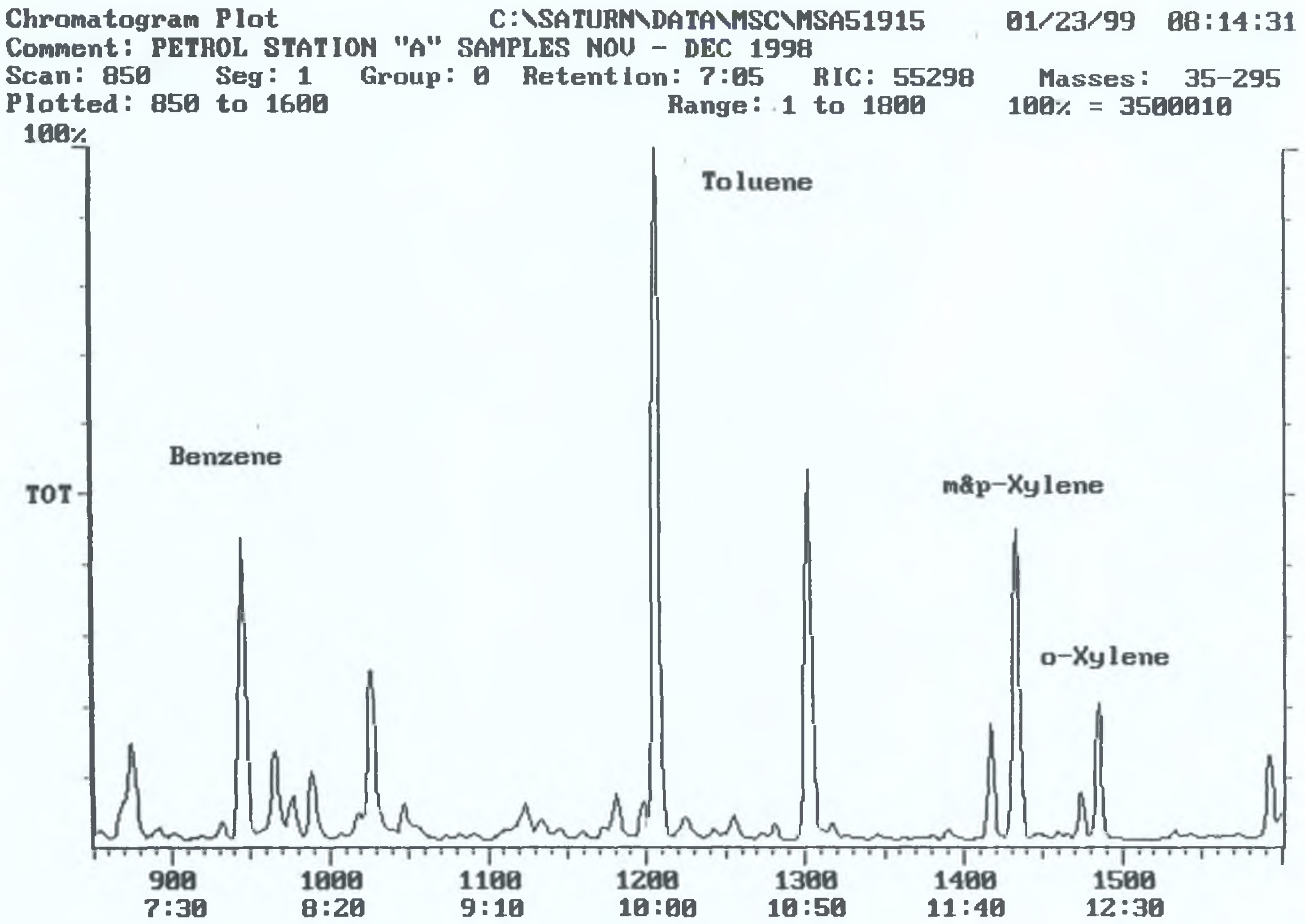


Appendix 3a. Standard chromatogram showing benzene, toluene and m-xylene peaks.



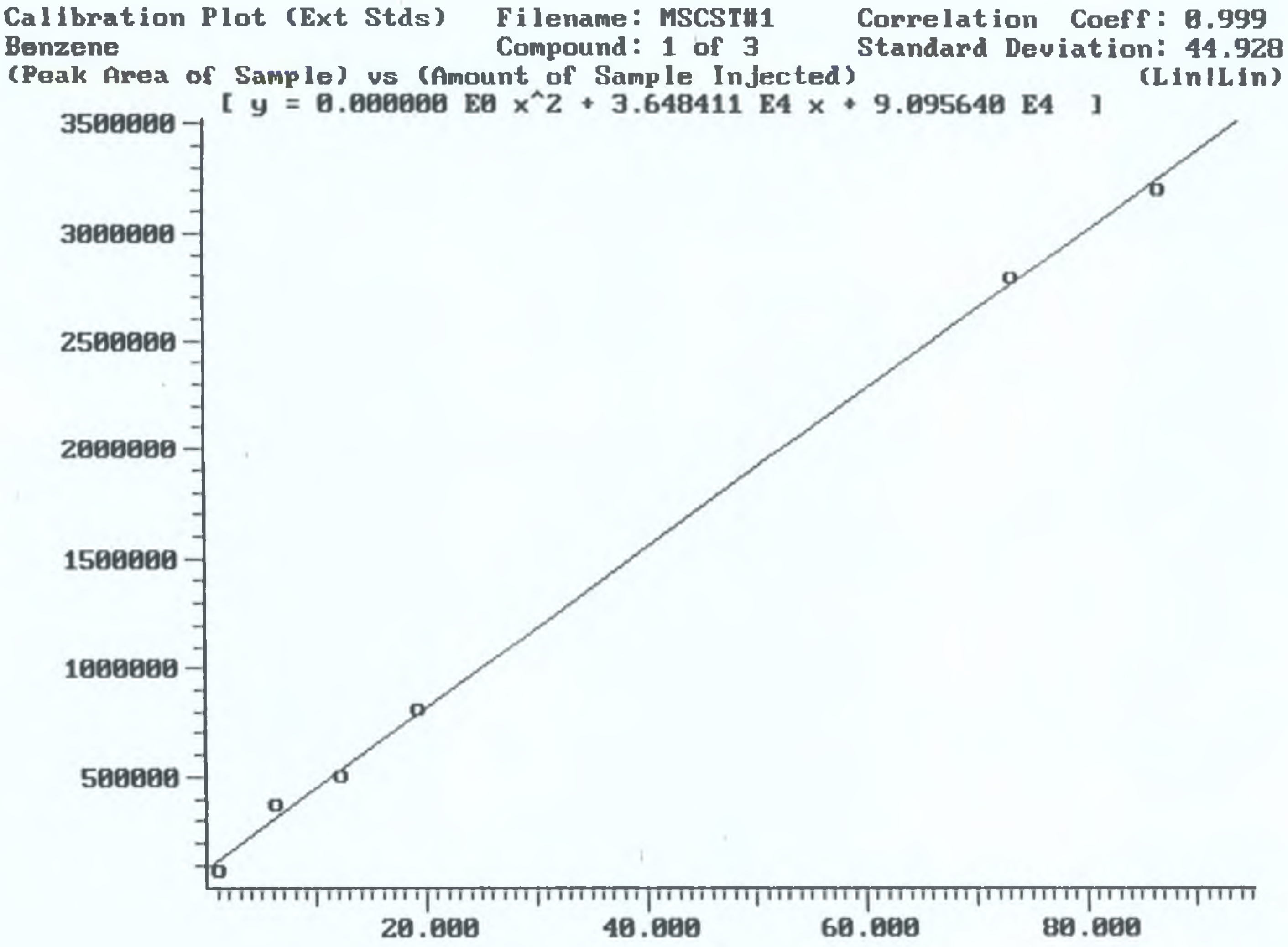
```
Chromatogram Plot              C:\SATURN\DATA\MSC\MSCAST03      01/22/99  14:33:08
Comment: PETROL STATION "A" BTX STANDARDS
Scan: 850    Seg: 1   Group: 0  Retention: 7:05   RIC: 21348    Masses:  35-296
Plotted: 850 to 1600                        Range: 1 to 1799     100% = 2124047
```

Appendix 3b. Sample chromatogram showing benzene, toluene and xylene peaks.



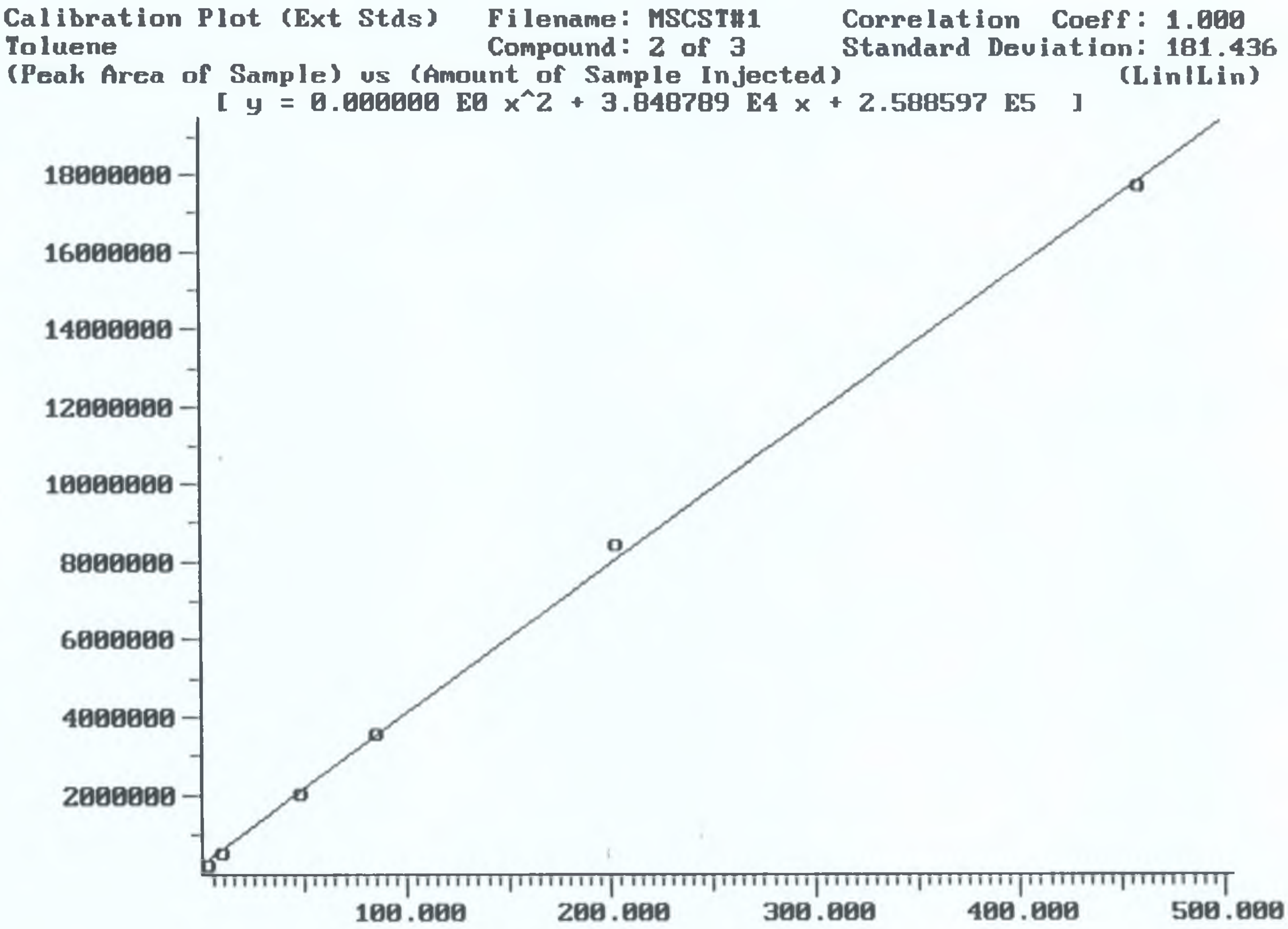
```
Chromatogram Plot               C:\SATURN\DATA\MSC\MSA51915     01/23/99  08:14:31
Comment: PETROL STATION "A" SAMPLES NOV - DEC 1998
Scan: 850    Seg: 1   Group: 0  Retention: 7:05   RIC: 55298    Masses:  35-295
Plotted: 850 to 1600                          Range: 1 to 1800     100% = 3500010
```

Appendix 4a. Benzene calibration curve.



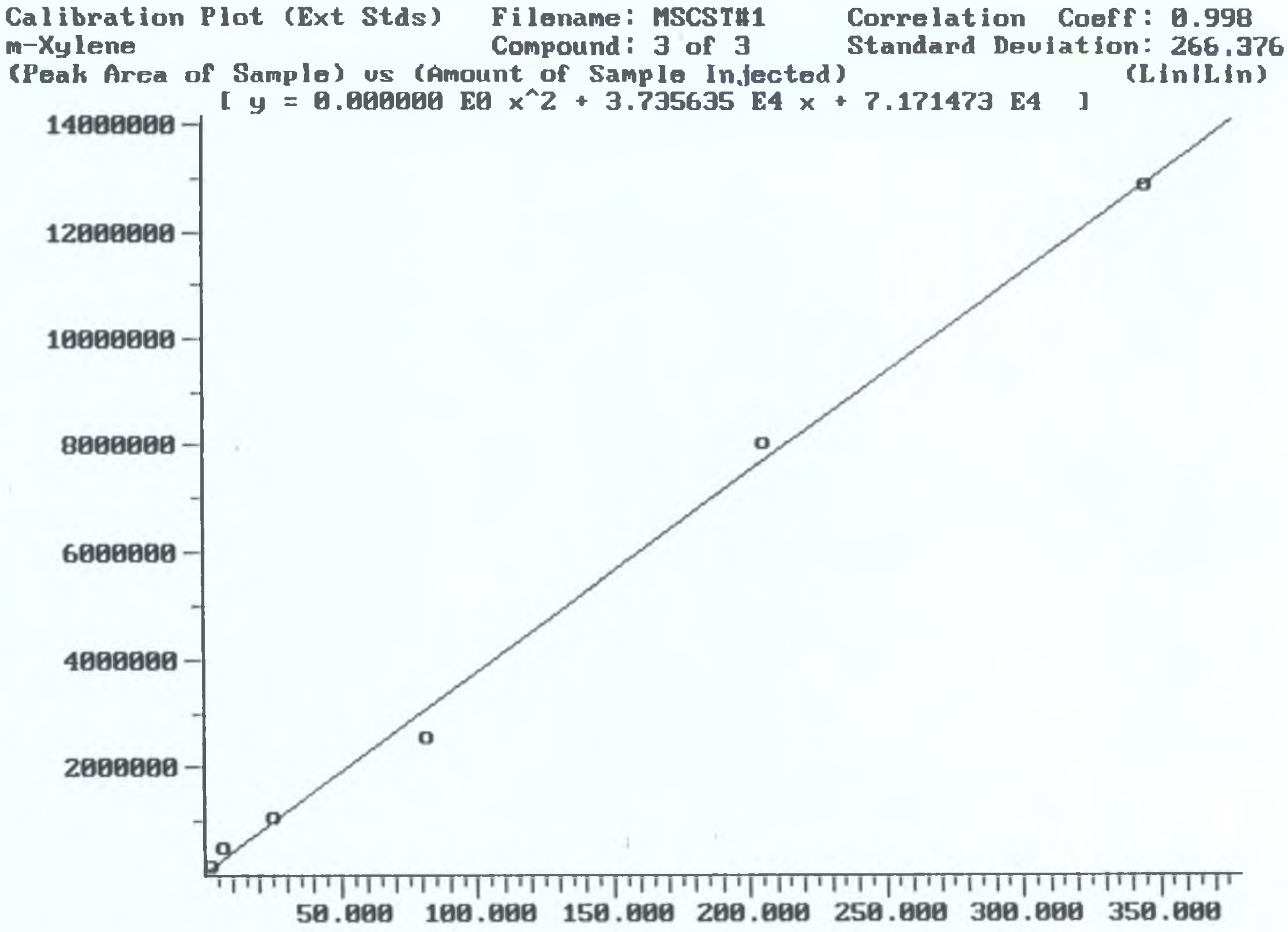
```
Calibration Plot (Ext Stds)    Filename: MSCST#1     Correlation  Coeff: 0.999
Benzene                        Compound: 1 of 3      Standard Deviation: 44.928
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin|Lin)
          [ y = 0.000000 E0 x^2 + 3.648411 E4 x + 9.095640 E4   ]
```

Appendix 4b. Toluene calibration curve.



```
Calibration Plot (Ext Stds)   Filename: MSCST#1     Correlation  Coeff: 1.000
Toluene                       Compound: 2 of 3      Standard Deviation: 181.436
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin|Lin)
             [ y = 0.000000 E0 x^2 + 3.848789 E4 x + 2.588597 E5  ]
```

Appendix 4c. m-Xylene calibration curve.



Calibration Plot (Ext Stds)   Filename: MSCST#1   Correlation Coeff: 0.998
m-Xylene   Compound: 3 of 3   Standard Deviation: 266.376
(Peak Area of Sample) vs (Amount of Sample Injected)   (Lin|Lin)
[y = 0.000000 E0 x^2 + 3.735635 E4 x + 7.171473 E4]

Appendix 5. Mass spectrum of 4-bromoflurorbenzene (BFB), mass spectrometer 'tune' compound.