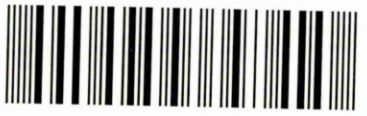

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Air Quality Assessment and the use of Specific Markers to Apportion Pollutants to Source.

By

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A thesis submitted in partial fulfilment of the requirements of Sheffield Hallam University for the degree of Doctor of Philosophy.

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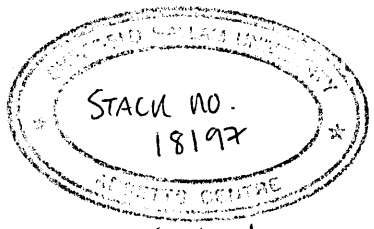

LEVEL 1

Abstract.

The contributions of specific polluting sources to both indoor and outdoor atmospheric pollution are difficult to determine, as solid and gaseous products from different combustion sources are often similar. Sometimes, however, a marker compound can be identified that is unique to a pollution source (or at least not present in most other local combustion sources) and which will allow assessment of the contribution of that source to total atmospheric pollution.

The aim of this study was to identify suitable marker compounds and methods for the apportionment (assessment of percentage contribution) of specific sources to atmospheric pollution. The sources selected were diesel exhaust emissions in outdoor, and environmental tobacco smoke (ETS) in indoor environments. Studies with controlled (laboratory) atmospheres would be followed by field studies using these methods and markers to produce apportionments for these sources to air pollution in selected environments. Initial analysis of such polluting sources was therefore the qualitative analysis of volatile compounds and particulate associated material, both organic and inorganic. Volatile organic compounds were adsorbed onto various resins, while particulate material was sampled onto various filter paper types. Organics were determined by GC-AED and GC-MS, and elements by ICP-MS.

1-Nitropyrene was identified as a suitable marker for diesel particulate emissions (≤5μm). A large volume air sample from Sheffield city centre using 1-nitropyrene as a marker suggested that 63% of atmospheric particulate material (≤5μm) might be of diesel origin. However the concentration of 1-nitropyrene is low in atmospheric samples, and in the volumes used in routine sampling the amount of 1-nitropyrene was below the limit of detection on the instrument used. In an alternative approach the aliphatic alkane tetracosane (C24) was used as a diesel marker for urban air, with a 1-nitropyrene:tetracosane ratio derived from the average results from laboratory experiments with a diesel engine running at various speeds and loads. This approach yielded apportionment values ranging from 5-85% for the diesel contribution to particulate material (≤5μm) in the urban air of Sheffield. No volatile marker compound was found for diesel apportionment.

The contribution of ETS to atmospheric pollution has previously been estimated from the measurement of respirable suspended particulates (RSP), which was superseded by total UV absorbance and total fluorescence of a methanol extract. More recent work has suggested the use of solanesol or scopoletin as marker compounds. This thesis shows that the non specific methods overestimated the particulate contribution of ETS in some atmospheres, and that solanesol is a better marker compound than scopoletin. Preliminary studies from a small number of smokers homes and offices, with solanesol as a marker compound for particulate ETS, indicated that ETS contributions to total particulate material (≤5μm) ranged from 6 to 49% in homes and 11 to 28% in offices.

Pyrrole was used as a marker for ETS contribution to volatile organic pollution, and studies with controlled atmospheres with a smoking machine allowed calculation of the ratios of pyrrole to other volatile organic compounds (VOC's) in ETS. Samples from the field study were used to produce apportionment percentage levels of benzene, toluene, o-xylene and p+m-xylene associated with ETS.

In addition the use of tree bark as a atmospheric sink for airborne particulates was investigated. Six nitrated polycyclic aromatic hydrocarbons associated with diesel emissions were quantified in bark extracts and levels of these were found to be highest during winter months.

.....and the scientist panned through it like a prospector crouched over a mountain stream, looking for the gold of knowledge among the gravel of unreason, the sand of uncertainty and the whiskery eight-legged swimming things of superstition.

"Witches Abroad", Terry Pratchett.

Dedicated to Mum and Dad (I followed the carrot!), Hazel (without whom, this would not have been bearable), Nick, Sue ,Gill (and families) and the boys (you know who you are!) many thanks for the continuous support and encouragement during my lengthy career in education.

1. Introduction.

The Royal Commission on Environmental Pollution defined pollution as:-

"The introduction by **MAN** into the environment of substances or energy liable to cause hazard to human health, harm to living resources and ecological systems, damage to structure or amenity or interference with legitimate use of the environment"(1).

Pollution is deemed to include products from the combustion of carbonaceous material, be it for energy production (oil, coal and gas), transport propulsion (petrol, diesel and kerosene) or from waste disposal. These are known as anthropogenic sources of pollution. Emissions from naturally occurring events including volcanic eruptions, vegetation or the decay of natural material are not deemed to be pollution in this context. Naturally occurring emissions are known as biogenic sources.

Air pollution includes any airborne material such as solid (particulate material), liquid (aerosols) and gases. Once emitted into the atmosphere, the organic material can be transformed chemically and/or physically prior to producing environmental damage. Such atmospheric reactions include :-

Photochemical formation of ozone from hydrocarbons.

Formation of acid rain from SO_2/NO_2 and rain water.

Other visible pollution phenomena include :-

Soiling of buildings by particulate material.

Respiratory damage by acidified aerosols.

Pollution can include highly toxic molecules often at trace levels which can have a direct effect on individuals, as well as pollution which can cause more general atmospheric damage such as chlorofluorocarbons on the ozone layer. The general structure of the atmosphere is shown in Figure 1.1.

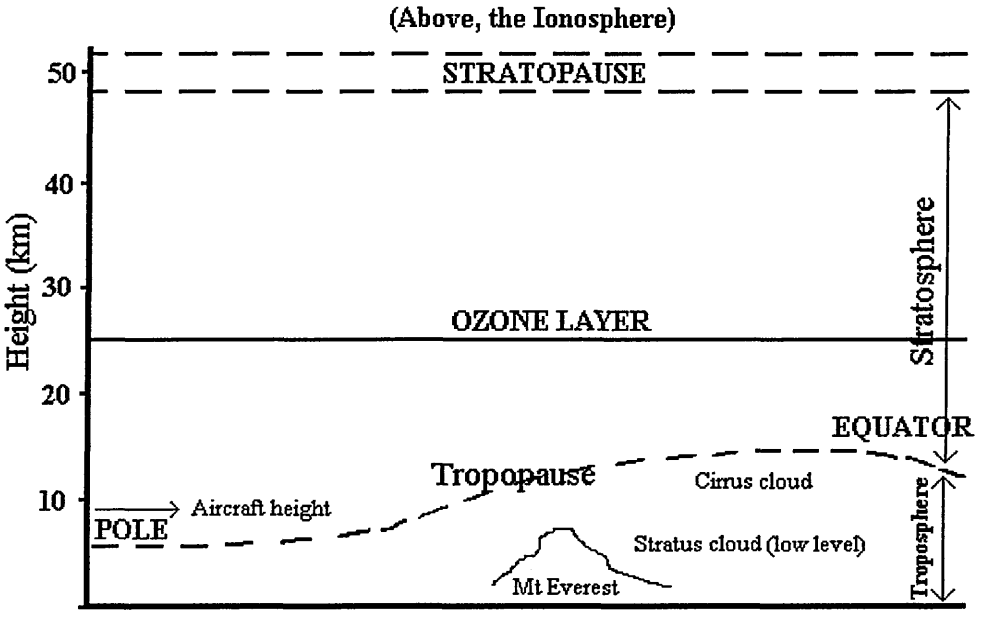

Figure 1.1: Structure of the Atmosphere, Identifying the Variation in Troposphere Depth with Latitude Variation.

The troposphere can be described as the "chemical processor" of the atmosphere, where partial or complete degradation of nearly all organic compounds released into the atmosphere occurs. The exceptions to this are chlorofluorocarbons (CFCs) and some Halons (small, bromine containing molecules used in portable and fixed extinguisher systems (2)). These compounds are relatively inert and slowly diffuse through the troposphere to the stratospheric layer. Here low wavelength UV radiation degrades these molecules to free chlorine and bromine radicals (Cl• and Br•). These are now known to destroy ozone, a vital compound that protects the earth's surface from harmful low wavelength UV radiation.

1.1 Atmospheric Pollutants.

1.1.1 Small gaseous polluting molecules.

There have been several major pollution contributors through history, which have had a major impact on plants and animals. These include:-

1 Carbon Monoxide

2. Carbon Dioxide

3. Sulphur Dioxide SO_2

4. Nitrous oxides NO_x ($NO + NO_2$)

5. Ozone (formed indirectly)

SO_2 and NO are deemed to be primary pollutants as they are produced directly from anthropogenic combustion material. NO_2 is seen as both a primary and secondary pollutant as it is not only released directly from a polluting source, but it can also be formed during atmospheric chemical reactions. Ozone is almost entirely a secondary pollutant with formation from atmospheric chemical reactions.

Pollution increased steadily from the 16th century due to the increased use of fossil fuels such as coal and oil for heat and energy, by the escalating population and industry (3). The 19th century saw the start of an explosive increase in anthropogenic emissions, people began to live longer due to improvements in health care and expected a more comfortable lifestyle with heat, light and access to energy. These improvements further increased the levels of CO, CO_2, SO_2, and NO_x in the atmosphere.

1.1.1.1 Carbon Monoxide (CO).

Carbon monoxide (CO) is formed during the combustion of any carbon containing material with insufficient oxygen to complete the combustion process to carbon dioxide. The combustion of fossil fuels produces a large quantity of CO, along with elemental carbon. This toxic gas acts as an asphyxiant by combining with haemoglobin to form a very stable molecule via a reversible reaction. The absorption of oxygen by the

haemoglobin molecule is prevented, hence reducing the level of oxygen in the blood. The present major source of CO is petrol driven vehicles. However, the use of catalytic converters can reduce CO emissions by up to 90%, and therefore CO emissions from petrol driven vehicles should, in the future, be significantly reduced.

1.1.1.2 Carbon Dioxide (CO_2).

Carbon dioxide (CO_2) is a major biogenic emission associated with the carbon cycle. However, since the industrial revolution the atmospheric concentration of CO_2 has steadily increased as the combustion of carbonaceous material has escalated. Major sources of CO_2 include power stations, domestic coal burning, and industry. Emissions from these sources have been decreased since 1970. However, conversely, emissions from transportation have steadily increased during the same time period.

The recent summit in Kyoto (Japan) discussed ways of reducing emissions of this gas because of its effect on the world's climate. It has been associated with a universal increase in temperature of the planet. CO_2 hinders solar radiation from leaving the atmosphere. The phenomena known as "Global Warming" is a cause for concern, since melting ice-caps and increasing sea levels caused by global warming would put many millions of lives at risk.

1.1.1.3 Sulphur Dioxide (SO_2).

There are several biogenic sources of SO_2. These include volcanic activity, the emission of dimethyl sulphide (DMS) by marine photoplankton, and its subsequent oxidation to SO_2, in addition to hydrogen sulphide (H_2S) emitted by natural decomposition. However, the amount of SO_2 released world-wide from these sources is heavily outweighed by man made production. Three quarters of all sulphur emissions are in fact man made (3).

Sulphur is found in most fossil fuels due to the presence of a small percentage (0-4%) of sulphur compounds (mainly organic thiol derivatives and sulphides). Their combustion releases the majority of this sulphur into the atmosphere as SO_2. Hence emissions of SO_2

increased in parallel with the increasing use of fossil fuels from the 19th century to the 1960's. However, since the mid 1960's the levels of SO_2 released by Europe as a whole has slowed and even began to fall from the late 1970's onwards.

The reason for this European reduction was the change of fuels used by power stations. These were identified as the major source of SO_2 (prior to 1970), with 72% (4) of the UK emissions being from this source. During the 1960's and 1970's British coal was the major fuel for power stations. This had an average 1.7% sulphur content (3) producing 6.5 million tonnes of SO_2 per year. The sulphur was mainly in the form of Iron pyrites (Iron sulphide FeS_2), an intrusive mineral which was not removed prior to or after combustion. SO_2 levels have recently dropped to 2.5 million tonnes per year due to the increased use of oil and gas power stations (as natural gas has nearly all of its sulphur (H_2S) content removed). The decline of British coal during the 1980's increased the opportunity of importing low sulphur content coal. The reduction of coal fires in the home in favour of gas central heating has also helped lower total emissions.

Emissions could be reduced even further with the removal of any remaining SO_2 from power station emissions. These can be fitted with flue gas desulphurization systems. These can utilise the SO_2 by reacting it with various compounds to produce useful by-products, including gypsum, (hydrated calcium sulphate) and calcium sulphide for use in the cement industry, or sulphuric acid (3). Such systems increase the cost of electricity, and are not in widespread use in the UK. However, world-wide SO_2 emissions have continued to climb (3) due to the increased use of coal in developing countries.

1.1.1.4 Nitrogen Oxides (NO and NO_2).

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the two oxides of nitrogen that are collectively known as NO_x. NO_x values are often quoted for combustion emissions, with NO being up to 90% of the total primary emission (3,5). However, the major UK source of NO_x is not related to the combustion of coal but is associated with the use of crude oil and its related compounds. Formation of these gaseous molecules is based on a thermal reaction between nitrogen and oxygen, which are described by the Zeldovitch mechanism:-

$$N_2 + O \longrightarrow NO + N \quad 1$$

$$N + O_2 \longrightarrow NO + O \quad 2$$

The reaction is endothermic so occurs readily in hot areas of the combustion zone.

From the 1960's the UK production of NO_x from industry has been falling. However, total emissions were constant from 1960-1990, due entirely to the increase in vehicle emissions. Since 1990 the total of NO_x has now begun to fall, as a result of the fitting of low NO_x burners to power stations and the addition of catalytic converters to vehicles (3).

Nitric oxide (NO) and nitrous oxide (N_2O) are also produced in nature by nitrifying bacteria found in soil. Nitric oxide is thought to be the predominant molecule released. Little scientific analysis has been carried out in this area, with a proposed emission value of 2-5% of total NO being released by biogenic sources.

NO and NO_2 also react with ozone to produce an equilibrium reaction which varies throughout the day and night. High levels of ozone and NO (rapidly used in other atmospheric reactions) are produced during the day, while low levels of ozone with high NO_2 concentrations being produced at night. NO_2 has been identified as causing respiratory problems at levels exceeding 300ppb, in addition to causing leaf damage and being a pre-cursor for the formation of nitric acid in the atmosphere (6).

1.1.1.5 Ozone O_3.

Naturally occurring ozone is found predominantly in the stratospheric layer of the atmosphere, which is positioned between 15 and 50km above the earth's surface (see Figure 1.1). This layer protects the earth from harmful high energy photons of wavelength (≤300nm) due to the high absorption coefficients of these photons by ozone (7).

90% of all ozone is found in the stratosphere, due to the formation of ozone by the reaction between oxygen and UV radiation from the sun. Radiation of wavelength

242nm and below have enough energy to split diatomic oxygen into two monatomic atoms - **3** (3).

$$O_2 + h\nu\ (\leq 242nm) \longrightarrow 2O \qquad \mathbf{3}$$

These monatomic oxygen atoms are then capable of reacting with a diatomic molecule of oxygen (in the presence of an impartial molecule such as nitrogen) to produce ozone - **4**.

$$O + O_2 + M \longrightarrow O_3 + M \text{ (where } M = O_2 \text{ or } N_2) \qquad \mathbf{4}$$

A current major issue is the depletion of this protective ozone layer due to the breakdown of ozone molecules by chlorofluorocarbons, but this will not be discussed in this thesis.

Ozone is a secondary pollutant, i.e. it is not released in any quantity by a polluting source. However, it is produced from chemical reactions that can occur with primary pollutants. The relationship between ozone and NO_x will be discussed later (see Section 1.4.1). NO_2 produced from vehicle emissions decomposes photolytically in daylight by absorbing UV radiation at <420nm, and decomposes to NO and monatomic oxygen, **5**. This oxygen can react further to produce ozone, **4**.

$$NO_2 + h\nu\ (280\text{-}430nm) \longrightarrow NO + O \qquad \mathbf{5}$$

This results in a photochemical equilibrium of lower NO_2 during the day, while the reverse reaction dominates during night-time, increasing levels of NO_2 - **6**.

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad \mathbf{6}$$

The formation of ozone from photolytic degradation of NO_2 produced from anthropogenic emissions, is likely to be only a minor contributor to ozone formation in the troposphere. Ozone is produced in greater quantities from a complex series of reactions that take place between hydrocarbons, radicals, in addition to an indirect route to the formation of NO_2 from NO, **7-9**.

Ozone production via atmospheric reactions of hydrocarbons.

Any hydrocarbon (saturated or unsaturated short hydrocarbon molecules) in the atmosphere can react with a hydroxy radical (OH•) via hydrogen abstraction, producing an alkyl radical. These react rapidly, and almost solely with a molecule of oxygen to form organic peroxyalkylradicals (RO_2) (3,8).

$$RH + OH\bullet \longrightarrow R\bullet + H_2O \qquad \mathbf{7}$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet \qquad \mathbf{8}$$

These radicals readily react with NO, to form NO_2 depleting the NO level in **6**, pushing the equation in favour of O_3 accumulation (3,8).

$$RO_2\bullet + NO \longrightarrow RO\bullet + NO_2 \qquad \mathbf{9}$$

This increase in NO_2 formation from a secondary source can undergo photochemical reduction, as seen in **5** to ultimately produce ozone - **4**.

A variation in ozone concentration occurs throughout a 24 hour period, with an increase of hydrocarbons, NO and NO_2 during morning rush hours. As the UV radiation increases, these primary pollutants undergo the previously described reactions, increasing ozone concentration and causing NO and NO_2 to fall. The initial high input of NO from diesel combustion hinders the formation of ozone and increases levels of NO_2 in **6** (9).

As the day progresses, this reaction is reduced in importance and ozone is formed in larger quantities. During late afternoon, UV begins to reduce in intensity. Along with this, the ozone level begins to fall, increasing the concentrations of NO_2 and NO during late evening. These levels stay high until early morning, when the cycle begins again.

Daytime formation of ozone in addition to airborne particulate material are responsible for smog formation during the summer months, when the length of time for the production of ozone from the above routes are at their highest. It has been observed that

there is a yearly cycle of tropospheric ozone production, with the highest levels during the summer months, reducing to the lowest levels during colder winter months (10). A number of studies have identified many adverse effects of high ozone levels. These include damage to agricultural and natural vegetation, disease in human beings (11), eye irritation and breathing difficulties (3).

The by-products of these reactions include formaldehyde and peroxyacyl nitrate (PAN) which are both toxic and irritants. Nitric acid is also produced leading to an increase in the acidity of aerosol droplets.

In order to control vehicular pollution a reduction in the primary sources which produce hydrocarbons, NO and NO_2 is required. These sources are invariably road traffic and in particular diesel engines, since these engines produce NO and NO_2 as well as hydrocarbons. Petrol fuelled vehicles produce mainly hydrocarbons and very little NO or NO_2 as petrol contains few nitrogen containing compounds. NO can be produced in the high temperature regions of the engine via the Zeldovitch mechanism (see Section 1.1.1.4) (3). Of the NO_x produced by a petrol vehicle, less than 10% is NO_2 (12). During the winter, increased quantities of NO_2 have been observed, with the mechanism for the conversion of NO to NO_2 being unclear. However, the presence of high concentrations of hydrocarbon material in the exhaust is thought to have an effect (12).

Unfortunately the solution to these problems is not achieved by simply reducing NO_x. The formation of ozone can be increased with a reduction in NO_x if volatile organic compound (VOC) emissions stay constant. A reduction in VOC does produce an overall drop in ozone formation, therefore in order to reduce tropospheric ozone, a reduction in hydrocarbons released into the atmosphere needs to be achieved. The advent of catalytic converters for petrol cars appears to be a step forward, along with the development of hybrid vehicles which use both a conventional engine and an electrical motor which can be used when driving through urban areas (13), reducing urban emissions. However, with diesel engines releasing large quantities of hydrocarbons into the atmosphere and an ever increasing vehicle fleet world-wide, this problem is unlikely to be resolved in the near future.

1.1.2 Acidic species.

Daytime conversion of primary to secondary pollutants can be attributed to various oxidative radical reactions. These are initiated by photolytic reactions with various oxygenated species. These then react with primary pollutants causing oxidation and the start of many pathways to degradation of chemicals in the atmosphere.

However, oxidation of some primary pollutants can ultimately produce acidic species. Such species can have an adverse effect on a wide variety of surfaces when they are deposited back to the earth. These surfaces include vegetation, both natural and agricultural, aquatic systems and buildings (14).

Acid rain was reported more than one hundred years ago (15), and more recent work has identified certain acidic species as being long range pollutants (14). Long distances of deposition are possible under favourable meteorological conditions, since the average residence times of these acidic species and their pre-cursors in the atmosphere is between 2-5 days (16,17). Emissions of SO_2 and NO_x from the combustion of anthropogenic material can ultimately produce HNO_3 and H_2SO_4. These acidic species can be formed from gas phase reactions or heterogeneous reactions between gases and particulate surfaces. Reactions can also occur within aerosols after primary pollutants and oxidative species have been dissolved into the droplet.

European studies originally completed in Scandinavia during the early 1970's (18) found that quantities of acids were being transported from combustion sources in other European countries, to Scandinavia. Here they were deposited to earth and were causing environmental damage. This has been eleviated to some extent with the reduction in SO_2 emissions over the last twenty years due to the change in fuels used for electricity production, (See Section 1.1.1.3).

NO_x is still a major pollutant, with an ever increasing quantity being produced from vehicle emissions, especially diesel engines. Therefore the production of nitrogen containing acidic species is likely to increase.

1.1.3 Particulates.

Particulate material is a very important component of atmospheric pollution due to probable irritation of and possible toxic effects on the respiratory system. The extent of this health response is dependant not only on the individual in question (and the condition of their airways), but also upon the size and possibly the composition of the particles.

Particulate material can be produced from direct primary emissions or through atmospheric chemical reactions which produce secondary particulate material. These particulates can be solid, or liquid (aerosols), and can vary widely in size from a few nanometers to micrometers. The sources of atmospheric particulate material can be quite diverse, and range from coarse materials including soil particles and industrial dusts, to finer particles, produced from combustion sources (19).

Particulate material can be categorised into three size dependant groups which can to some degree, help to clarify this complex area of atmospheric particulate pollution.

1. Nucleation <0.2μm.

These exceptionally fine particles are often produced from processes that involve hot vapour condensation including incinerators, smelters and possibly combustion sources (specifically diesel particulate emissions (see Section 4.3.2)).

Atmospheric formation of acidic aerosols (i.e. $SO_2 \rightarrow H_2SO_4$ and $NO_2 \rightarrow HNO_3$) can produce fine particulate material if they react further with ammonia (NH_3). This produces ammonium sulphate or ammonium nitrate which once formed, agglomerate to form larger particles.

2. Accumulation. 0.2-2μm.

These particles are often formed from the clustering of smaller nucleation particles, producing larger agglomerates of irregular shape (see Section 4.3.2) (19). Such particles

include material produced during combustion. Particles this size are the most stable and can have an atmospheric lifetime of between 7-30 days (20). Their extended lifetime is due to the lack of mass, and this prevents rapid removal due to physical deposition and the inefficiency of wet deposition on this particular particulate size. Wet deposition effectively removes both larger and smaller particles from the atmosphere via different processes (20).

3. Course >2μm.

Particles of this size are often produced from natural sources, including silicas from soil erosion, as well as re-suspended street dusts, and salt crystals formed from sea spray (19).

Particulate material of 10μm (PM10) are regularly found suspended in atmospheric air. Therefore inhalation of such material can occur, with deposition being possible in the respiratory system at three possible sites depending upon the size of the particulate:-

1. Nasopharyngeal
2. Tracheobronchial
3. Alveolar.

Both the nasopharyngeal and tracheobronchial areas use a combination of hairs (cilia) and mucus to trap and remove particulate material from the inhaled air. These areas can effectively cope with particles >2.5μm, as the particles mix with the mucus and are removed from the airway by the wafting type movement of the cilia hairs. This moves the mucus/particulates up the airway to the trachea/oesophagus intersection, allowing the cleared particles to be swallowed and dealt with by the digestive system.

However, particles of <2.5μm (often produced from anthropogenic combustion (19,21)) are capable of penetrating deeper into the lung and being deposited at the alveolar region, where oxygen is absorbed and carbon dioxide is released by the blood. These regions of the lung are unciliated, so particulate material is removed far less efficiently by macrophages which transport the particles to ciliated areas or deposit them directly into

the lymphatic system. This also suggests that material contained on/in the particulate could cause detrimental health effects, including lung disease (22).

Other particles found in the atmosphere are the inorganic salts formed from atmospheric reactions. These include ammonium sulphate and ammonium nitrate produced from reactions between ammonia and sulphuric or nitric acid. The acids are themselves produced from SO_2 and NO_2 and converted to mineral acids through other atmospheric chemical reactions. (Acid chemistry is dealt with in Section 1.4.3).

1.1.4 Metals/Inorganics.

All atmospheric elemental material (with the exception of mercury) are associated almost entirely with particulate material. Elements including aluminium, chromium, cerium, chloride, sodium and manganese are biogenically released from crustal rock, soils and marine sources (23,24). Other elements including lead, bromine, zinc and vanadium (24) have been identified as major components of anthropogenic emissions. This was especially true when tetraethyl lead was added to petrol as an "anti-knock" additive for engines. However, with increased knowledge of the effects of lead on health, leaded petrol was superseded by unleaded petrol, resulting in the steady reduction of lead in atmospheric samples. Lead is still released into the atmosphere from leaded petrol cars (with the lead content being reduced to 0.15g/l from 0.4g/l in January 1986), diesel emissions, (see Section 2.2.6.4) and industrial emissions.

Transport of these elements can be quite extensive as nickel, lead and zinc have been found in the Arctic (25).

1.1.5 Organic compounds.

The organic compounds that are released into an indoor or outdoor environment can be classified into the three following types:-

1. Volatile.
2. Semi-volatile.
3. Non-volatile.

This is not a precise way in which to describe all organic compounds, but it helps to identify some of the many problems encountered when sampling and analysing atmospheric samples.

1. Volatiles.

These are organic molecules which are found almost entirely in the gaseous phase. Such molecules are often small in size and include methane (CH_4), small aliphatic chain lengths (possibly oxidised) in addition to benzene and associated compounds such as toluene and xylenes. The major route of removal of these compounds from the atmosphere is physical dry and wet deposition to a sink or surface. The rest of these molecules react with the various radicals present in the atmosphere, including the hydroxy ($OH\bullet$) and nitrate radical ($NO_3\bullet$). They undergo radical reactions which invariably increase polarity while reducing carbon number. This continues until they are either oxidised to CO_2 and/or H_2O, or removed from the atmosphere by wet or dry deposition before this occurs.

2. Semi-Volatiles.

Semi-volatile organic molecules are compounds which associate partly with particulate material, as well as being present in the gaseous phase. Straight chained alkanes from C15-C22 can be found in both these phases and also various PAH and heterocyclic compounds. However, this is dependant upon the ambient temperature and the compounds individual vapour pressure.

3. Non-volatile compounds.

These are organic compounds which are associated totally with particulate material. These include the larger straight chained alkanes often identified as unburnt or partially combusted anthropogenic fuel and lubrication oil, larger PAH compounds, PAH derivatives, in addition to heterocyclic and polar compounds.

1.2 Physical Atmospheric forces.

A wide range of chemicals can be released as pollutants into the atmosphere from a variety of sources. As stated previously, such chemicals include organic, inorganic and organometallic material. These gaseous or particulate associated chemicals, from either anthropogenic or biogenic sources, can be subjected to physical and/or chemical forces before their fate of removal from the atmosphere is determined.

The troposphere is a very good environment for this to occur, since mixing due to wind and small scale turbulent air (often associated with the lower region (1-2km) (23) of the troposphere) helps to induce intimate mixing of all pollutants. This is very important as all pollutants are able to mix well prior to significant dilution, allowing chemical reactions to occur and hence transforming molecules before dispersion. All but the most inert compounds (CFCs and some halons) are transported, transformed and finally removed either by complete oxidative processes, or physical deposition to a certain sink (continental area or sea).

It can be seen that atmospheric conditions will ultimately control the fate of any one pollutant. Wind variations, temperature, pressure, solar radiation, and relative humidity due to the time of year and the site of emission will help/hinder the various possible reactions that can occur. It has been explained in previous sections that radical formation is increased with increased UV radiation (the summer months) (10), and a more complete overview of basic atmospheric chemical reactions are discussed as a whole in Section 1.4.

1.2.1 Physical deposition for pollutant removal.

Physical deposition is the major method by which pollutants are eventually removed from the atmospheric environment. This can occur by two routes, dry deposition when gaseous and particulate material deposit directly to a surface or sink, and wet deposition, where pollutants are removed due to various interactions with atmospheric water molecules (e.g. rain, snow or fog).

1.2.1.1 Dry deposition.

Dry deposition is poorly understood compared to wet deposition, as the process is very difficult to follow. This is due to the slow rate of dry deposition compared with wet deposition. Dry deposition mainly occurs through collisions of the pollutant with a surface, reducing velocity and producing deposition of the pollutant due to range of parameters. These vary according to the physical state of the pollutant.

Particulates.

Parameters effecting the rate of dry particulate deposition include the size and shape of the particle, as well as the velocity of the prevailing wind (23).

Gaseous.

Important characteristics of dry deposition for gaseous pollutant are physiochemical, and include chemical reactivity, polarity, water solubility and molecular weight (23).

Surface.

The type of recipient surface also has an effect on the overall rate of dry deposition, i.e. whether it is wet or dry, hot or cold, rough or smooth. The variations in these parameters make it very difficult to accurately quantify dry deposition. Various mathematical equations have been devised to quantify this route of deposition (23,26). However, variation of certain parameters make the quantitation uncertain (23).

1.2.1.2 Wet deposition

Several routes to wet deposition have been identified. These include the collision of water droplets with a polluting particle or gaseous molecule. This can result in the dissolution of the pollutant (depending upon its solubility) or the deposition of the wet particle due to its heavier mass. This mainly occurs below cloud level, while other processes including nucleation and brownian capture often occur at cloud level.

Nucleation is where a particulate acts as a nucleus for the formation of a water droplet. Once the droplet has increased to a sufficient size, it drops to earth removing the polluting particle from the atmosphere. Brownian capture also occurs at cloud level, and is where water droplets come into contact with pollutant particles through kinetic motion.

Wet precipitation has a major effect on the routes of removal of atmospheric pollutants, especially particulates and the associated organics, in comparison to gaseous organic molecules (27). Chemical reactions can also occur, with atmospheric water droplets, inducing the formation of various mineral acids from gaseous SO_2 and sulphate ions as well as NO_x molecules.

1.3 Transportation

The majority of polluting sources emit close to the surface (exceptions to this include aircraft and volcanic activity) hence the pollution is expected to be deposited in relatively close proximity to the polluting source, producing an accumulation of that pollutant close to the point of origin. However, this is not the case for many pollutants, with the distances travelled by certain pollutants being dependant upon a number of parameters. These include not only the physical climate that the pollutant is exposed to, but also the chemical stability of the pollutant in question. Residence times of various organic species can be varied, with some being as little as a few seconds (radicals) while others can last a few days, or even years (low reactive compounds).

As previously stated, the CFC and Halon families are highly stable (inert). However, these molecules are small and light, often rising to the stratosphere in preference to deposition back to earth. Other pollutants can have a relatively large residence time (days/weeks) in the atmosphere, thereby increasing the possibility of being transported great distances from their source of origin (28), prior to deposition. This has been clearly identified with the discovery of various pollutants in areas originally thought to be "clean" of such human activity. Examples include the identification of radioactive material found world-wide after weapons testing (29) and more recently, the discovery of chlorinated hydrocarbons (28,30) and mercury in the Arctic (30). It has been hypothesised that unreactive organic molecules are transferred from warmer to colder regions by a number of successive deposition and re-emission steps (26,28,30). This is due to evaporation and condensation of these volatile elements and organic compounds with the variation in atmospheric temperature, until reaching a more permanent sink in the colder aquatic polar regions (30).

Larger residence times increase the possibility of some degradation either from the various oxidative species produced indirectly from solar radiation, or from species introduced into the body of atmosphere in which the pollutant is present. Chemicals with a residence time of a few days associated with favourable atmospheric conditions, are capable of diffusing over an entire continent (11). Species with residence times longer than this (weeks/months) are capable of diffusing throughout the troposphere, and can even diffuse into the lower stratosphere (11).

1.4 Photochemical Degradation.

In this section, various relevant atmospheric reactions that can occur will be discussed, along with the possible effects these can have on primary pollutants emitted into the atmosphere.

Many of the photochemical degradation reactions that occur in the atmosphere, are induced by radical chemistry and initiated by UV radiation. Such atmospheric reactive

species include OH•, OH_2, CH_3O_2, NO_3•, peroxides and their related radicals, in addition to ozone, oxides of nitrogen, SO_2, atomic oxygen, along with various acidic and basic species (23). These can cause degradation via various pathways using either homogeneous (in one phase, i.e. gaseous phase) or a heterogeneous reactions (where volatile or involatile molecules are adsorbed to a surface, catalysing a chemical reaction) (23). The phase partitioning of these organic molecules is very much related to the compound's vapour pressure, along with the atmospheric temperature and pressure at the time. The partitioning of compounds between the gaseous and particulate associated phase can therefore be predicted by using the vapour pressures of the organic compounds under investigation (26).

As has been previously described, a large proportion of the pollution material is removed from the atmosphere by physical processes. However, during its atmospheric lifetime organic pollutants are available for reactions with many of the reactive species previously stated. The result being that each individual organic compound has numerous possible routes of degradation. Major radicals identified as having an effect on organic pollutants include OH•, NO_3•, and ozone.

1.4.1 Daytime atmospheric reactions.

A comprehensive description of all possible atmospheric chemical reactions is a thesis in itself. However, the following description and schematic of possible reactions that can occur during day and night activity will identify the complexity of this environment.

Hydroxy radical (OH•) production.

The OH radical is produced from the photochemical degradation of tropospheric ozone to an oxygen molecule and an excited oxygen atom - **10**.

$$O_3 + h\nu(<320) \longrightarrow O_2 + O(^1D) \qquad \textbf{10}$$

The reaction only occurs during the day, as UV radiation is needed for the initial photochemical degradation of O_3 to occur.

The excited oxygen molecule can do one of two things:-

1. It can de-excite with a diatomic molecule of nitrogen or oxygen - **11**, which can then react further with an oxygen molecule to re-produce ozone - **4**.

2. Or it can react with a molecule of water to produce two hydroxy radicals - **12**.

$$O(^1D) + M \longrightarrow O(^3P) + M \qquad \text{(where } M = O_2 \text{ or } N_2\text{)} \qquad \mathbf{11}$$

$$O(^1D) + H_2O \longrightarrow 2OH\bullet \qquad \mathbf{12}$$

Even though OH• is only found at very low concentrations in the atmosphere (typically sub ppt/volume) (31), it plays a major role in the oxidation of organic compounds in the atmosphere.

Hydrocarbon degradation.

Alkanes (produced from incomplete anthropogenic combustion and vegetation) do not undergo photolysis in the atmosphere, or reactions with ozone at any measurable rate (32). However, they do react with OH• and NO_3• radicals, as well as chlorine atoms. Reactions with the OH• radical are seen to dominate over the other possible reactions, and proceeds via hydrogen abstraction from the carbon chain -**7** in the day, the night time reaction can be seen in **13**.

Night-time $\quad RH + NO_3\bullet \longrightarrow HONO_2 + R\bullet \qquad \mathbf{13}$

These alkyl radicals react almost entirely with diatomic oxygen to form alkyl peroxy radicals - **8** (3,8).

These alkyl peroxy radicals can react with a number of atmospheric species. Species available include NO, NO_2, as well as HO_2 and RO_2 radicals, with their relative concentrations dictating which reactions are likely to occur. It is thought that the major reactions that occur include those with NO, NO_2 and the HO_2 radical (8).

The reaction with NO produces NO_2 and an alkoxy radical **9**. The NO_2 molecule is available for ozone production by photolysis **4-5** (3,8) or Peroxyacyl nitrate (PAN) formation - (33).

Another possible reaction which the alkyl peroxy radical can undertake is with NO and oxygen, - **14**, to produce analogous aldehydes and ketones.

$$RO_2\bullet + NO + O_2 \longrightarrow \text{aldehydes/ketones} + NO_2 + HO_2\bullet \quad \mathbf{14}$$

The production of aldehydes and ketones (33) introduces various routes of degradation due to possible breaking of the carbon chain at the ketone active site, or even isomerization (8,34). This has also been shown to occur with atmospheric alcohols (35).

The alkyl peroxy radical can also react with hydro peroxy radicals to produce a hydro peroxide - **15** (8).

$$RO_2\bullet + HO_2\bullet \longrightarrow ROOH \text{ (hydroperoxide)} + O_2 \quad \mathbf{15}$$

These hydroperoxides are themselves removed from the atmosphere by wet or dry deposition, photolysis, or by various reactions with OH•(8).
The alkoxy radical (RO•) produced in **9**, as well as the aldehydes and ketones formed in **14**, can react under favourable conditions to form peroxyacyl radicals - **16-18** (33).

$$RCO\bullet + O_2 \longrightarrow RC(O)O_2\bullet + NO_2 \quad \mathbf{16}$$

$$\text{Aldehydes} + OH\bullet + O_2 \longrightarrow RC(O)O_2\bullet + H_2O \quad \mathbf{17}$$

$$\text{Ketones} + OH\bullet + OH\bullet + O_2 + h\nu \longrightarrow RC(O)O_2\bullet + H_2O \quad \mathbf{18}$$

These peroxyacyl radicals can undergo several reactions, including a reaction with hydroperoxy radical to produce a hydroperoxide - **19-20** (8).

$$RC(O)O_2\bullet + HO_2\bullet \longrightarrow ROOH + O_3 \quad \mathbf{19}$$

$$RC(O)O_2\bullet + HO_2\bullet \longrightarrow RC(O)OOH + O_2 \quad \mathbf{20}$$

Under cooler atmospheric conditions these peroxyacyl radicals can react with NO_2 to produce a peroxyacyl nitrate (PAN) - **21** (33).

$$RC(O)O_2\bullet + NO_2 \longrightarrow RC(O)O_2NO_2 \qquad \textbf{21}$$

PAN is stable in the atmosphere at low temperatures however, it readily decomposes to NO_2 and the peroxyalkyl radical at higher ambient temperatures. This can act as a possible route for transportation of NO_2 over large distances, before decomposition due to temperature (33).

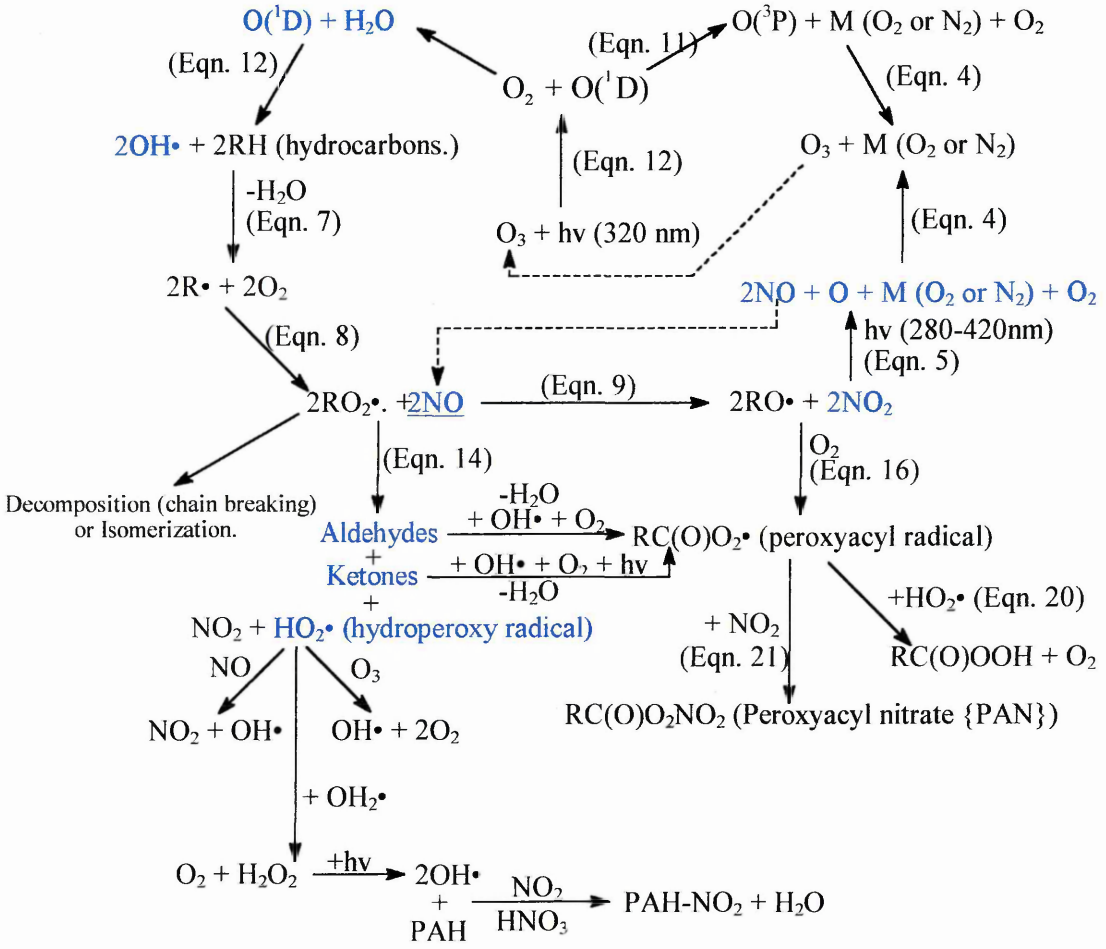

Figure 1.2: Schematic of Daytime Reactions.

The "natural" daytime atmospheric cycle is disrupted with the introduction of anthropogenic emissions released into the atmosphere. For simplicity, and in order to

identify the major pre-cursors for atmospheric reactions, only NO, NO_2, SO_2 and hydrocarbons, will be discussed. All these emissions are released by combustion sources.

Many other compounds are released from combustion sources, but these can often follow similar routes of degradation to that of a hydrocarbon chain. However, the degradation routes of many groups of compounds found at relatively low concentration in atmospheric samples are yet to be clearly identified. Certain nitrated PAH have been shown to photodegrade to quinone type compounds (36,37). However, exhaustive work has yet to be undertaken to clarify the favoured degradation routes of these and many other compounds.

The increase in levels of NO and NO_2 effects the equilibrium of a range of chemicals found in the atmosphere. The photolytic reduction of NO_2 to NO and an excited oxygen atom, **5** results in the formation of ozone. Equally, NO reacts with ozone to produce NO_2 and O_2, resulting ultimately in a stable equilibrium. However, the formation of other species effects this equilibrium and leads to a net increase in the formation of ozone during the day. This excess ozone can react with UV light and water vapour to produce hydroxy radicals (OH•) as well as other oxygenated species, and radicals capable of causing atmospheric oxidation of organic molecules.

With a sufficient quantity of UV radiation, the cycle is initiated, and these reactions can begin to remove organic material from the atmosphere, **7-9**. The degradation pathways produce other oxygenated radicals/species capable of oxidising compounds to their analogous oxidative species, **10** and **12**, while ozone is formed from NO_2 photolysis, **5**. It is this continuous daytime formation of oxygenated species, especially the hydroxy radicals, which plays a predominant role in the daytime cycle (31) and degrades hydrocarbon material to oxygenated alkanes (33). These compounds can either degrade (chain break), isomerise, or form oxygenated peroxyacyl compounds (33).

Laboratory experiments have shown that these reactions do indeed occur (3), with levels of ozone and PAN compounds steadily rising during the daytime. After an initial increase in NO_2, the NO_2 levels steadily decrease as they are consumed not only through ozone formation but also through PAN formation. PAN has been identified as a possible

accumulation compound as it can have a relatively long residence time at low temperatures (33). However, PAN (as previously stated), does decompose rapidly in warm atmospheres (33).

Therefore, it can be seen that during the summer months, daytime reactions produce and accumulate ozone in the lower troposphere. High levels of aldehydes, peroxyacyl nitrates (PANs), and fine particulate material are partially responsible for the smog formation seen around major polluted cities today. It was first recognised as a potential pollution problem in California in the 1950's (38,39). Reduced visibility, due to absorption and the scattering of light by the fine particles, causes the haze known as smog.

1.4.2 Night-time atmospheric reactions.

The onset of night-time causes many daytime reactions to cease, due to the loss of UV radiation needed to initiate the photolytic reactions. However, night-time reactions take over, producing sinks for reactive oxidative species or routes for the removal of some atmospheric compounds. Ozone, formed during the day is used in various reactions, including the formation of nitrate radicals.

Nitrate radical ($NO_3\bullet$) production.

$NO_3\bullet$ radicals are produced from nitrogen dioxide reacting with ozone, to form a nitrate radical and an oxygen molecule - **22.**

$$NO_2 + O_3 \longrightarrow NO_3\bullet + O_2 \qquad \textbf{22.}$$

Nitrate radicals rapidly react photolytically in daylight - **23**, so concentrations are low during the day. However, concentrations rise during the night-time to measurable levels (8), providing a sink for ozone as well as forming a reactive nitrogen species.

$$NO_3\bullet + h\nu \longrightarrow NO + O_2 \qquad \textbf{23.}$$

Nitrogen dioxide is capable of continuing the atmospheric reactions, producing PAN type molecules - **21** from various radicals (including peroxyacyl) formed during the day, **16-18.**

Nitrogen dioxide can also react with the recently formed NO_3 radical to produce dinitrogen pentoxide **-24**, another nitrating species available for night-time reactions.

$$NO_3\bullet + NO_2 \longrightarrow N_2O_5 \qquad \textbf{24.}$$

Dinitrogen pentoxide has been shown to react with gaseous PAH during the night to form specific isomers of nitrated PAH (see Section 4.2.3.3) (40-42).

$$N_2O_5 + PAH\ (g) \longrightarrow PAH\text{-}NO_2 \qquad \textbf{25.}$$

The rate determining step of this reaction is the volatility of the PAH during the night, as many PAH molecules are associated almost entirely with particulate material. Nitration of these PAH molecules can proceed via a different route (see Section 4.2.3.2), as it has been shown that the reaction of gaseous N_2O_5 with particulate associated PAH material is of minor consequence (43)

Many daytime reactions are driven by the hydroxyl radical, which can be produced from various photolytic reactions. However during the night the concentration of this radical is reduced and can be "stored" in the molecule HNO_2 (sometimes written HONO), produced from the reaction of the hydroxy radical with NO, **-26.**

$$OH\bullet + NO \longrightarrow HNO_2 \qquad \textbf{26.}$$

Along with this gas phase reaction are heterocyclic night-time routes to HONO formation , such as: - **27** (44,45).

$$NO + NO_2 + H_2O \longrightarrow 2HONO \qquad \textbf{27.}$$

Initially it was thought that this reaction occurred rapidly, due to catalysis from the surface it was adhered to (44,45). However, work by Pitts et al (46) identified that the rate of reaction was far slower , producing little nitrous acid in a real atmosphere.

HONO has been shown to increase during the night due to its direct release from exhaust emissions (47). Levels steadily accumulate due to little photolytic degradation and also through a second heterocyclic reaction between NO_2 and water - **28** (45,46,48).

$$2NO_2 + H_2O \longrightarrow HONO + HNO_3 \qquad \textbf{28}$$

HNO_2 (HONO) is a stable molecule during the night, however daylight causes the reaction to reverse thereby being an early morning source of OH radicals (33,49).

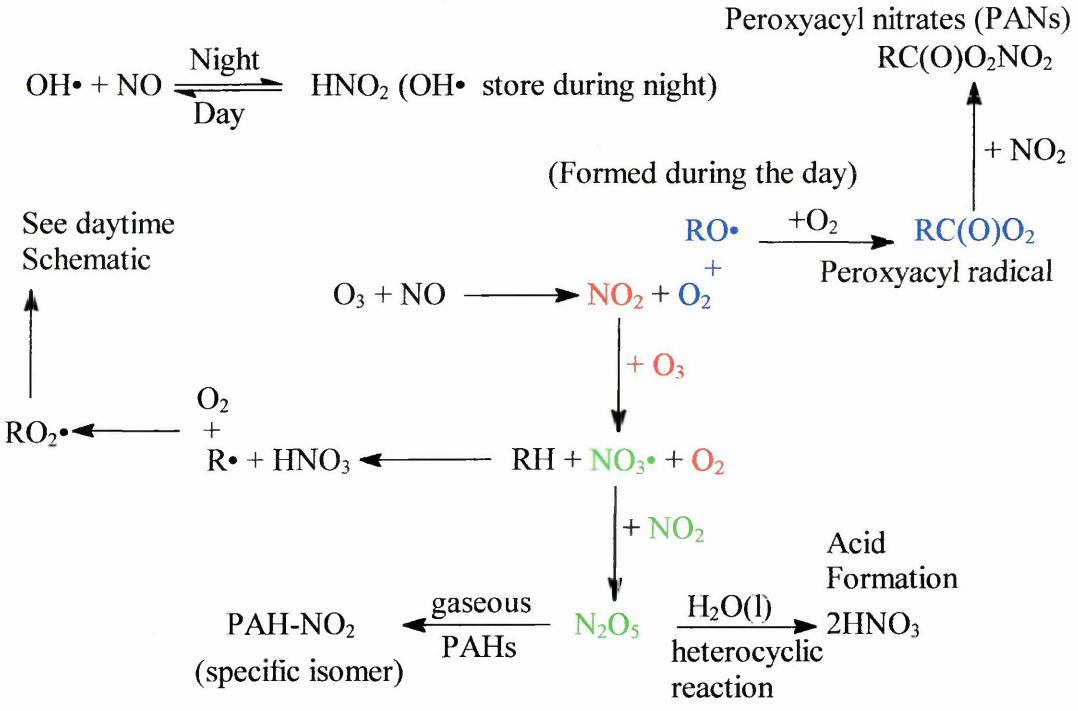

Figure 1.3: Schematic of Night-time Chemical Reactions.

1.4.3 Acid Formation.

The following rapid overview of acid rain formation is by no means comprehensive. However, it does show the main routes to certain mineral acid formation in the

atmosphere. For a more comprehensive description of atmospheric reactions to atmospheric acid production Finlayson-Pitts, et al (21) is a good point of reference.

Anthropogenic sources are once again mainly responsible for the formation of acidic molecules formed in the atmosphere. The release of sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) are the precursors for the formation of sulphuric and nitric acid respectively.

Sulphur Dioxide (SO_2)

The most likely route to the oxidation of ground state SO_2 is by OH• which produces an adduct, **29**, as observed by Hasimoto. et al (50)

$$SO_2 + OH\bullet\ (+M) \longrightarrow HOSO_2\bullet\ (+M) \qquad \mathbf{29}$$

Reaction **30** described by Calvert. et al (51) is thought to be endothermic (52) so is unlikely to occur at any great rate at ambient temperature. After absorbtion into water droplets or adsorption to surfaces, oxidation by various species can possibly occur.

$$HOSO_2\bullet + O_2 \longrightarrow SO_3 + HO_2\bullet \qquad \mathbf{30}$$

Alternative exothermic reactions include :-

$$HOSO_2\bullet + H_2O \longrightarrow HOSO_2\bullet OH_2 \qquad \mathbf{31}$$

$$HOSO_2\bullet OH_2 + O_2 \longrightarrow H_2SO_4 + HO_2 \qquad \mathbf{32}$$

and

$$SO_2 + O(^3P) + (M) \longrightarrow SO_3 \qquad \mathbf{33}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad \mathbf{34}$$

The atmospheric sulphuric acid formation after the initial oxidation of SO_2, **29** is often written as

$$HOSO_2 \rightarrow \rightarrow \rightarrow H_2SO_4 \qquad \mathbf{35}$$

All routes to the formation of sulphuric acid need oxidative pre-cursors for the initial oxidation to occur. This ensures that there is a seasonal variation in the production of atmospheric sulphuric acid, with larger concentrations produced the warmer summer months (53).

Nitrogen Dioxide (NO_2)

The following daytime reaction, **36** dominates the production of atmospheric nitric acid during the summer period due to the large amount of OH• produced from photolytic reactions (33).

$$NO_2 + OH\bullet + M\ (N_2 \text{ or } O_2) \longrightarrow HNO_3 \qquad \mathbf{36}$$

However, night-time reactions also produce nitric acid. A heterocyclic reaction of gaseous N_2O_5 with water vapour can produce liquid HNO_3 (54) - **37**.

$$N_2O_5\ (g) + H_2O\ (l) \longrightarrow 2HNO_3\ (l) \qquad \mathbf{37}$$

The night-time reaction is dominant during the winter months when night-time levels of N_2O_5 are at their highest (53). Another route to night time formation of HNO_3 is a reaction between the $NO_3\bullet$ and a hydrocarbon - **38** (55).

$$NO_3\bullet + RH \longrightarrow HNO_3 + R\bullet \qquad \mathbf{38}$$

The possible formation of nitric acid during both the daytime and night time removes the independence of the reaction from photolytic OH• production, (as with sulphuric acid) resulting in nitric acid being present in the atmosphere throughout the year.

These acid molecules can be removed from the atmosphere by either wet or dry deposition. However, these inorganic acids can be partially neutralised by reacting with ammonia released into the atmosphere from various sources (both biogenic or

anthropogenic). These reactions produce fine particles of ammonium nitrate and ammonium sulphate.

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \qquad \mathbf{39}$$

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4 \qquad \mathbf{40}$$

Along with carbonaceous particulate material, these inorganic salts are partially responsible for the visible smog hazes seen around polluted cities during heavy pollution episodes due to the scattering of light. These inorganic particles are temperature sensitive, with higher temperatures reducing the ammonium salts to ammonia and the relevant inorganic acid.

Other cations available to react with nitric acid include sodium ions, released into the atmosphere predominantly from sea salt. Sea salt is mainly associated with the coarser fraction of particulate material (>2μm) thereby resulting in the identification of nitrate in coarse particulate material (56).

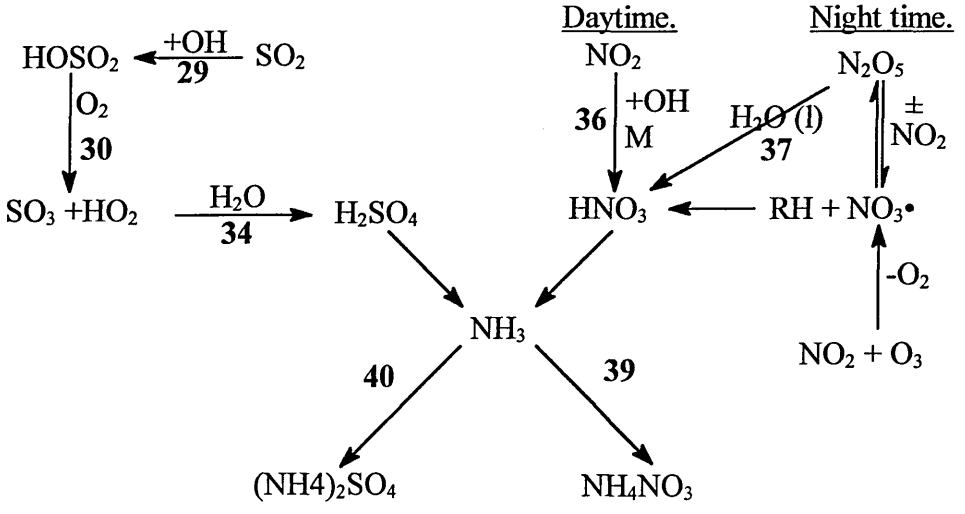

Figure 1.4: Schematic of Acid Formation.

It can be seen from this generalised overview that atmospheric chemistry is highly complex, with minor constituents having major effects on the reactions occurring in any outdoor atmosphere. Daytime reactions are generally powered by OH• radicals with ozone and NO_x continually reacting (often photolytically) to produce various amounts of

reactive precursors at any one time. The OH• radical is able to control oxidation of many manmade and naturally occurring compounds emitted into the earth's atmosphere (Figure 1.2) (31).

As night falls and the UV radiation diminishes, other reactions begin to take control. Hydroxyl radicals and other precursors form compounds, such as HONO where OH• can be "stored" until the next morning before pholatolysing back to OH• and NO at the start of a new day. Oxidation as such, stops at night. However, nitration becomes the major reaction occurring at night with NO_3• and N_2O_5 being two species capable of reacting with organic atmospheric pollutants.

Acidic species and fine ammonium salts are produced under the right conditions producing another group of toxic compounds that are detrimental to plant and animal life.

We can therefore see that there are many factors which can effect gaseous and particulate associated organic pollutants once they have been released into the atmosphere. Physical processes can remove them, before or after chemical reactions have occurred with the numerous radicals or reactive species (found in the atmosphere during the day or night). This can produce a whole range of possible secondary compounds from one primary pollutant, resulting in the eventual removal of the pollutant from the atmosphere. Re-emission of compounds after degradation whilst deposited at a sink can also occur, showing that pollutants both organic and inorganic can undergo a wide and diverse existence, before complete degradation or final deposition to a specific sink occurs.

1.5 Sources.

The sources of air pollution are very much dependent upon the type of context the air sample is taken from. For example, samples can be from inside a building or from an outdoor environment, be it urban or rural. Specific sources will be discussed later, however, in general possible sources for pollutants in indoor and outdoor air include:-

Outdoor air.

Primary emissions

1. Road transport including petrol and diesel emissions.
2. Power generation.
3. Residential and commercial combustion.
4. Industrial combustion.
5. Construction emissions.
6. Quarrying emissions.

Secondary emissions.

Chemical reactions ; formation of fine particles of ammonium sulphate/nitrate.

Indoor air.

1. Fuel combustion/cooking emissions.
2. Tobacco smoke.
3. People.
4. Animals.
5. Building materials.
6. Furnishings.
7. Outdoor air diffusing in.

It can be seen that a sample from either of the environments will be complex, with a number of contributing sources being possible. The development of methodology by which specific sources could be identified from a sample, would therefore be very useful. Ultimately, ways of reducing the effect of such a source, could be investigated.

1.5.1 Outdoor Air.

The major sources of pollution in outdoor air have changed quite considerably over the last 50 years, as the chemistry of the atmospheric environment has become understood, and the detrimental effects of certain pollutants has become apparent. Coal was the main source of industrial and residential heat and power up to and including the 1950's and 60's. Air pollution during this time was considerable with "dirty smog" regularly occurring in urban areas due to the high concentrations of particulate material, and SO_2 released from coal combustion, e.g. the London smog episode of 1952 (57). This was caused by exceptionally high levels of total suspended particulate (TSP) material and SO_2 over a four day period in December. Average concentrations for that time of year were 120-440$\mu g/m^3$ and 0.07-0.23$\mu g/m^3$ (TSP) and SO_2 respectively. These levels rose to highs of 4460$\mu g/m^3$ and 1.34$\mu g/m^3$ for (TSP) and SO_2 during this time. This large increase in atmospheric pollution was in part due to the "still" meteorological conditions that were situated over the south of England, in addition to the pollution emitted continuously during this period. The high concentrations had a major effect on mortality (specifically chronic respiratory and cardiac deaths) with an estimated 3500-4000 excess deaths due to the air pollution. 90% of the deaths occurred in individuals over 45 years of age, with between 60-70% over the age of 65. The number of deaths in children under 1 approximately doubled. The increase in deaths was seen mainly associated with older individuals often with respiratory or cardiac problems or young children whose respiratory and cardiac systems were still developing (57). The 1952 smog pollution was a major reason for the introduction of the Clean Air Act of 1956.

The advent of gas central heating and smokeless areas where the residential combustion of coal or wood is prohibited, along with the conversion of power stations from coal, to gas and oil, has drastically reduced the emissions of particulate material and SO_2. However, other sources have begun to increase in recent years, specifically the emissions from motor vehicles. Levels were reduced slightly with the introduction of unleaded petrol in 1986. However, urban areas are now under the threat of increased pollution from vehicle emissions and specifically diesel emissions.

1.5.1.1 Vehicular Emissions.

Vehicular emissions are similar to all anthropogenic emissions, containing quantities of carbon monoxide, carbon dioxide, particulate material, NO_x, organic compounds and metals at varying concentrations. The emissions from any one vehicle can be very different to similar vehicles due to physical engineering factors and the manner in which the vehicle is driven. For example a car driven at a relatively slow constant speed will produce different emissions to a vehicle driven hard and fast in a lower gear.

Diesel emissions have become an increasingly important source of urban pollution. They are likely to become even more significant in the near future due to many, if not all of the following reasons.

1. From 1993, all new petrol powered cars were required to emit a reduced level of CO, CO_2, unburnt hydrocarbons and NO_x (58). This was achieved by many car firms by fitting catalytic converters, which was made law in 1993 (59). However, due to the different characteristics found in the various types of diesel engine, there is as yet, no commercially available catalytic converter for diesel vehicles. Their contribution to an atmosphere will therefore become more pronounced as the number of petrol engines with catalytic converters increase.

2. Diesel cars have also begun to become more common on the roads as their popularity has increased. In 1991, diesel cars occupied 5-6% of the new car market, by 1993 this had risen to 25% (60). The increase in the share of the new car market by diesel was due to the prices of diesel and petrol powered cars becoming comparable. Petrol cars had to be fitted with emission reducing systems pushing the price of the car up. Diesel cars became more attractive due to the similar price and also due to the financial gains associated with diesel car. These were that the car was more economical to run due to better fuel efficiency, along with the maintenance of the vehicle being less than for an average petrol powered vehicle. This is due to diesel engines using compression ignition in the combustion region, which is known to be less wearing on engine parts compared to petrol powered spark engines. Diesel cars were also seen as the cleaner more environmentally friendly mode of transport as they emit less CO_2 than petrol cars.

3. A comparison of emissions from petrol vehicles (both with and without catalytic converters) and a diesel engine (61) identified that the major emitter of CO, total hydrocarbons and NO_x was the standard petrol driven car with no catalytic converter. Emissions from a petrol car with catalytic converter released slightly higher levels of CO, compared to the diesel engine, however the diesel engine released slightly more NO_x and total hydrocarbons compared to the petrol car with catalytic converter. Particulate material released in the exhaust emissions was also measured. A measurable quantity was found only in the diesel emissions.

4. Particulate material from a diesel engine consists of approximately two thirds elemental carbon and one third organic carbon (62). Particulate material released from leaded petrol consists mainly of organic carbon, lead and bromine (from anti-knock and scavenging agent additives, respectively) (63). With the introduction of unleaded petrol, the lead particles around which much of the petrol particulate material was formed is no longer present. This caused the amount of particulate material in petrol emissions to drop to levels where certain diesel vehicles can release up to an order of magnitude more particulate material into the atmosphere than an unleaded petrol vehicles (61).

It can therefore be seen that a major source of urban particulate emissions in the future is likely to be from diesel engines, due to the increase in diesel cars, along with the emissions from various light goods vehicles (LGV's), heavy goods vehicles (HGV's) and buses. Particulate material is likely to be even more specific to diesel compared to petrol engines due to the elevated levels found in diesel emissions. If a method for specifically identifying vehicle emitted particulate material, (e.g. diesel particulates) can be found, a contribution to an atmosphere for diesel emissions could be identified. Other urban particulate material which would account for the unknown percentage would include re-suspended street dusts, particles from tyre debris and other worn car parts. However, these particles have been identified as being mainly associated with larger particles >2.5μm (64).

Diesel.

There are two main types of diesel engine:-

1. The direct injection (DI) engine where fuel is injected directly into the combustion chamber, and ignition is induced via compression. This type of engine is used for LGV's, HGV's and buses. The DI diesel engine is more fuel efficient and as a consequence produces a higher quantity of NO_x and particle material in its exhaust emissions (compared to indirect injection diesel engines). Higher quantities of NO_x and particulate material are produced per volume of fuel as there is a certain amount of heat loss when the burning fuel flows into the cylinder from the pre swirl chamber (in indirect injection diesel engines). This heat loss results in lower combustion efficiency and ultimately lower particulate emissions (per volume of fuel). The average temperature of an indirect diesel engine is also lower, reducing the amount of NO_x produced by the Zeldovitch mechanism.

2. Indirect injection (IDI) diesel engine is a quieter engine compared to the DI. Fuel is injected into compressed air in a pre (swirl) chamber where it ignites and combustion begins. The combustion mixture then flows directly into the combustion chamber where the power is generated. Due to its quieter running this type of engine is mainly used in diesel cars.

Diesel particulates contain elemental carbon, with some sulphate and water. These elemental particulates are formed in the pre swirl or combustion chamber into which a fine spray of fuel is injected and ignited. Fine particle <0.2μm are formed along with pyrolysed fuel. These combustion products along with CO, CO_2, NO_x, VOCs and unburnt fuel are released into the atmosphere through the exhaust system. As these emissions pass through the exhaust they are capable of reacting with other emissions at the elevated temperatures to produce an increased variety of organic compounds. As they pass into the atmosphere (or cooling tunnel when samples are being taken) the emissions cool, high temperature boiling point organic compounds and some of the unburnt fuel condense out and coat the elemental carbon particles which begin to coagulate forming larger particles from between 0.2-2μm. These particulate emissions

have been linked with possible detrimental health effects as they are small enough to penetrate deep into the lung (Section 1.1.3). Particulate material has in some studies been linked with mortality/morbidity (Section 1.6) however, the direct mechanism for this is not yet understood.

100% of the particulate material released by diesel vehicles has been shown to be of a size less than 10μm in diameter, and 92% of all emitted particulate diesel material is below 2.5μm (58). Petrol driven vehicles (not including cars with a catalytic converter) produce on the whole larger particles than diesel engines, with only 70% of the particulate material being <2.5μm in diameter (64).

The increased levels of particulate material found in the urban environment has been attributed to vehicle exhaust emissions, of which the majority is likely to be from diesel engines. An estimated 2-10 times more particulate material is generated by diesel cars compared to petrol powered cars and 5-50 times more particulate material is released by larger HGV type vehicles compared to petrol driven cars. Over-all in 1995 it has been estimated that 5 times more particulate material was released by diesel powered vehicles compared to petrol driven vehicles throughout the UK (64). An accurate quantitative value is very difficult as little work has been published on the average particulate emissions from petrol engines.

The emissions of particulate material, hydrocarbons and CO increase from a diesel engine with the use of lower speeds, acceleration and deceleration due to urban speed ramps, sleeping policemen and other traffic control measures (however, contradictory evidence to this is found in literature (65)). Such driving increases fuel consumption by the engine due to inefficient fuel combustion, especially during acceleration, compared to the constant speeds of a duel carriageway or motorway. Urban areas are where this type of driving is found in most profusion thereby increasing levels of pollution in urban environments. This is especially true for buses owing to their constant stopping and starting, to pick up and alight passengers along their route. It has been estimated that 86% of all PM10 material in Greater London can be attributed to road traffic (64), a major proportion of this is likely to be from diesel emissions.

Previous work to identify if vehicular traffic did increase pollution in an urban environment has been completed. PM10 samples taken from roadside sites in central London were compared to PM10 samples taken at three roadside "background" urban sites on the outskirts of the city. Averages over the years 1986-89 identified an approximate increase in PM10 levels of between 2.5-3 times at the central roadside samples compared to the background samples. This increase was attributed almost entirely to vehicle emissions (66).

Another study centred on London identified that up to 77% of all particulate polluting material was from vehicular emissions (67). It identified that particulate material and lead varied throughout the year with highs in the winter (from increased use of vehicles during cold weather and the prevention of dispersion of the pollutants emitted at ground level sources due to stable atmospheric conditions) and lows in the summer (67). More recently, a daily variation has been observed for particulate matter with peaks at 8.00am and 5.00pm during week days, adding further evidence to the increased levels of particulate material in urban environments as being from transport (66).

As described earlier in this section, much of the diesel particulate emissions originally released are of very small size, <0.2μm in diameter. These can be extremely difficult to accurately measure especially if a filter with a pore size of 1μm is used. Even if they are successfully sampled, the small size causes little contribution to the actual sampled particulate mass. However, it has been shown that these ultra fine particulates can be present in the immediate vicinity of the source at very high concentrations. For example measurements in central Birmingham three metres from a main road gave particulate counts of 10^3-10^6/cm^3 (Average 180000/cm^3) (66). Counts under similar weather conditions at a background site several hundred metres away gave an average particulate count of 27,000/cm^3. This 6-fold reduction is likely to be due to dilution through mixing with cleaner air, agglomeration of the smaller particles into larger particulates, or adhesion to surfaces.

Thus, the indication here, is not only that the mass of particulate material is important in identifying the major polluting sources but, just as important, is the number of smaller particulates released into the atmosphere. The high levels of finer particulate material

released into the atmosphere, adjacent to the source is considerable, and also it is known that these particulates are capable of penetrating deep into the lung to be deposited into the alveolar region (21). Work by Jones and Harrison (66) has identified that the number of particles does not drop after the morning rush hour unlike many components of vehicle emissions such as PM10. This indicates that they have a longer life-time in the atmosphere and are hence respirable throughout the day.

Conclusion.

In this section it has been shown that petrol and diesel propelled vehicles are likely to contribute different amounts of polluting emissions to any one atmosphere. However, in an urban environment it is likely that diesel engines will emit the largest quantity of particulate emissions, as they release approximately 5 times more particulate material than petrol powered vehicles. The contribution from diesel vehicles is likely to escalate with the expected increase in the numbers of LGV's, HGV's and buses over the next few years (60). The increased amount of stopping and starting of these vehicles in the urban area and the increasing number of diesel cars will also exacerbate the situation. These factors along with the health implications of fine particulate material and access to a diesel engine in an exhaust sampling laboratory led to the initial aim of this project. To identify a convenient method capable of identifying the contribution of diesel emissions to an urban environment.

1.5.2 Indoor Air.

People spend the majority of time in an indoor environment these days, be it either at home or at work. The vast quantity of air that we breath is therefore indoor air which until recent years was an area of the atmosphere that was not well researched. Notice was originally taken around 1973 and coincided with the Middle East oil embargo, which identified the necessity for an increase in overall energy conservation. This was achieved by improving combustion efficiency for heating, along with improvements in insulation. However, increased insulation produced a reduction in ventilation of buildings (especially during colder climatic times), which led to increasing levels of indoor pollution, such as volatile compounds (68). Health complaints associated with indoor air were seen to

increase with this variation in indoor air. Levels of various pollutants did not necessarily exceed those permitted by current legislation. However, the long term exposure to these lower concentrations (chronic exposure), in conjunction with outdoor pollution could have induced the health problems observed.

Major sources of indoor pollution include biological pollutants, with humans mainly emitting odorants, water vapour and CO_2. Other biological emissions include those from pets and micro-organisms releasing CO_2 and odorants as well as skin, hair and waste material. Combustion due to heating and cooking can release various pollutants including CO, NO_x, particulate material and formaldehyde. Buildings and their contents can emit various chemicals including volatile organic compounds and formaldehyde from insulation, paints and varnishes. Human activity releases a whole array of substances into the indoor environment with cleaning releasing organics and odorants and environmental tobacco smoke (ETS) producing CO, particulate material and odorants (69).

Groups that are found to spend the majority of their times in an indoor environment include the elderly, the young (children) and the sick. Their movements are often restricted by climatic variations with an increase in heating during the winter associated with a reduction in time outside. At the same time, levels of indoor air pollution increase due to reduced ventilation and increased combustion emissions. All these groups (elderly, the sick, and children) have been identified as being highly susceptible to some forms of air pollution and climatic variations. This is discussed further in Section 1.6.

A recent study by the Department of the Environment in collaboration with Bristol University (70) undertook a study investigating child health, child development, and indoor air. The main objectives of the study was to investigate the concentrations of various compounds in the air and the variation of these due to house characteristics and human activity. Variation of chemical and microbial concentrations throughout the year were also investigated

The highest average concentrations of NO_2 were generally found in the kitchen, and gas cookers were identified as the major source. Levels were high during the winter months and when the dwelling was situated in an urban environment, adding weight to the idea

that outdoor pollution penetrates the indoor environment. This has been identified as occurring for both gaseous and particulate pollutants (72). Concentrations of NO_2 in some households were found to be regularly above levels found in outdoor air, depending on the season (68).

Mites, fungi and bacteria were found mainly in the living room and bedroom. The seasonal fluctuation of mites and fungi indicated that higher levels were present during the summer months, this was mirrored to a lesser extent by bacteria.

Volatile organic compounds were found to be up to ten times higher in indoor environments compared to outdoor environments. There are therefore major sources of organic compounds to be found in indoor areas which are not being diluted or transported from indoors due to poor ventilation. Formaldehyde is a fairly ubiquitous compound, which has been found to be released in higher concentrations from newer houses than from older houses. There was also an annual fluctuation of formaldehyde release with higher levels found during the summer months. Major sources of volatile organic compounds were found to be houses where painting was or had recently taken place along with a household in which there was a smoker (68).

The sponsors of the work reported in this thesis, Rothmans International were interested in comparing indoor air quality of households/workplaces with smokers to household/workplaces without smokers, and measuring the effect a smoker has on an environment. Using a measure of vehicle (diesel) emissions a value for outdoor air penetrating into an indoor environment could also be investigated, along with the contribution associated with ETS.

1.5.2.1 Environmental Tobacco Smoke (ETS).

Environmental tobacco smoke (ETS) describes the tobacco emissions a non-smoker is exposed to when in the presence of a smoker. ETS is of greater significance in an indoor environment since the accumulation of emissions due to reduced dilution is possible. ETS is of less importance in an outdoor environment due to the large dilution possible from the overall atmosphere.

ETS is the overall name given to tobacco smoke released from various parts of burning tobacco, be it a cigarette, cigar or pipe. ETS can be divided into three specific sources. These include :-

1. Side-stream smoke (SS), which is the emissions released from the burning end of the cigarette, directly into the atmosphere, and the major source of ETS (74).
2. Main-stream smoke (MS), which in itself contains two components, the smoke exhaled from the lungs by the smoker and the emissions exhaled that don't reach the lungs after the initial inhalation of the cigarette. Little inhaled material is subsequently exhaled (73).
3. The final emission type includes material released through the paper of the cigarette.

The chemistry of tobacco combustion is extremely complex and consists of a number of chemical reactions that occur in the combustion zone. Oxidation is the major reaction occurring. However, there is seldom enough oxygen for complete combustion, therefore an array of partial and completely oxidised compounds are produced. Other reactions include pyrolysis (transformation of a compound to one or more different compounds due to heat alone) as the temperature at the end of the cigarette can reach temperatures in excess of 800°C (73). This ensures that the 2000 compounds identified in the tobacco blend can produce up to twice this number in ETS.

The type of tobacco being smoked can also produce variations in emissions. For example, cigarette tobacco, cigars and pipes all contain different blends of tobacco and tobacco that has leaves cured in different ways. The majority of cigarette tobacco leaves are flue-cured, where warm air is passed over the leaves to dry them. On the other hand, cigar and pipe tobacco is often allowed to dry more naturally. This causes a variation in the sugar content of the tobacco as the warm air associated with flue curing activates enzymes in the leaf to convert starch into sugar, while the naturally dried leaves produce little conversion of starch to sugar. Tobacco blends vary from brand to brand and additives (a list of which can be found reference in 75) and their respective concentrations all ensure that ETS is a highly complex mixture (74).

Another added complexity of ETS is that the concentrations of many of the compounds released in ETS vary with time, this is known as ageing. Both vapour phase and particulate associated organic chemicals released from the cigarette are susceptible to chemical conversion once released into the atmosphere. Particulate material is also likely to change due to the original particle containing a high proportion of water. These particles are susceptible to surface adhesion, removing them from the respirable atmosphere quite rapidly.

However, particulate material and vapour phase organic compounds can be inhaled (by both smokers and non-smokers) deep into the alveolar region of the lungs, as much of the particulate material released by cigarette smoke is of <2.5μm. The health effects this can cause will be dealt with in Section 1.6. However, as ETS contains gaseous molecules of CO and NO_x, vapour phase organic compounds including benzene, toluene, xylenes, nicotine and various derivatives in addition to particulate associated organics including PAH compounds, we can identify that exposure to such organic material is likely to be increased in households/workplaces where individual(s) smoke.

1.6 Health Effects.

A great deal of literature has been published on the effects of both indoor and outdoor air pollution on health. The following section is aimed to further clarify the importance of accurate measurements of air pollution and their sources, due to the possible adverse health effects.

1.6.1 Health Effects Associated with Outdoor Air Pollution.

The difficulty in trying to discuss the contribution of air pollution to increased health problems is immediately apparent to anyone who reads the literature associated with this area. The biggest problem being how you quantify if a person fell ill purely through the inhalation of polluted air, or if they would have fallen ill anyway? Is the polluted air purely speeding up an illness that is exacerbated by air pollution? Is it caused by pollution that is present at low concentrations over a long period of time (chronic exposure)? Pollution that is present at higher than normal concentration for short periods of times (acute exposure)? Does it effect certain age groups? Does it preferentially effect people with respiratory problems? Is it a specific pollutant from one source or a combination of pollutants from various sources? Are these adverse health effects occurring during the summer months (of high ozone and secondary particulate material) or winter months (low ozone and high levels of particulate material). There are more question than answers at the current time. However, some interesting correlations are to be found.

A lot of work found in the literature relates to a specifically high pollution episode in a specific place due to certain weather conditions (often anticyclones preventing air movement). Such conditions restrict the dispersion of the constantly emitted pollutants producing extremely high concentrations in the atmosphere. Such episodes include those seen in London in 1952 (57,76) discussed earlier, the 1962 London episode and another, again in London in December 1991 (77). These studies have been used to identify increases in the morbidity, mortality rates during the pollution episodes and relate them to the high concentrations of pollution at that time.

Other studies on atmospheric health effects use groups of individuals (be they young or old, symptomatic or asymptomatic of asthmatic type problems), who keep records of illnesses or health problems for a period of time. Research in America has used these diary exercises to good effect. These real time studies produce possible statistical increases in health problems due to atmospheric pollution.

Chamber studies (where volunteers are exposed to levels of pollutants) and in vitro studies (where animals are exposed to pollutants) can all add to the understanding of the possible effects of pollutants on individuals. All these types of studies were investigated to try and identify the major contributory effects associated with atmospheric pollution.

Nitrogen Dioxide.

Nitrogen Dioxide is mainly released in vehicle emissions into the outdoor atmosphere and is often associated with urban areas. NO_2 is also a major pollutant of indoor air, associated with gas cooking facilities (69). Analysis of outdoor exposure has been extensive however, the health effects are still valid for NO_2 exposure indoors. High levels have been observed in several cities around the world, including the London high of 1991 (77). In that instance, the highest ever levels of NO_2 in the UK were recorded. However, this pollutant was found not to significantly contribute to the increase in mortality/morbidity. Conversely, other studies have found a statistical increase in overall mortality due to elevated NO_2 (78). However, these same workers identified that this increase was not associated with respiratory or cardiac deaths (79). Difficulties arise from specifically associating increases in mortality to NO_2, as increases in particulate material concentrations are often associated with NO_2 variations, due to their similar sources.

Even though mortality association is unclear for NO_2, there has been literature which has associated respiratory problems with an increase of this pollutant. Admissions to hospitals do seem to increase, with an increase in asthma admissions (80) other respiratory problems (79), specifically in children (81), and circulatory problems including chronic obstructive pulmonary disease (COPD) (82). NO_2 has also been identified as effecting asthma sufferers (83-85), associated with causing a reduction in

lung function (86) and inducing an inflammatory response of the respiratory tract (83,87). A reduction in mucociliary activity has also been observed after exposure to NO_2 for only a short period (88). This type of response may cause increased sensitivity of the airways and produce an enhanced sensitised response to allergens solely due to NO_2 (89,90) or in association with other atmospheric pollutants such as SO_2 (91).

We can see from the studied literature that an understanding of the health effect of NO_2 in the atmosphere on individuals is not complete. Even though statistical evidence of increased mortality (78) has been attributed to NO_2 in certain elevated episodes, other pollutants are often present causing a great deal of uncertainty about the specific contribution associated with NO_2. However, we can conclude that NO_2 could possibly induce increased sensitivity to the respiratory system (especially in asthmatics and individuals with other respiratory problems). The increased sensitivity and possible airway permeability (84) can then be aggravated by other pollutants present in the atmosphere, such as SO_2 (91,92), and/or particulate material (78), during the winter and ozone (93) during the summer months, when the levels of ozone are high. Circulatory problems could be associated with the formation of NO-Haemoglobin and met-Haemoglobin, i.e. haemoglobin that reacts with NO and NO_2 respectively, preventing them from carrying oxygen around the body (94).

Particulates.

Particulate material is a complex atmospheric pollutant, due to the size, shape and composition all depending on which source the particles arise from (See Section 1.1.3). Particulate material and its effects on health have therefore been investigated a great deal. However, even after extensive investigation, there is still no known biological mechanism by which particulate matter effects the health of individuals. The smaller particulate material <2.5μm in diameter (PM2.5), are able to penetrate into the alveolar region of the lung. Sources of this material are vehicular emissions and secondary production of ammonium sulphate and nitrate. The fine fraction from vehicle emissions therefore consists of carbon particles which can have various metals and organic compounds associated with them, in addition to ammonium sulphate/nitrate. The smaller

sized particulates are thought to induce the adverse health effects rather than coarser material. However, there is as yet no proof of this (79,95).

Numerous studies (after correcting for possible errors for individuals that smoke, or are exposed to high levels of ETS or occupational exposure due to work) have identified particulate matter PM10 as causing an increase in overall mortality/morbidity (96) and hospital admission cases (97). Problems can occur in this type of study from the use of death certificates, as the stated cause of death can be mis-leading from the actual cause of death which may be due to stresses on a weakened area from an associated problem. For example many respiratory deaths in America are recorded as cardiovascular or circulatory deaths (98). However, correlations are still identified in many mortality/hospital admissions, these include respiratory disease (97-100) cardiovascular deaths (97-99,101) and a number of respiratory associated hospital admissions and deaths, due to levels of particulate material (85,102,103). Wordley et al (102) identified elevated concentrations of PM10 material with increased mortality/admissions of people with ischaemic heart disease (IHD) and acute cerebrovascular problems.

Identification of increased irritation due to air pollution of asthmatic and "healthy" children has also been investigated in the USA (104) and Europe (100,106,107), while a study of adult individuals using respiratory medication was undertaken in Europe (108). Children were seen to be more effected than adults. Children both symptomatic and assymptomatic (of asthma symptoms) were found to show reduced peak expiratory flow (PEF) and an increase in symptoms of respiratory disease. The effects were seen to be most significant in the symptomatic children (105). The identification of a lag time was also observed, with the effects of a high pollution episode of increased PM10 causing an increase in mortality/respiratory associated problems (99,105,109) for up to four days after the original high emission. Work in the USA also identified an increase in the hospital admissions of people with cardiovascular problems (110) and respiratory problems (111,112) who were aged 65+. Several atmospheric pollutants were measured during the time of the study, including PM10, ozone, SO_2 and CO. Statistical independent association was observed between congestive heart failure, PM10 and CO (110). While independent PM10, levels were found to statistically increase the admission of ischaemic heart disease (110).

Anderson, et al (77) found that with the elevated levels of pollution (including particulate material and NO_2) in the London pollution episode of 1991, led to a statistical increase in all mortality (excluding accidents) compared to the immediate previous weeks. The number of respiratory problems for the elderly (65+) part of the population was also observed to increase. Control values were also obtained from other parts of the country for the same weeks, where no increase in air pollution was apparent. All levels of mortality increased for respiratory type diseases, in all age groups, including respiratory infections, and obstructive lung disease. A statistical increase was also seen for deaths from cardiovascular diseases. The increased levels of particulate material were found to be statistically associated with the increase in deaths and admissions for respiratory and cardiovascular problems. As stated previously, NO_2 was not found to cause any health effect in this study. Several more recent studies have investigated the effects of air pollution and health in London (101,113,114) along with a study carried out in Birmingham (102) and a European study including results from six cities (115). The Birmingham study identified a higher level of mortality due to particulates compared to the London and European studies but all studies identified a statistical correlation between particulate pollution and increased mortality.

One possible mechanism for this increase in health effects is believed to be due to the acidic fine fraction of the atmospheric particulates released from anthropogenic sources and secondary formed particulates (116,117). These ultra fine particles are capable of penetrating deep into the alveolar region of the lung, where they cause lung inflammation as well as increasing blood coagulation resulting in cardiovascular deaths. It is proposed that it is the number of these fine particles (which have little mass) and not the overall mass of material inhaled which can cause detrimental effects. A recent study on rats showed that an exposure to high numbers of fine particulate material induced bronchoconstriction and resulted in the deaths of some of the rats (118). Such reasoning would help to explain why people susceptible to atmospheric pollution are likely to be elderly house bound individuals (since traffic emissions are capable of penetrating indoor areas (91,97,119) rather than industrial workers who are often exposed to a larger mass of particulate material but of a coarser size.

It can be seen from the literature reviewed in this section that an increase in particulate pollution does seem to cause ill health both directly (respiratory problems) and indirectly (cardiovascular/cardiopulmonary). Particulate pollution has been linked with chronic effects, leading to increased mortality/morbidity (79). Investigations have also identified a statistical increase in respiratory and cardiovascular problems in the elderly 65+ (77) along with problems for asthmatics with increased problems for asthmatic children (106). We can therefore state that particulate material does seem to cause an adverse effect on the health of individuals. Those at most risk include children and the elderly, especially those with medical conditions. A recent UK government report stated that 8100 premature deaths were caused by particulate material along with 10500 additional hospital admissions (79).

Sulphur Dioxide (SO_2).

SO_2 is present in the atmosphere and is the only combustion product discussed in this section which is known to cause respiratory irritation and bronchoconstriction, especially to asthma (79) and bronchitis sufferers (115). However the mechanism for this reaction is not yet known (79).

Several recent studies from six European cities (79,104) have shown that there is a statistical increase in the number of over-all deaths from cardiovascular and respiratory illnesses with an increase in SO_2. Similar trends were also noted in a review by Lebowitz (120). Hospital admissions have been observed to statistically increase with increasing SO_2 levels, in the case of elderly, (79,101) respiratory, (111) and asthma admissions (100,103). Other health effects due to elevated SO_2 levels include an increase in wheezing and use of bronchodilator medicines and also a reduction in peak expiratory flow (PEF) in children with chronic respiratory symptoms (106). Similar results were seen in a study of adults with respiratory disease (121). A recent UK report stated that the possible number of premature deaths due to SO_2 pollution was 3500 and the number of additional hospital emissions of a respiratory nature was also 3500 (79).

From the literature investigated it is observed that SO_2 does have an effect on the health of individuals. As with NO_2, the problem with discussing the health effects of SO_2 is that

its present sources such as vehicle emissions also produce particulate pollution at the same time. An elevated concentration is therefore likely to correspond with high levels of NO_2 and particulates making the identification of their individual contribution to adverse health effects very difficult. However, it can be determined that SO_2 even at relatively low concentrations can produce a cumulative effect with other pollutants such as NO_2 (91,92) and/or particulate material (78). SO_2 also contributes to the secondary pollution through the formation of sulphate particles along with the primary SO_2 gaseous pollution.

Ozone.

Studies have shown that ozone can cause inflammation of the respiratory system resulting in a reduction in lung function (122). Once again, no mechanism has yet been identified linking ozone with effects in health, but trends and statistical data from various studies show that some effects can occur. Contradictory results have been obtained from several studies looking at the increase in mortality due to an increase in ozone in an atmosphere. A European study of several cities identified ozone as a cause of a statistical increase in total mortality (78,103,113,114,123), for sufferers of cardiovascular and respiratory problems. Some studies from the USA agree with these findings, as they also found an increase in mortality due to an increase in atmospheric ozone (100,124). However, other US studies disagree with this hypothesis since no statistical increase in mortality was found due to ozone (125).

The European study indicated that there was a specific increase in cardiovascular and respiratory mortality with admissions for respiratory problems in all age groups. COPD admissions and asthma admissions all statistically increased with increased ozone (103,114,123). Respiratory admissions for the elderly (65+) population also increased in a US six city survey (113,125) along with elderly COPD admissions (112). An increase in the admission of pneumonia cases has been observed and identified as statistically significant with respect to ozone (125).

The short term effects of ozone on the respiratory system have been discussed, with brief exposure to certain concentrations causing increased lung permeability and reactivity

(124). Other detrimental effects include a reduction in forced expiratory volume (FEV_1 in 1 second) (126) and PEF (115,121,127), often associated with higher previous day concentrations. However these expiratory flow results were contradicted by similar studies carried out on children, which identified no statistical reduction in FEV_1 (107) or PEF (126), due to high ozone levels (107).

Ozone toxicity at the levels often found in the atmosphere is difficult to quantify, as a great deal of contradictory evidence is available from the literature. Effects of ozone from minor short term problems to hospital admissions and fatalities have at some point been shown to be statistically significant. However there also seems to be an equal number of studies which find no such significance in ill health due to ozone. The result of this is therefore slightly more tentative than for previous pollutants. Ozone possibly causes detrimental health effects, especially in susceptible individuals, with this increasing when other pollutants such as SO_2, NO_2 or particulate material are present.

Carbon Monoxide (CO).

Several studies have identified a statistical increase in overall mortality (128,129) and cardiovascular admissions (129,130) due to an increase in CO levels. These are often associated with elevated PM10 and SO_2. The increase in admissions has been investigated further and statistical increases in myocardial infarction, heart failure and circulatory disease admissions (101) have been identified. Increases in admissions of congestive heart failure in the elderly (131) due to elevated CO concentrations have also been observed.

As CO is released from combustion emissions it can be seen that an elevated level of CO will probably correlate with an increase in other combustion products including SO_2, NO_2 and particulate material. Such effects will be evident in both indoor and outdoor environments. It can therefore be said that CO has a role to play in the health effects that occur through atmospheric pollution both individually and cumulatively. The mechanism by which CO causes detrimental health effects is uncertain. However, the statistical increases in admission and fatalities are all associated with the circulatory system and the heart. The effect that increased CO levels have on the oxygen levels in the blood can

cause health problems especially in elderly (131) or individuals with cardiovascular (101) or heart problems (101).

1.6.2 Health Effects Associated with Indoor Air Pollution.

Environmental Tobacco Smoke.

For some time the health effects of direct smoking (i.e. the inhalation of tobacco smoke directly from the cigarette) has been known to be a cause of chronic respiratory disease, cardiovascular disease, in addition to cancers of the lung and various other sites including oral and throat (132). It has also been stated that half of all regular smokers are eventually killed by tobacco related illnesses. This works out to be approximately 1/5 of all deaths in the UK, attributing 120,000 deaths a year to tobacco related disease (132).

The determination of a link between increased illness and ETS has been much harder to accurately identify. Numerous studies have been published identifying/not identifying a link between non-smokers and exposure to ETS at work or at home. Increased respiratory problems including asthma have been identified, along with middle ear infections for children often present in ETS atmospheres due to parental smoking (132). ETS has not only been linked with an increased likelihood of respiratory and cardiovascular disease but also to possible incidences of increased coronary heart disease (133). However, reanalysis of results published in this area by LeVois and Layard (134) identified bias towards falsely high relative risk values for coronary heart disease associated with ETS exposure.

Even with the extensive array of literary sources, the conflicting information makes it difficult to determine the health effects of ETS. However, the following section will attempt to identify the major effects of ETS to an atmosphere, and why it is therefore necessary for accurate analysis of indoor environments to identify the contribution that ETS makes to an atmosphere.

ETS was originally described as having a similar chemical composition to main stream (MS) cigarette smoke, and therefore contained several known carcinogens/mutagens previously identified in MS smoke, which were identified as causing lung cancer. The concentration was simply diluted due to the mixing of ETS with air in the atmosphere (132). However the simple presence of the compounds does not directly necessitate that ETS should be classified as a class A human carcinogen (135) (which it has been by the US EPA (136)) as many of these compounds had not been identified as carcinogenic at the concentrations found in ETS, or when inhaled into a biological system (137). Also certain publications identify ETS as causing cancer "beyond reasonable doubt" (138), while other publications strongly refuted this (135,139).

In fact ETS is a complex combination of side stream (SS) and exhaled MS smoke which has a different chemical composition than inhaled MS smoke due to the adsorption of major quantities of constituents from MS smoke into the body of the smoker. It has been stated that over 90% of inhaled MS particulate material is retained in the respiratory tract (140,141). Non-smokers retain a much smaller proportion of ETS particulate material (estimated to be 11% by Hiller (141), and 34%/26% in men and women respectively (142)), due to their better lung clearance compared to a regular smoker. The emitted particulates and gases are then diluted by the atmosphere (increased by circulation and ventilation) along with various ageing processes that change the chemical composition of ETS. Therefore the identification of ETS as diluted MS smoke is likely to produce erroneous results, but has in the past been used to estimate ETS exposure. Tobacco smoke carcinogenicity due to direct inhalation has also been identified as being reversible in action, i.e. the risk of damage reduces when the smoker stops smoking for a period of time. They never attain the lower level of risk associated with a non-smoker, indicating that a small amount of permanent damage is left (135). However the lungs do recover to a great extent. Recent toxicological work using A/J rats that inhaled ETS (side stream) for a number of hours per day for five months, were then allowed to recover (no ETS exposure), did show a significant statistical increase in the number of rats that produced lung tumours against a control group (143). However two studies were unable to identify a significant increase in the number of lung tumours found in A/J mice when one group were exposed to ETS while a control group was not (144,145). The major difference was the use of a recovery period in the experiment in which a significant

increase was seen. This identified that a recovery period was necessary for the full carcinogenicity to become evident.

Numerous studies have identified a link between ETS and various respiratory illnesses (136). Epidemiological studies of lifetime non-smokers who have lived with a smoker were shown to have an increased likelihood (relative risk = 1.24) of developing lung cancer (146). The study also identified a relationship between the average number of cigarettes smoked and the length of time of exposure with increased risk (146). Overall averaged relative increased risks due to ETS has been stated as being between 1.38 and 3.11 (136) (although a study by Cardenas et al (147) identified a far lower relative risk of 1.2 for non smoking women and 1.1 for non-smoking men married to smoking spouses). The higher risk factor (RR = 3.11) is in fact higher than some relative risks identified in studies looking at women who actively smoke (135,136). Direct measurement of ETS exposure by analysis of marker systems/compounds identify that levels are far lower than those estimated by epidemiological studies with relative risks of 1.04 for women and 1.07 for men with smoking partners, identified by Lee et al (148) (by biological cotinine measurements), while other extrapolated exposures have been identified as being from 1.003-1.07, (measurements of ETS particles and nicotine atmospheric concentrations (135)).

Disagreement in relative risk, especially the higher risks identified by epidemiological studies have been published, in which confounding factors are found to cause the increase in lung cancer associated with non-smokers who live with smoking partners. Such factors include diet, air pollution, life style, mis-diagnosis and various biases including recall, publication and misclassification (Tobacco Manufacturers' Association 132) and hereditary disposition (135). They identify that data from written reports or interviews can be unreliable and that questioning can sometimes miss important factors such as a non-smokers previous smoking habits, which are seldom taken into consideration (135).

One bias identified as causing a major influence on data available in the literature included bias by the authors/editors preference to publish data identifying a statistical significance. In fact, a mathematical data analysis on the identification of ETS causing

lung cancer in non-smokers was investigated by Givens et al (149). They used a funnel plot to identify bias of US EPA data which identified a link between ETS and lung cancer. Givens (149) identified that up to five studies which displayed no increase in relative risk between ETS and lung cancer had not been published, and that the excess risk may be overestimated by up to 30%. These results were later "found" in 1994 (150).

Another major confounding factor for higher levels of risk associated with ETS in epidemiological studies could be due to the socio-economic level of certain individuals along with their diet (135). It has been identified that people on low incomes that volunteer/chosen for epidemiological study are more likely to smoke (135,151) and may spend periods of time unemployed. This increases the average length of time at home, possibly increasing the length of time a non-smoking partner or infant is exposed to ETS. Similar trends are identified in smoking mothers and associated infant and school child studies (151). It is stated in Sterling et al (151) that 34 reports of epidemiological studies of non-smoking women with smoking husbands were reviewed and none considered the socio-economic position of the individuals in the study.

Dietary information along with socio-economic position and ETS exposure has also been investigated. Levels of fruit and vegetable intake seem to be associated with such grouping with lower levels consumed by families containing a smoker (often the husband (135,152)) compared to non-smoking families. These are of importance as carotenoids and vitamin A, found in fruit and vegetables induce a protective effect with respect to lung cancer (153,154). High levels of saturated (animal) fat in the diet has also been linked with possible increases in lung cancer (155). High consumption levels of saturated fat and low quantities of fruit and vegetable consumption have been identified as being most prevalent in low socio-economic families (135). These confounding factors can skew the results towards high risk responses, and it has been commented that the removal of such cases reduces the cancer risk from ETS to a nonsignificant level (135).

Further factors that can cause over estimation of ETS damage were identified by Phillips et al (156) where salivary cotinine analysis was used to help identify the validity of the questionnaires when individuals stated if they were smokers or non-smokers. 34 individuals (out of 327 (10.4%)) were rejected due to the salivary cotinine result being

above 25ng/ml, originally identified by Lee (148) as a level associated with a smoker. Questionnaire results can therefore also introduce a great deal of error into any study.

A European working group identified a weak association of increased lung cancer when a partner smoked and explained this association was due to confounding factors and that there was in fact no elevated risk of lung cancer due to ETS (157). This material is discussed in the report on tobacco and health (132), and is subsequently disregarded as it was submitted by tobacco companies, due to it stating no link between the increased probability of various illnesses due to ETS. However, little of the "rejected" material (presumably of the type discussed in the previous paragraphs) is referenced or discussed in this 1998 government publication (132) so that conclusions cannot be drawn from both perspectives by the reader. This conclusion was recently confirmed by a European study published in The Journal of the National Cancer Institute which also identified a weak positive correlation (non significant of 1.17) due to spousal smoking (158). The report discusses in great depth the literature published on ETS and the adverse health effects this can have on various individuals. The following paragraphs cover these areas, adding where necessary any literature that contradicts or disagrees with the conclusions drawn by these publications, as this was not done in the government report (132).

A large quantity of material has been published on the effects of ETS on children where one or more of the parents smoke. Illnesses identified as being associated with possible increased likelihood of developing include sudden infant death syndrome (SIDS) and lower respiratory tract illnesses in pre-school children. Prevalence of asthma and respiratory symptoms have also been identified in school children with links to ETS. Possible responses included bronchial reactivity, allergic sensitisation, an increased prognosis of asthma and ear infection (132).

The government report (132) states that there is an elevated risk of SIDS (2.08), and asthma (159) if maternal smoking is present while the increased risk of lower respiratory illness is increased by maternal ETS for pre-school infants. Socio-economic factors also appeared in this study with children from poorer backgrounds and a maternal smoker being more likely to be diagnosed with asthma than children from more educated families

with a smoking mother. Factors including better living conditions and diet are possible reasons for this observed difference (159).

Maternal smoking again had the greatest effect on school children, with an increased risk being identified for asthmatic symptoms, including wheezing with colds, or a persistent wheeze (where which parent that smoked was found to be irrelevant (160)) bronchial hyper-reactivity, ear infections and respiratory symptoms (132). No relationship was identified between parental smoking and allergic sensitisation (132). The exposure of siblings to ETS mainly identify statistical increases in most studies published (some studies identify little or no statistical increase (161)), discussing the respiratory illness with ETS exposure from a parent (especially maternal exposure, (161)). Sensitivity of child respiratory systems is probably due to the immaturity of the system, unable to cope with the type and quantity of material inhaled in ETS.

The disagreement for the relative risk of ETS to an indoor atmosphere seen between epidemiological and direct measurement studies is a cause for concern. Further work is needed to identify if there is a major overestimation in some epidemiological work due to confounding factors stated earlier including poor questionnaire (mis-classification) information, diet, socio-economic situation and bias needed to be strictly controlled to produce a more concrete risk factor for ETS inhalation.

The more disturbing results are those that identify illnesses increased in children due to parental smoking and the inhalation of ETS both pre-school and during school age. The respiratory system of infants will still be developing with the effects of ETS probably being more pronounced in these individuals.

1.7 Conclusion.

It can be seen from this rather detailed chapter that atmospheric pollution (both indoor and outdoor), can be highly complex with the source pollutant containing an array of compounds/elements. All of these may be subjected to both chemical and physical processes. This produces a plethora of compounds/elements which may be harmful to animals or plants. However due to the often trace levels of many of these compounds it

is very difficult to identify specific pollutant chemicals and relate them to a specific health effect. In fact, a great deal of contradictory evidence is identified when epidemiological studies are investigated (especially associated with ETS, and to a lesser extent individual outdoor pollutants).

These pollutants and their sources are thought introduce toxic material into the atmosphere. Therefore, the sources of these pollutants need to be identified and quantified to enable a reduction of some if not all of them. The particulate material seems to cause many detrimental health effects, ranging from increasing short term symptoms to increased admissions to hospitals and deaths. The mechanisms for these are unclear, so measurement of those outdoor particulates which arise from diesel emissions and ETS from indoor environments needs to be performed.

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2. Apportionment of Pollutant Sources in Air Quality Measurements.

2.1 Previous methods for contribution determination.

2.1.1 Diesel.

Source apportionment of vehicle emissions (specifically diesel emissions) in an urban environment, have been attempted in previous studies. The first study to identify the contribution of vehicles in an urban environment (London), used black smoke measurements, and was published in 1977 by Ball and Hume (1). Lead concentrations related to black smoke measurements were used to identify a percentage apportionment for vehicle emissions (mainly leaded petrol cars, although diesel vehicles also emit lead (see Section 2.2.6.4)) into the atmosphere. Values were identified as being around 77%, rising to as high as 89% during high pollution episodes throughout the winter months.

More recently, a study by Horvath et al, (2) was able to identify the contribution of diesel emissions to urban atmospheric particulate material in Vienna, Austria. All diesel fuel used by vehicles in Vienna was stored at one refinery just outside the city. The addition of a tracer compound to the fuel at the refinery meant that all diesel fuel sold in Vienna during the experiment contained the added tracer molecule. A tracer molecule was added as a specific diesel associated tracer had not been identified. The tracer molecule added was tris-dipivalyl-methanato-dysprosium ($Dy(CH(COC(CH_3)_3)_2)_3$. The organometallic compound was sufficiently soluble in diesel, and dysprosium was found in the emissions at a measurable level (2). The percentage contribution of diesel emissions to particulate material was quantified at between 12-32%. Vienna has an extensive fleet of leaded petrol powered road vehicles contributing to particulate material. During the time of the experiment (1982) diesel vehicles made up only 7% of the total vehicle fleet (2). Many of these diesel vehicles were used for commercial purposes thereby using a larger proportion of the fuel consumed in Vienna for that year. In fact, 32% of the total fuel used in Vienna during 1982, was diesel.

An even more recent study, (1996) described in the 3rd QUARG (Quality of Urban Air Review Group) report (3) discussed the correlation between particulate concentrations (PM10) and CO emissions. They found that the correlation was most useful during the winter months, and that a value for the fraction of particulate material (PM10) that could be attributed to traffic emissions could be calculated. Values from across the UK produced a range of fraction values of between 0.66 and 0.79. The publication then stated that these fraction values identified that 40-50% of PM10 particulate material in those samples were from traffic emissions.

The values for traffic related emissions were very high during the mid 1970's with between 77-89% of total particulates attributed to vehicle emissions (1). Leaded petrol and diesel powered heavy goods vehicles (HGVs) were the major sources of particulate material. The introduction of unleaded petrol in 1986 (4) reduced the amount of petrol related particulate emissions, as the lead acted as a nuclei for particulate formation. Diesel emissions have increased in importance since this time. The Vienna study (2) indicated that 12-32% of particulate material was due to diesel emissions. Particulate emission values were found to be higher in the UK during 1993 with a value of 40-50% being identified by the PM10/CO correlation method (3). The contribution of diesel vehicles can therefore be seen to be rising, due to the continuing success of diesel cars and the increasing number of buses and HGV's on urban roads. Recently, a possible diesel catalytic converter (5) has been produced. However, it is likely to take some time before the invention becomes commercially available, or fitted as standard to diesel vehicles. Thus diesel emissions are likely to rise for the foreseeable future. For these reasons, and taking into account the detrimental health effects of particulate material (see Section 1.6.1), there is a need for a diesel tracer molecule that can be used to identify the contribution of diesel emissions to an atmosphere.

2.1.2 Environmental Tobacco Smoke (ETS).

Environmental tobacco smoke is a highly complex mixture of compounds that are released through the combustion (oxidation or pyrolysis) of tobacco leaves. The

measurement of tobacco associated emissions has been researched a great deal, with over 3800 compounds having been identified in emissions (both vapour and particulate associated) released through smoking (6). A number of standard methods along with several "tracer" methods have been published in the literature.

Initial methods for the identification of tobacco smoke used the total respirable suspended particulate (RSP) value (7,8), as an elevated quantity is found in households where a smoker is an inhabitant (9). The quantity of particulate material sampled on a filter paper at a certain flow for a period of time produces a mass value of particulates per cubic metre of air. The problems associated with this method for ETS determination is that not all particulate material sampled in a smokers environment is due to ETS. Therefore values obtained are always over estimates of the actual contribution of ETS (8), in fact it has been suggested that this over estimation could be as high as 50% (7).

To reduce this over estimation, more specific methods have been introduced. These include total UV absorption (10) and total fluorescence (11) measurements of a methanol extract from a particulate filter sample. No column is used in the HPLC systems for total UV or total fluorescence quantitation. Quantitation is achieved by comparison with a specific standard associated with the relevant technique (See Section 2.2.5.2). Both methods have been shown to be more specific than total RSP. However, a value is obtained even when there is no ETS present, suggesting that these methods also over estimate the contribution of ETS to any environment (See Section 3.5.3). Therefore, to accurately measure the contribution of ETS in an atmospheric sample, a tracer compound specific to tobacco smoke is required.

Several requirements have been suggested by the National Academy of Sciences (12) for a tracer for ETS. These include :-

1. "The compound be unique, nearly unique to ETS; that is, there is a low contribution of the species from other sources".
2. "There is a determination method available for the species even for low level measurements".
3. "There is a similar emission factor for the marker from various cigarette products".

4. "The marker is present in constant proportion to the ETS components, which cause adverse health effects".

The identification of a tracer compound is complicated by the fact that both volatile and non-volatile compounds are released in ETS. Some compounds are therefore found in the gaseous phase while others are found associated with particulate material, in addition to some being found distributed between these two phases. The identification of tracer compounds will therefore depend upon the distribution of the specific compound between these two phases and also the speed by which this compound degrades (ages) in an atmosphere.

The ageing of ETS complicates the accurate determination of ETS contribution to an atmosphere, as the distribution and concentration of compounds (especially volatiles) can vary quite significantly in a short period of time (13). Major factors identified as occurring during the ageing of ETS include:-

1. Coagulation of particulate material, causing a change in the size distribution of particles in ETS (7,14,15).
2. Variation in the distribution of semi-volatile compounds between the gaseous phase and particulate associated phase (7,16).
3. The possibility of reactions between other available chemicals or radiation, to induce chemical reactions degrading compounds in various phases (16,17).
4. Variation in chemical composition due to recirculation and dilution with outdoor air (7,18).

It is necessary for a tracer molecule to be stable over a period of time for accurate sampling to be possible.

Many specific tracer molecules have been identified in ETS. These include nicotine (14), along with several similar molecular compounds, such as cotinine, nicotyrine or myosmine (14), and 3-ethenylpyridine (19-21). All these tracers identify the contribution ETS has on the gaseous phase of the environment, as the compounds are found almost entirely in the gaseous phase. Tracer compounds that are less volatile, and identify the

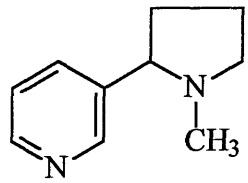
contribution of ETS associated with particulate material include, solanesol (17,22) and scopoletin (23). An elemental marker of cadmium was also identified as a possible tracer for particulate associated ETS (24).

Volatile tracers.

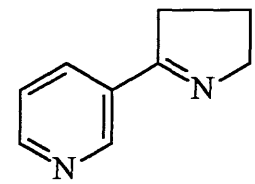
In the past, nicotine has been the major tobacco related compound that has been identified as an ETS tracer compound (6,14,25,26). Its inherent specificity to tobacco products would seem to identify nicotine as the ideal tracer compound for ETS. However, variation in concentrations from different sampling devices introduce uncertainty for this compound as a marker. Nicotine is found almost entirely in the gaseous phase (16,27) in fresh ETS. However, gaseous nicotine is rapidly removed from an environment compared to particulate ETS (13,18,19,28) and particulate associated nicotine (19). Particulate associated nicotine also decreases rapidly compared to particulate material itself (13). This is due to nicotine either reacting with UV radiation (14,16), desorbing then re-adhering to surfaces (20), or associating to non ETS particulate material as the ETS ages (29). However, the relative removal rate is dependant upon factors associated with the sampling site. These can include air circulation, the presence of people, in addition to the types of furnishings and wall paper (7).

Nicotine measurements were at one time used to quantify the contribution of ETS to the particulate phase. The concentration of nicotine could be related to respirable suspended particulate material (14,30), as ratios of nicotine to RSP were known and did not appear to vary with brand (31). Recently this was shown to be a far more complex situation and such a ratio system was found to be invalid (7,32). The faster removal of gaseous nicotine resulted in an underestimate of nicotine, and therefore an underestimate of particulate associated ETS in an indoor atmosphere (28). Nicotine is unique to ETS emissions, it is easily measurable in environmental samples and is emitted at similar concentrations from different brands. However, the concentration of nicotine is not found to be constant in an indoor environment. Thus, it is not an ideal tracer molecule for ETS.

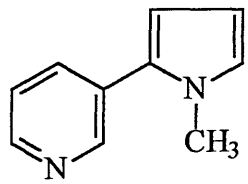
Other nicotine type compounds have been identified as possible ETS tracer molecules. These include compounds of similar structure to nicotine, such as myosmine (16,32) and nicotyrine (14). In addition, 3-ethenyl pyridine (16,20,28,32), a pyrolytic product of nicotine (20), was identified as a possible gaseous ETS tracer molecule along with isoprene (7) and pyrrole (20).



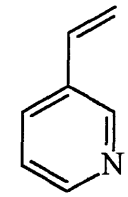
Nicotine.



Myosamine.

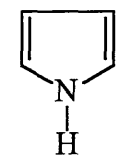


Nicotyrine.



3-Ethenyl pyridine.

$H_2C=CH-C(CH_3)=CH_2$ (Isoprene).



Pyrrole.

Myosmine and nicotyrine are both found almost exclusively in the gaseous phase (7,16,19) and are specific to tobacco smoke emissions. However, they are present in lower concentrations than nicotine, making them harder to accurately quantitate. Myosmine and nicotyrine also react rapidly with UV radiation (14).

3-Ethenyl pyridine has been identified in many studies as being a more robust gaseous phase tracer molecule for ETS (7,13,19,28). It is more stable than the nicotine type compounds to UV degradation (16), and is also the fourth most abundant compound found in ETS, behind only nicotine, isoprene and 1,3-Butadiene (7). However, although it appears ideal, 3-ethenyl pyridine is not quantitatively sampled onto XAD-4 resin using flows of several litres per minute (28), which are used for sampling nicotine (28). Several studies have used XAD-4 resin as the sampling media for 3-ethenyl pyridine (21).

Quantitative adsorption of 3-ethenyl pyridine is achieved by a multisorbent thermal desorption tubes containing Tenax-TA, Ambersorb XE-340 and activated carbon, producing a method for attributing percentage contribution to volatile compounds (20).

Isoprene has also been reported as being a possible tracer molecule for ETS (33). Although not necessarily totally unique to ETS, the emissions from other sources into indoor atmospheres seem to be trivial when compared to the amount released in tobacco smoke.

Therefore there were a number of possible compounds that could be quantified to identify the contribution of ETS in any environmental sample. It was decided that nicotine would be analysed using XAD-4 resin tubes as the sampling device (due to its selectivity in sampling only vapour phase nicotine (28)), as recommended by the following accepted standard methods (28,34-36). These XAD-4 resin tubes were positioned directly behind the particulate filter samplers (see Section 2.2.2.2). Nicotine associated with particulate material was also quantified.

Apportionment of volatile organic compounds would be quantitated by using ATD/GC/MS with 3-ethenyl pyridine or pyrrole as the tracer molecule.

Particulate associated tracers molecules.

The improvement of UVPM and FPM apportionment of ETS is significant as they reduce the over-estimation by RSP measurements that was originally used for ETS apportionment. However, these methods still produced an over-estimation of ETS to any environment, as UV absorbance and fluorescence at the relevant wavelengths were obtained in background samples. A particulate phase marker was therefore necessary for the specific identification of ETS particulate material in a sample.

Solanesol was the first and most widely used tracer molecule for particulate ETS. It was originally identified in flue cured tobacco in 1956 (37) as a primary terpenoid alcohol. The compound was later correctly identified as having a trisesquiterpenoid long chain (C45) structure (38):-

$CH_3–C(CH_3)=CH–[CH_2–CH_2–C(CH_3)=CH]_8–CH_2–OH$

Structure of Solanesol (3,7,11,15,19,23,27,31,35-Nonamethyl-2,6,10,14,18,22,26,30,34-hexatriacontanonaen-1-ol), (39).

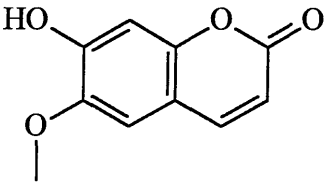
Solanesol has been regularly studied in tobacco leaves (40-43) but was only recently identified as being present in ETS (39). Due to solanesols large molecular weight, the compound is very involatile, and was found entirely associated with the particulate emissions of ETS (44). Studies on solanesol in the tobacco plant have identified solanesol in the laminae of the tobacco leaf, and not in the stalk or stem (45). Solanesol has also been identified in higher concentrations in the new leaf growth (46). Solanesol is found in many plants from the Solanaceae family, of which one member is the Nicotiana genus. Other members of the family known to contain solanesol include tomato plants, potato plants, eggplants and pepper plants. Therefore, sources other than ETS for solanesol include certain possible cooking emissions. However, the interference is thought to be of only minor consequence (39).

The original analysis by capillary GC of solanesol was complicated by the interference of solanesenes, produced from the pyrolysis of solanesol and solanesyl esters during smoking. The break down of solanesol at high temperatures in the GC oven also hindered the direct quantitation of solanesol by GC analysis (44). However, by derivatising the alcohol group with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) analysis by capillary GC was possible (17,44). The extraction and sample manipulation methods varied between the groups that completed the work. However, all were time consuming and specific only to solanesol determination and capillary columns lost chromatographic performance over a relatively short period of time (39). Although the performance could be restored through washing, or the use of guard columns, the situation was far from ideal (39).

A HPLC method using UV detection at λ=205nm from a methanol extract of a particulate filter sample was found to be just as quantitative as the GC method. The methanol extract could also be used to determine total UVPM and FPM values for the

determination of ETS in the sample (44). A slightly modified version of this method was used for solanesol determination in this thesis, (See Section 2.2.5.2).

Another compound that has recently been identified as a possible particulate associated ETS tracer molecule is scopoletin (6-methoxy-7-hydroxy-coumarin) (47). It has been identified in tobacco leaves (48,49) and has also recently been detected and quantified in particulate ETS (23).



Scopoletin.

Scopoletin is extracted into methanol from particulate material collected on teflon impregnated glass fibre filters. Quantitative analysis can be achieved using reverse phase HPLC and fluorescence detection (Ex=342nm, Em=464nm (23)). A slight variation of the method in reference (23) was used to quantitate scopoletin in this study (See Section 2.2.5.2). The method of sampling and extraction can be used to produce a sample that can quantitatively determine UVPM, FPM, solanesol and scopoletin, reducing the number of samples that need to be taken. These four ETS parameters along with RSP were determined in an attempt to obtain an accurate apportionment of ETS in field samples, and also to identify the average overestimation of ETS by UVPM and FPM measurements.

Long chained iso (2-methyl) and anteisoalkanes (3-methyl) (C29-C34) have been used to identify the contribution of ETS particulate material to an outdoor environment in Los Angeles (50). These marker compounds were not investigated further as the four previously described particulate methods seemed sufficient to quantify ETS particulate contributions in both indoor and outdoor air.

Elemental

Several studies have been undertaken to identify possible elemental markers for ETS (51,52). These identified a number of elements to be present in tobacco smoke. These were determined by a range of methods, including:

1. Neutron Activation Analysis (51,52).
2. Atomic Absorption Spectroscopy (51,52).
3. Inductively Coupled Plasma - Mass Spectrometry (52).
4. X-ray Fluorescence Spectroscopy (52).

Elements determined included: Arsenic (As), Cadmium (Cd), and chromium (Cr) (specific to tobacco), while Lead (Pb), copper (Cu), Potassium (K), nickel (Ni), Zinc (Zn), thallium (Tl), thorium (Th), Iron (Fe), lithium (Li), and bromine (Br) were identified in the ETS. These were identified at varying concentrations. However, many of these elements are retained in a higher concentration in the cigarette ash, specifically Fe and Ni (52).

Cadmium has been proposed as a possible particulate marker for ETS (24), with quantitative analysis being achieved using neutron activation analysis employing Compton suppression (24). Elevated quantities of cadmium were found to be present in ETS atmospheres compared to ETS free atmospheres, and similar quantities were found in various types of tobacco leaf. It was identified that around 44% of the cadmium was released into the atmosphere associated to ETS particulate material (90% of which is associated with particles $<1\mu m$) after smoking. The removal of cadmium from the atmosphere was found to be relatively slow, making it ideal as a marker element for ETS (24).

The possibility of Cd as a marker element for ETS prompted the decision for elemental analysis of ETS to be undertaken. The acquisition of a HP4500 Series inductively coupled plasma - mass spectrometer (ICP/MS) introduced an ideal method for a semi-quantitative analysis of ETS for possible elemental markers. A more rigorous

determination of cadmium as a marker element or any other compound found to be relatively specific to ETS could then be performed.

2.2 The identification of marker compounds and their phase distribution in diesel emissions and ETS.

2.2.1 Sampling.

2.2.1.1 Diesel.

Diesel exhaust samples were taken from a four cylinder, 4-1, non-inter-cooled direct injection diesel engine with turbo charger, in a controlled test environment. The engine could be run at a number of different revolution per minute (rpm) speeds, for example the engine idle, at 1300, 1600 and 2300 rpm. Each speed could then be subjected to various rated powers, increasing or decreasing the work that the engine had to do. This was undertaken to investigate the variation in emissions from an engine moving heavy or light loads.

The exhaust emissions were split after leaving the exhaust (Figure 2.1). Half of the emissions were released into the atmosphere, while the other half passed into the dilution tunnel (Weslake Developments Ltd, Figure 2.2). Here, the emissions were mixed with air to reduce the temperature of the exhaust gases to below 52°C. This was done to prevent chemical reactions such as oxidation and nitration of organic compounds, which were collected on glass fibre filter papers at the end of the dilution tunnel. It has been hypothesised that the filters used to collect particulate material could cause possible variations in the distribution of organic compounds between the gaseous and particulate phases. For example, compounds being blown off sampled particulate material or gaseous compounds adsorbing to sampled particulate material (53). We have assumed in this sampling regime that this occurrence is negligible.

Due to the partitioning of organic compounds between the gaseous and particulate phases, the following sampling procedures were carried out.

Particulate material was sampled onto 12.5cm glass fibre filter papers (Whatman) (The silver filter holder can be seen in Figure 2.3). Each filter paper was changed every 20-30 minutes to prevent clogging by the sampled particulate material. Placed directly behind the filter paper was a XAD-4 resin tube with a flow of approximately four litres a minute passing through it (the resin tube was attached to the black rubber tubing protruding from the left of the copper "T" section in the foreground), collecting any volatile compounds that passed through the filter paper, not associated with the particulate material (Figure 2.3).

This side line from the dilution tube made it possible to sample exhaust volatiles directly onto a tenax resin tube (containing 0.16g of Tenax) at a lower flow rate of approximately 100ml/min, with the use of a flow regulator.

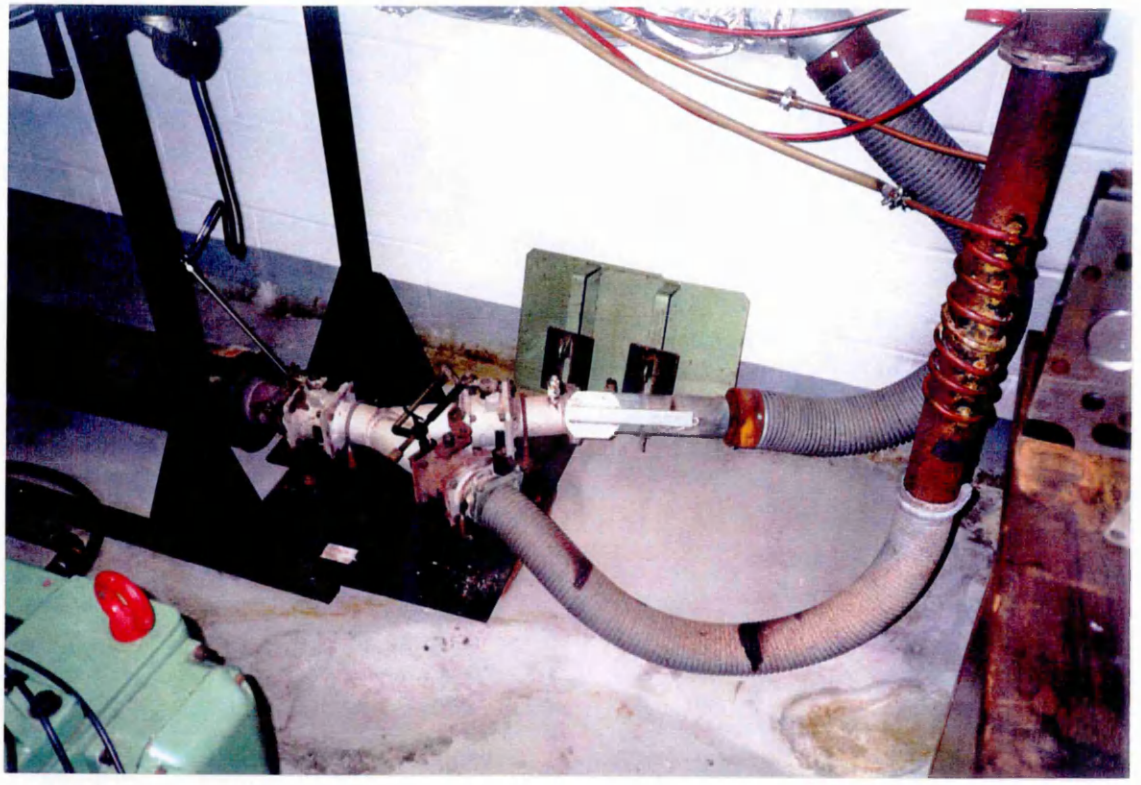


Figure 2.1: The exhaust emissions from the diesel engine are split, with half being vented to the atmosphere and half continuing into the dilution tunnel.

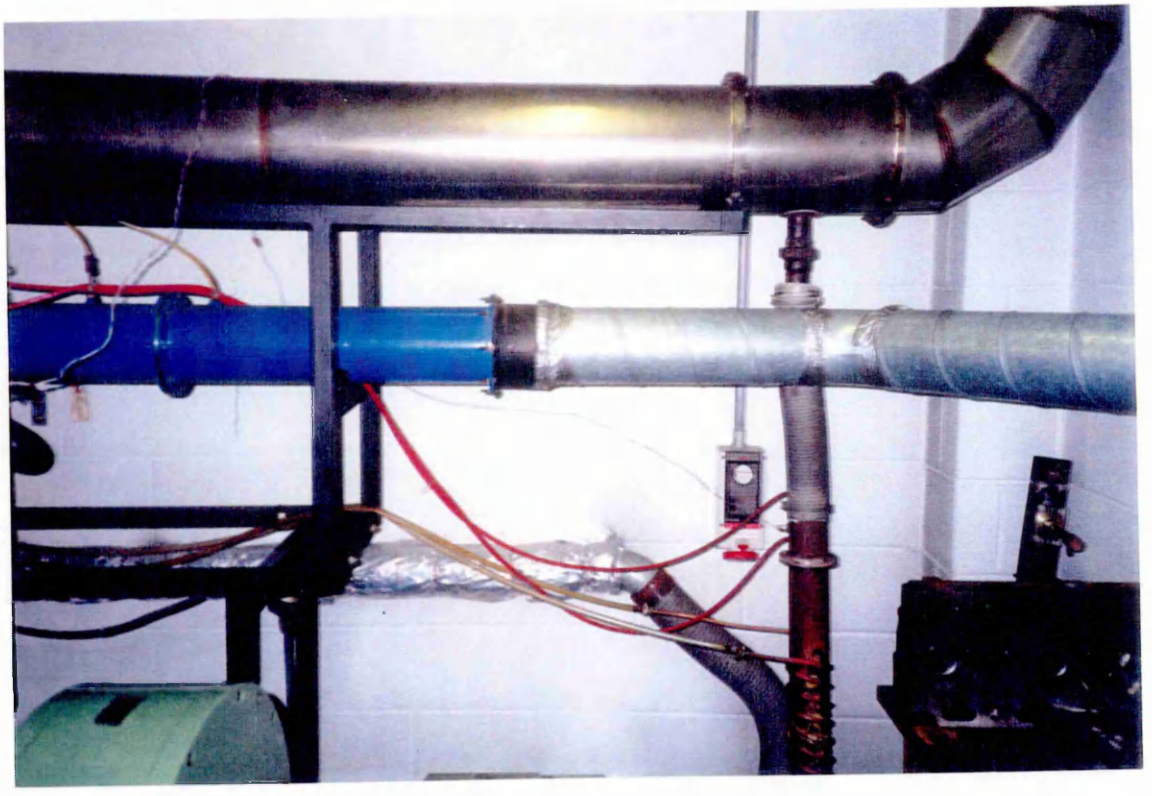


Figure 2.2: Emissions continue from the exhaust split into the large silver dilution tunnel.

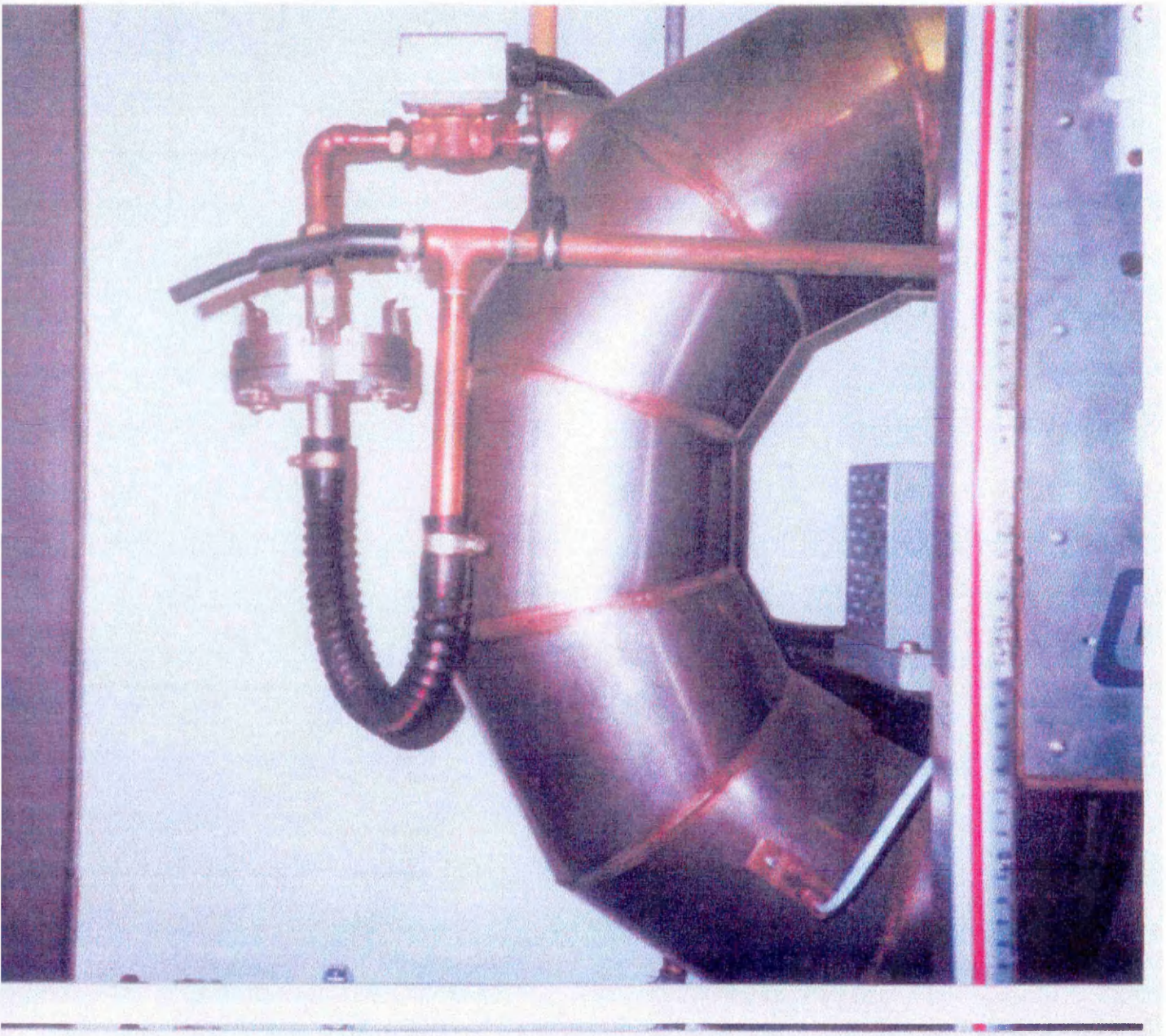


Figure 2.3: Filter holder with tubing for volatile sampling situated directly behind the filter holder, connected by the black tubing.

2.2.1.2 Environmental Tobacco Smoke.

Controlled ETS sampling was kindly undertaken by Rothmans International at their research and development facility in Basildon, Essex.

Each cigarette was smoked by a Borgwaldt smoking machine (situated in a smoke generation room attached to the main sampling room - Figure 2.4) which smokes each cigarette to the international standard ISO 3308 (54). Main stream smoke was trapped on a Cambridge filter and the main stream vapour emissions were piped directly out of the smoke generation system.

The smoke generation chamber was 0.7m (wide) x 0.849m (long) x 0.795m (high), producing a volume of $0.472m^3$ (Figure 2.4). Access to the smoking machine positioned within was achieved through a hinged door. Rubber gaskets ensure an air tight seal forms around the door edge. An electric cigarette lighter penetrates through the door via an airtight slip ring gasket that enables ignition of the cigarettes while maintaining a closed atmosphere. Fresh ETS was transferred from the smoke generation chamber to the main room via an interconnecting duct. This was achieved with the use of the recirculation system (Figure 2.4). This draws air from the main chamber through the base of the smoke generation chamber, and back into the main room through the interconnecting duct, taking with it the freshly produced ETS.

ETS produced in the smoke generation chamber was circulated into a model room which is 2.745m (wide) x 3.245m (long) x 2.3m (high), producing a total volume of $20.78m^3$ (Figure 2.4). The walls were constructed of interlocking panels of heavy duty PVC coated "galvatite" sheet metal. Three main chamber walls were hollow, including a serpentine void in which thermostatted air was recirculated via a temperature control/fan unit positioned in the roof. Insulation of the room keeps the temperature constant at 21°C. The room floor is constructed of a composite material of PVC, glass fibre, and aluminium oxide bonded to the concrete floor. Samples can be taken directly from this room using sampling equipment or via sampling ports positioned in the door.

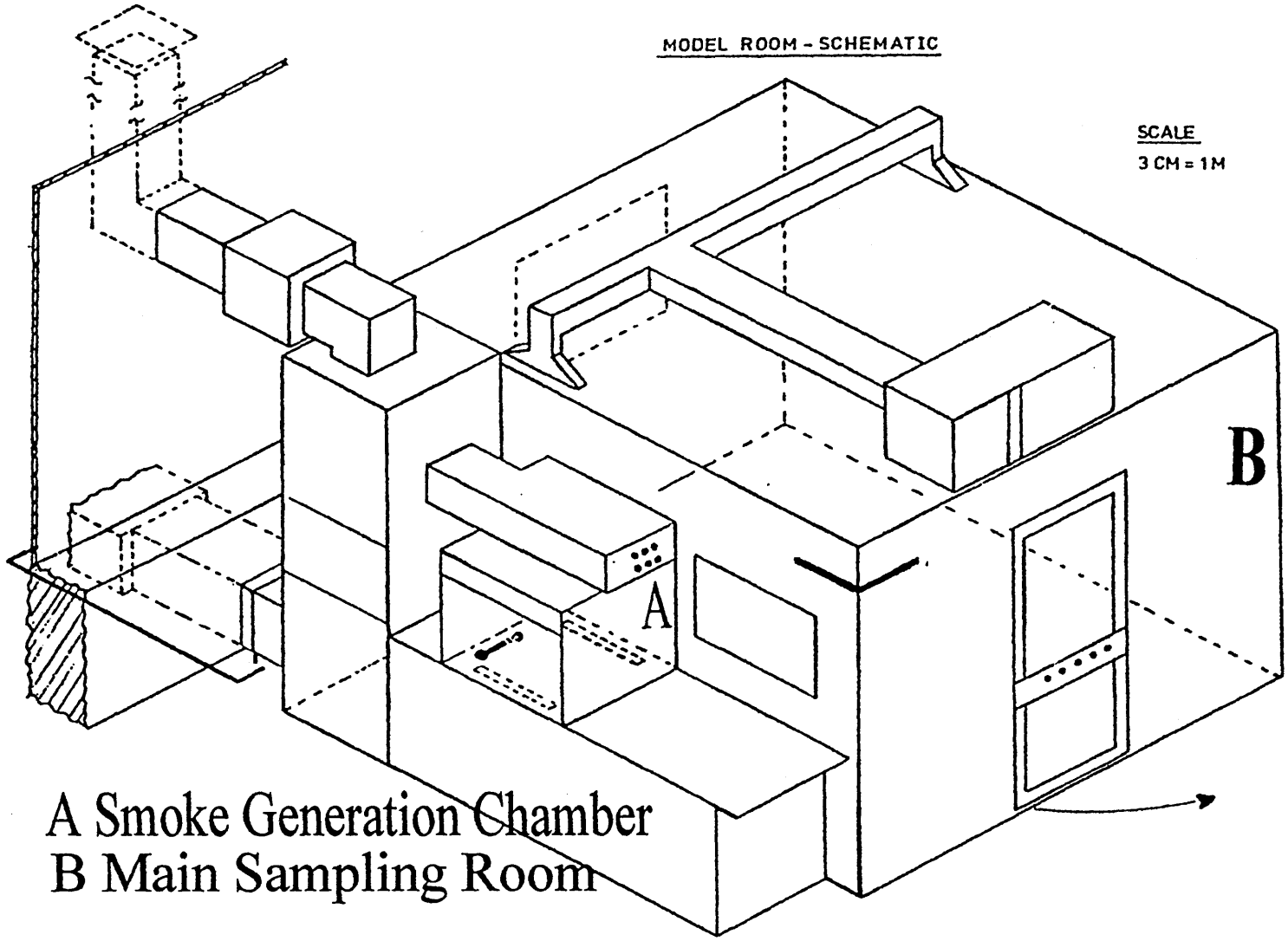


Figure 2.4: A schematic diagram of the smoke generation chamber and main sampling room used for the sampling of tobacco smoke emissions at Rothmans International, Basildon.

2.2.2 Samples.

2.2.2.1 Diesel.

Volatile, semi-volatile and particulate exhaust emission samples were taken from the test diesel engine at 1 speed (1600rpm), but at three different loads. All samples were taken in duplicate.

Table 2.1: Samples Taken from the Turbo Charged Diesel Engine at 1 Speed but Three Different Rated Powers.

	Volatiles	Semi-volatiles	Particulates	Metals
1/2 rated power (176)	2 tenax tubes	2 resin tube	2X4 filters	2X1filter
3/4 rated power (286)	2 tenax tubes	2 resin tube	2X4 filters	2X1filter
full rated power (373)	2 tenax tubes	2 resin tube	1X4 filters 1X6 filters 2X1 filter.	2X1filter

As we can see from Table 2.1, all samples were taken in duplicate, with the tenax thermal desorption tubes capped and stored prior to analysis while the other samples were extracted as necessary (see Section 2.2.3). All samples were taken to identify possible diesel tracer molecules/elements.

Alkane Quantitation.

Another specific experiment completed using the diesel engine was to obtain particulate samples from a number of different engine speeds (with various loads to identify an average alkane C24 (tetracosane) emission for a diesel engine. The previously described diesel engine was run for approximately thirty minutes to obtain each particulate filter sample. The range of speeds included 1300, 1600 and 2300 rpm (see Section 2.2.6.3).

All samples were run in duplicate, and the four filter papers were extracted for GC/MSD analysis, see Section 2.2.3.1.

2.2.2.2 Environmental Tobacco Smoke (ETS)

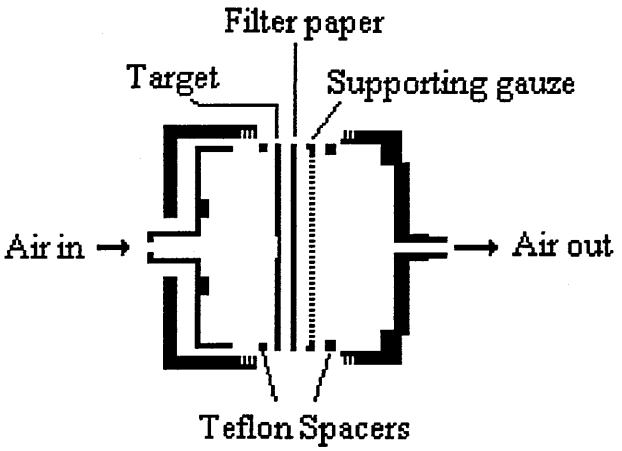
Two types of samples were taken from the smoking facility, These included :-

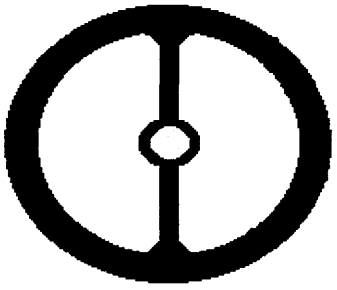
1. Volatile organic samples.

A low flow pump (Model 222-3, SKC Ltd, Dorset England) was used to sample ETS onto two automated thermal desorption (ATD) metal tubes. The first tube was filled with 0.16g of Tenax TA resin, 60/80 mesh (Supelco, Dorset, England), and the second tube contained 0.18g of Carboxen 569, 20/45 mesh (Supelco, Dorset, England) resin. Each sample was taken in duplicate to ensure a sample was available if an instrument fault should occur. The flow rate used for this sampling was 50ml/min with analysis of the sample by ATD/GC/MS.

2. Particulate samples.

Particulate material was sampled onto a 37mm teflon impregnated glass fibre filter paper (Gelman Science, Supelco, Poole, Dorset, England) in a round "target" type filter holder. The size of particulate material sampled could be determined by the flow through the sampling system. The "target" type filter head used the principle that larger particles hit and stuck to the target placed adjacent to the sampling orifice (grey area Figure 2.5b), while smaller particulate material was swept around the target and sampled on the filter paper (pore size 1μm) situated directly behind the target. Directly behind the filter head was an XAD-4 resin tube to collect any organic compounds found in the gaseous phase. The total flow through this sampling apparatus was 1l/min, achieved by a larger personal sampling pump (SKC Ltd, Dorset, England). The particulate material sampled at this flow was ≤5μm. Sampling was done in duplicate as two filter samples were needed to complete all the chemical analyses undertaken.





Particulate target (not drawn to size with sampler head).

Figure 2.5a Filter Head (apart) and 2.5b Target, Used in the Sampling of Particulate Material in Various Environments.

2.2.3 Extraction.

2.2.3.1 Diesel.

Volatiles.

The Tenax tubes were not extracted, but were placed directly into an automated thermal desorption instrument and analysed. Each tube was analysed separately. Quantitation was achieved using external calibration.

Semi-volatiles

The resin in the XAD-4 tubes was removed and placed into an amber screw topped vial. Dichloromethane (5mls) was added and the resin was extracted in an ultrasonic bath, for 30 minutes. The extract was reduced in volume using a dry flow of pure nitrogen, before being transferred to a 2ml autosampler vial and reduced to 1ml. D10-anthracene was added as an internal standard for alkane and PAH quantitation prior to analysis by GC/MSD and GC/AED.

Particulate associated organics.

The filters for each individually sampled speed and rated power were placed into a soxhlet apparatus and extracted for 24hrs with dichloromethane (80mls). The dichloromethane was reduced to a few mls by rotary evaporation, prior to reduction to a 100µl (using a flow of pure nitrogen) before fractionation using an amino/alumina tandem solid phase extraction (SPE) system (See Section 2.2.4).

The higher rated power engine load also had 2 single filters sampled. These were separately extracted into methanol (10ml) and heated to 50°C for 30 minutes. The methanol was reduced to 5ml and analysed by HPLC for the following:-

1. Total UV adsorption.
2. Total fluorescence.
3. Scopoletin.
4. Solanesol.

Metal samples.

The relevant glass fibre filters with diesel particulate emitted material were wet ashed with 10mls of nitric acid on a hot plate for 30 minutes. The filter material was not dissolved by this technique. This meant that the extract had to be filtered prior to analysis by ICP-MS. The acidic metal extracts were made up to a volume of 25ml with MilliQ water.

2.2.3.2 Environmental Tobacco Smoke (ETS).

Volatiles.

The Tenax tubes were not extracted but were placed directly into an automated thermal desorption instrument and analysed. Each tube was analysed separately, and quantitation was achieved using external calibration.

Semi-volatiles.

Each tube of XAD-4 resin with their glass wool plugs were emptied into a 7ml screw topped amber vial. The emptied XAD-4 glass tube was washed through with dichloromethane containing 0.01% triethylamine, (as nicotine adheres well to glass surfaces and the addition of triethylamine was found to ensure reproducibility in the resin extracts) (55). The washings were added to the vial along with more dichloromethane (DCM) until the extraction volume was 5ml. The resin was extracted for 30 minutes using an ultrasonic bath. The volume of dichloromethane was then reduced to less than 2ml, transferred to an 2ml amber autosampler vial and reduced to 1ml. Internal standards of quinoline for nicotine determination and D10 anthracene for alkane and PAH quantitation were added to each extract prior to analysis by GC/MSD and GC/AED.

Particulate associated organic compounds.

Filter 1. Dichloromethane (5ml) containing 0.01% triethylamine was added to the filter placed in a 7ml screw top amber vial. The sample was extracted for 30 minutes by ultrasonication, the filter was then removed. The dichloromethane extract was subsequently reduced to less than 100ul using a flow of ultra pure nitrogen. The sample was transferred to an 2ml autosampler vial containing a 200µl glass insert. 20µl of 100µg/ml solutions of D10-anthracene and quinoline internal standards were added. The sample volume was reduced to be 100µl prior to analysis by GC/MSD and GC/AED.

Filter 2. This filter was cut in half with the use if a ceramic column cutter to prevent as much elemental contamination as possible.

One half of the filter was placed in a 7ml screw top amber vial and methanol (5ml) was added. The vial was then heated to 50°C in an oven for 30 minutes. Analysis by all the appropriate HPLC methods (stated in 2.2.5.2) were completed.

The second half of the ETS filter 2 was wet ashed in an identical way as described in Section 2.2.5.2. The teflon filters did not disintegrate so filtering was not necessary with these samples. Another slight modification was that the acid extracts were diluted to 10ml and not 25ml (as for the diesel emissions). The extract was then analysed by inductively coupled plasma/mass spectrometry (ICP/MS).

2.2.4 Fractionation. (Organics)

2.2.4.1 Diesel.

Solid Phase Extraction

Solid phase extraction (SPE) was performed using polypropylene cartridges containing an amino bonded phase (200mg of sorbent with a 10ml reservoir, obtained from

International Sorbent Technology, Jones Chromatography, Mid Glamorgan, Wales, England) and an alumina cartridge (500mg of sorbent with a 6ml reservoir obtained from J.T. Baker. U.K. Milton Keynes, Bucks, England) in series. The cartridges were initially cleaned with acetone (30ml) to remove all adsorbed water. 15ml of each eluting solvent were then passed through the cartridges. This commenced with methanol and continued back through the solvents with reducing polarity to hexane, leaving a layer of 10ml of hexane in the top cartridge reservoir. The sample extract was loaded onto the cartridge using the smallest quantity of dichloromethane (often 50-100µl), introduced directly into the 10ml of hexane. Fractionation was achieved by elution of compounds with 10ml of the following solvents of increasing polarity:-

Table 2.2: Solvents of increasing polarity and the compounds they eluted from the solid phase extraction system (Amino-Alumina).

SOLVENT	ELUTING COMPOUNDS
Hexane	Aliphatics
Cyclohexane	Aliphatics
5% Dichloromethane : 95% Cyclohexane	2-4 ringed PAHs (up to Pyrene)
20% Dichloromethane 80% Cyclohexane	Larger PAHs and Nitrated derivatives
Dichloromethane	Polar Species
Acetonitrile	Polar Species
Methanol	Polar Species

The fractions were transferred to pre-weighed amber vials, and reduced to 100µl of solution with a dry stream of nitrogen. Two internal standards were added, (8-Nitroquinaldine (obtained from Sigma-Aldrich Co. Poole, Dorset, England, at 98% purity) and D10 anthracene (Supelco, Poole, Dorset, England), for alkane and PAH quantitation prior to analysis by GC/MSD and GC/AED.

2.2.5 Analysis.

The mass of the particulates that were sampled from various environments was determined using two balance systems.

Diesel engine samples.

These samples were taken using 12.5cm glass fibre filter papers that were weighed prior to and after the engine sample had been completed using a Satorius 2004MP five figure balance.

Environmental tobacco smoke samples.

Accurate determination of sample masses were required at μg levels for these samples. For this reason a Perkin Elmer PU-50 balance was used to identify the mass of the 37mm teflon impregnated glass fibre filter (Gelman Science, Supelco, Poole, Dorset, England) prior to and after the sampling. The balance was calibrated prior to use with NAMAS accredited weights. Accuracy at this low mass level can be effected quite markedly by static electricity. Such effects were removed by placing the filter in front of a Stat-attack anti-static fan (Stat-Attack) for a few seconds and obtaining three mass values within 3μg. An average of the three mass values was then used as the actual mass of the filter.

2.2.5.1 Volatile Organic compounds.

Automated Thermal Desorption (ATD)-Gas Chromatography/Mass Spectrometry (GC/MS).

A Perkin Elmer ATD 50 instrument was used for the thermal desorption, coupled to a Hewlett Packard 5890 gas chromatograph with a VG Trio I quadrupole mass spectrometer detector (VG Masslab, Manchester, UK).

Thermal desorption parameters.

The tenax and carboxen tubes were desorbed for 12.5 minutes at 250°C, with the trap temperature set at -30°C. The trap was then heated to 260°C with the transfer line to the GC set at 150°C, and the GC injector temperature set at 250°C. The carrier gas was helium, at a flow rate of 1ml/min.

GC/MS parameters.

A Restek Rtx-5 (Thames Chromatography U.K.) capillary column (50m x 0.25mm i.d.) with a film thickness of 1μm was used for analytical separation. The GC parameters were as follows:-
The initial oven temperature was 45°C hold for 1 minute, ramp 1: 10°C/min. to 250°C hold for 13 minutes, producing a total analysis time of 35 minutes. The mass spectrometer used a scanning range of 10-300mu.

2.2.5.2 Semi-volatile and particulate associated organic compounds.

Samples for analysis of organic compounds that could be analysed by gas chromatography, were reduced to the relevant solvent volume, and injected into GC/MSD and a GC/AED instrument for general qualitation. Several compounds were quantified using various analytical methods also reported in this section.

Gas Chromatography/Mass Spectrometry (GC/MS).

A Hewlett Packard 5890 Series II gas chromatogaph coupled to a Hewlett Packard 5971A Mass Selective detector were used for this analysis. All splitless injections were carried out by a Hewlett Packard 7973 autosampler which injected 1μl of sample (To ensure that all the injected sample went onto the column). A Restek Rtx-5 (Thames Chromatography U.K.) capillary column (30m x 0.25mm) with a film thickness of 0.25μm was used for analytical separation, with helium as the carrier gas set at 1ml/min. The injector temperature was set at 275°C, with following GC oven program :-

Initial oven temperature was 40°C, hold for 5 minutes, ramp 1: 10°C/min to 280°C, hold for 10 minutes, producing a total analysis time of 39 minutes. The mass spectrometer scanned over a range of 40-500mu. There was an initial solvent delay of 10 minutes.

Gas chromatography/mass spectrometry-selected ion monitoring (GC/MS-SIM). (For PAH quantitation).

The instrument described in the GC/MS section above was used in selected ion monitoring mode so that only the ions for the PAH eluting at any one time were analysed. This reduces the number of ions under investigation and increased sensitivity. The compounds and ions identified at specific times throughout the analysis were as follows:-

Table 2.3: The PAH and the associated ions used in the selective ion monitoring program.

PAH.	Ions.
Naphthalene.	127,128.
Acenaphthene, Acenathylene.	154,153,152,76.
Fluorene, Phenanthrene, Anthracene and D10 Anthracene (Internal Standard).	166,165,178,152,188.
Fluoranthene, Pyrene.	202,101.
Benzo(a)anthracene, Chrysene.	228,114.
Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene.	252,126
Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene, Indeno(1,2,3,c-d)pyrene	278,276,138

Gas chromatography with Atomic Emission Detection.

A Hewlett Packard 5890 Series II gas chromatogaph coupled to a Hewlett Packard 5921A Atomic Emission Detector were used for this analysis. 1µl of each sample was injected splitless with the use of a Hewlett Packard 7673 autosampler. Ultra pure helium was used as a carrier gas at a flow rate of 1ml/min. The GC/AED system was controlled with a Hewlett Packard 300 data station with pascal based software (HP 35920C). A Restek Rtx-5 (Thames Chromatography U.K.) (25m x .25mm i.d) capillary column with a film thickness of 0.25µm was used for the separation. The injector temperature was set at 280°with the detector temperature at 280°C and the cavity and transfer line set at 300°C. The GC oven temperature program was identical to that used in the GC/MS section above.

The wavelengths monitored were :- Carbon 496nm and 193nm, Hydrogen 486nm, Chlorine 479nm, Bromine 478nm, Sulphur 181nm, and Nitrogen 174nm.

Gas Chromatography with Negative Ion Chemical Ionisation Mass Spectrometry working in Selected Ion Monitoring mode. (GC/NICIMS-SIM.)

Analysis was undertaken using a Hewlett Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 3 mass spectrometer working in SIM mode. The reagent gas used for chemical ionisation was methane with an ion source temperature of 125°C. The NICI conditions were optimised by injecting a small quantity of methyl iodide via the septum inlet and tuning the instrument via the peak at m/z 127. A SIM experiment was set up monitoring each of the M-• shown in Table 2.4. The column used was a 60m x .32mm i.d. 5% diphenyl wall coated open tubular capillary column (Rtx-5, Thames Chromatography U.K.) with a film thickness of .25µm. The injector temperature was set at 275°C and the GC oven temperature program was:-
Initial oven temperature of 40°C, hold for 4 minutes, ramp 1: 25°C/min. to 175°C hold for 1 minute: ramp 2: 5°C/minute to the final temperature of 280°C, hold for 15 minutes. The carrier gas was helium at a flow rate of 1ml/min. 1µl of each sample was injected splitless.

Table 2.4: The Molecular ions used to quantify individual nitrated PAH.

Compound	SIM Molecular Ion
1-Nitronaphthalene	173
Internal Standard	188
4-Nitrobiphenyl	199
5-Nitroacenaphthene	199
2-Nitrofluorene	211
9-Nitroanthracene	223
3-Nitrofluoranthene	247
1-Nitropyrene	247

.Gas Chromatography with Electron Capture Detector (GC/ECD)

The instrument used in all cases was a Hewlett Packard 5880 Gas Chromatograph using a 5% diphenyl wall coated open tubular capillary column (Rtx-5, Restek, Thames Chromatography U.K.) (20m x .32mm) with a film thickness of .25μm. The carrier gas used was nitrogen, at a flow rate of 1ml/min, with nitrogen as the makeup gas yielding a total flow of 30ml/min. 1μl of each sample was injected splitless using a Hewlett Packard 7673A autosampler. The injector temperature was set at 275°C with the detector at 300°C. The oven program temperature used was:-
The initial oven temperature was 40°C hold for 4 minutes, ramp 1; 25°C/min to 145°C hold for 1 minute, ramp 2; 5°C/min to 280°C with a final hold time of fifteen minutes.

High Performance Liquid Chromatography methods.

Total UV absorption.

The analysis was carried out using a Pye Unicam PU 4015 isocratic HPLC pump with a Pye Unicam PU 4025 UV detector. The wavelength used for the analysis was set at

325nm (56). A 7125 Rheodyne injector with a 50µl loop was used for all manual injections. A Hewlett Packard HP3394 integrator was used to obtain the relevant integrated chromatograms. Methanol was the eluent, at a flow rate of 0.4ml/min, with no column used for analytical separation. 2,2',4,4' Tetrahydroxybenzophenone (Aldritch, Poole, Dorset U.K.) was used as an external calibration molecule against which the concentration equivalent of the total UV measurement was determined (10,56). A calibration graph of 0.05-10ppm was constructed to ensure linearity over this range.

Solanesol quantitation.

The pump and detector were the same as those described in the UV section above. The wavelength used for the analysis was 210nm (56). A 7125 Rheodyne injector with a 200µl loop was used for all manual injections. Integrated chromatograms were obtained from the system described in the UV section above. Methanol was the eluent, at a flow rate of 1ml/min, using a octadecyl silane (ODS) column (5cm x 4.6mm) for analytical separation. An external calibration graph of Solanesol (Aldritch, Poole, Dorset, U.K.) was used to quantify the solanesol in all the samples analysed.

Total fluorescence.

The HPLC system consisted of a Jasco LG-980-02 tertiary gradient pump, with a Jasco PU-980 intelligent HPLC unit. Injections were completed manually using a 7125 rheodyne injector, with a 20µl injection loop. The eluent used was 100% methanol, at a flow rate of 0.5ml/min. Detection was completed by a Jasco FP-920 intelligent fluorescence detector, (Ex =300, Em =420 (56)). No column was used for total fluorescence determination. Integration was completed by a Shimadzu C-R4A chromatopac computing integrator. Scopoletin was used as an external calibration molecule against which the concentration equivalent of the total fluorescence measurement was determined.

Scopoletin quantitation.

The HPLC and integration system were the same as that described in the total fluorescence section above. All manual injections were completed using a 7125 rheodyne injector, with a 20µl injection loop. The analytical column used was a Spherisorb ODS (25cm x 4.6mm) column with an eluent system of 90%/10% (water/methanol), hold for 5 minutes, followed by a 15 minute ramp to 100% methanol, which was held for 15 minutes. The flow rate of the eluent was 1ml/min. Detection was by a Jasco FP-920 intelligent fluorescence detector, Ex = 300, Em = 420 (56). Scopoletin was used as an external calibration molecule.

Inductively Coupled Plasma / Mass Spectrometry (ICP/MS).

A Hewlett Packard 4500 Series ICP/MS coupled to a Hewlett Packard Data station was used for the elemental analysis of particulate samples. A semi-quantitative method, found as part of the HP 4500 Chemstation software (HP 35920C - copyright 1992), was used to obtain data of elements found in particulate samples from diesel emissions and ETS. The semi-quantitative method took six readings across a peak, producing a maximum accuracy of 70% ±10-30% (57). A linear response for each element is assumed over the range investigated, with the variation in quantitation of any specific peak being the same from the semi-quantitative nature of the computer analysis.

Indium was added to all samples as an internal standard, as indium is a very rare element which is unlikely to be found in the atmospheric samples under investigation. Indium is ideal as an internal standard by ICP/MS as it has one major isotope, with 100% of the isotope being ionised in the plasma, giving excellent sensitivity.

A standard containing 12 elements at known concentrations, in addition to the indium internal standard, was run prior to analysis of any samples to identify any variation in ionisation or response of the instrument at that time. The elements in the standard were magnesium (Mg), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), strontium (Sr), molybdenum (Mo), cadmium (Cd), tin (Sn), barium (Ba), mercury (Hg) and lead (Pb). The responses of these elements are obtained and then using response factors found

in the semi quantitative program, a set of semi quantitative data for almost any element in the samples can be obtained.

2.2.6 Results and Discussion.

2.2.6.1 Volatiles.

Diesel.

The chromatogram seen in Figure 2.6 is typical for all the samples taken from the diesel test engine at the three different rated powers.

Analysis of the mass spectral data and library searches provided the identification of compounds emitted from a diesel engine, seen in Table 2.5.

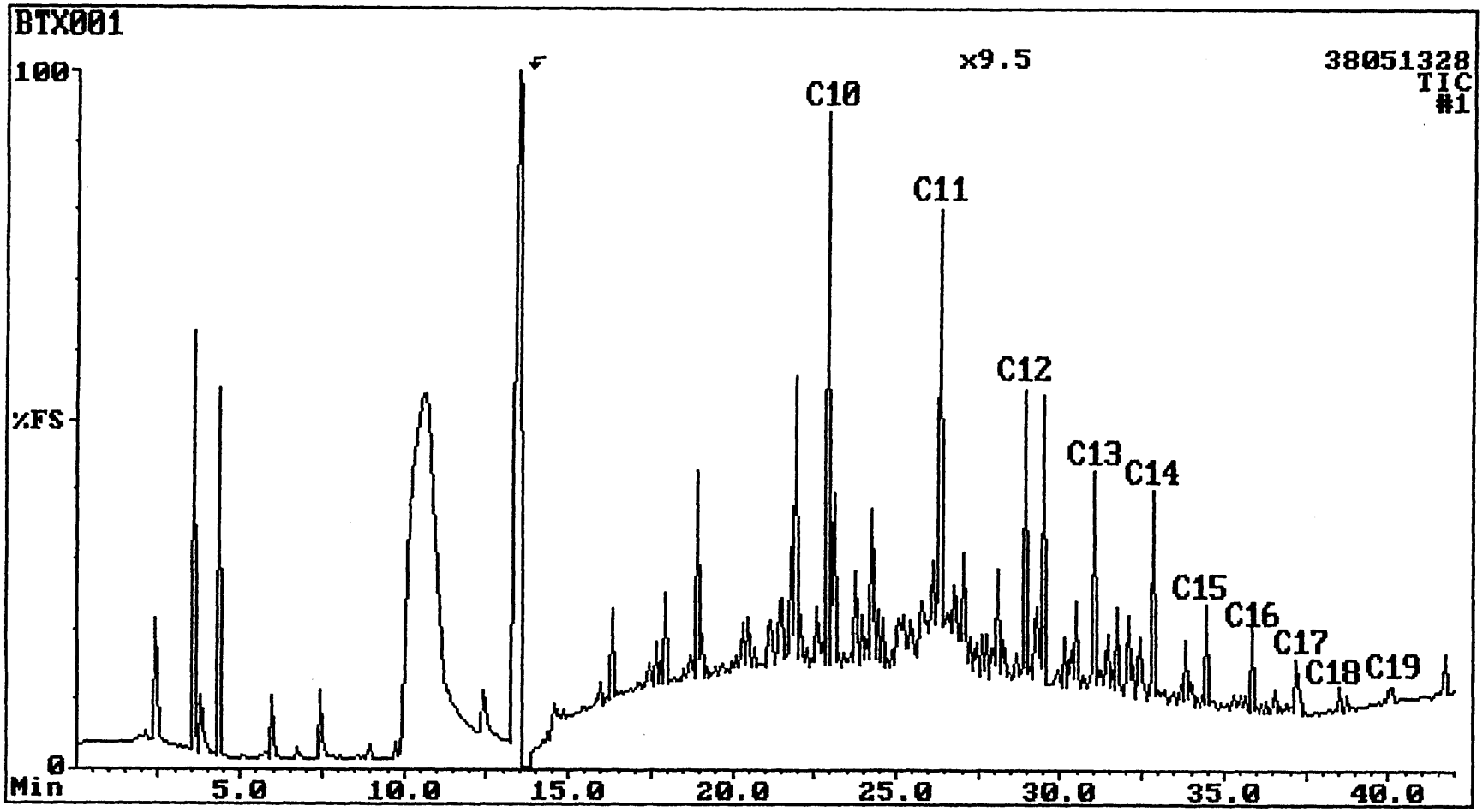


Figure 2.6: A ATD/GC/MS Chromatogram of a Volatiles Sample Taken from the Exhaust of a Diesel Engine.

Table 2.5: ATD Volatile Organic Compounds found in Diesel Exhaust Fumes.

Retention time	Standard	Retention time	Engine speed of 1600rpm at half load.	Retention time	Engine speed of 1600rpm at 3/4 load.	Retention time	Engine speed of 1600rpm at full load.
	Water	2.4	Water	2.4	Water	2.4	Water
	Acetonitrile	3.6	Acetonitrile	3.6	Acetonitrile	3.6	Acetonitrile
				3.79	Oxy bis ethane	3.79	Oxy bis ethane
4.35	Dichloromethane	4.33	Dichloromethane	4.37	Dichloromethane	4.37	Dichloromethane
		5.82	Formic acid				
6.00	Hexane	5.97	Hexane	6	Hexane	6	Hexane
		6.73	Acetic acid methyl ester	6.73	Acetic acid methyl ester		
		7.45	Methoxy ethanol	7.45	Methoxy ethanol	7.46	Methoxy ethanol
8.61	Benzene	8.6	Benzene	8.63	Benzene	8.63	Benzene
		8.95	Thiophene	8.95	Thiophene	8.95	Thiophene
9.68	1,2 dimethyl cyclopentane						
10.05	heptane						
		9.73	Trifluoroacetamide	9.75	Trifluoroacetamide	9.75	Trifluoroacetamide
						10.33	Methyl benzene
		12.43	Pyridine	12.42	Pyridine	12.48	Pyridine
13.37	Toluene						
		15.97	Formic acid pentyl ester	16	Formic acid pentyl ester	16	Formic acid pentyl ester
		16.3	Bromo pentane	16.33	Bromo pentane	16.33	Bromo pentane
		17.45	Unknown	17.47	Unknown	17.47	Unknown
17.65	ethyl benzene	17.63	ethyl benzene	17.65	ethyl benzene	17.67	ethyl benzene
		17.77	methyl octane	17.78	methyl octane	17.8	methyl octane
17.97	(p,o) Xylene	17.93	(p,o) Xylene	17.98	(p,o) Xylene	17.99	(p,o) Xylene

Retention time	Standard	Retention time	Engine speed of 1600rpm at half load.	Retention time	Engine speed of 1600rpm at 3/4 load.	Retention time	Engine speed of 1600rpm at full load.
				18.63	Unknown	18.63	Unknown
		18.93	Dimethyl hexane	18.95	Dimethyl hexane	18.95	Dimethyl hexane
19.03	(m) Xylene	19.01	(m) Xylene	19.05	(m) Xylene	19.03	(m) Xylene
		20.31	Dimethyl octane			20.33	Dimethyl octane
20.32	isopropylbenzene						
		20.43	propyl cyclohexane	20.48	propyl cyclohexane	20.48	propyl cyclohexane
						21.55	Unknown
		21.79	Unknown			21.82	Unknown
		21.92	Benzaldehyde	21.95	Benzaldehyde	21.95	Benzaldehyde
		22.05	Trimethyl benzene			22.05	Trimethyl benzene
				22.56	methyl propyl cyclohexane		
		22.9	Decane	22.95	Decane	22.93	Decane
		23.08	Trimethyl benzene	23.11	Trimethyl benzene	23.12	Trimethyl benzene
		23.77	Dimethyl nonane			23.78	Dimethyl nonane
23.97	Dichlorobenzene	23.95	Dichlorobenzene	23.98	Dichlorobenzene	23.98	Dichlorobenzene
						24.23	Unknown
		24.3	Methyl ethyl benzene	24.3	Methyl ethyl benzene		
		24.42					
		24.58	Benzenemethanol	24.62	Benzenemethanol		
		25	Dimethylnonane	25	Dimethylnonane		
		25.1	Unknown	25.13	Unknown		
		25.17	Unknown				
				25.2	Methyl propyl benzene		
		26.32	Undecane	26.35	Undecane	26.35	Undecane
				26.75	Chloro methoxy benzene		
		28.92	Dodecane	28.94	Dodecane	28.95	Dodecane

Retention time	Standard	Retention time	Engine speed of 1600rpm at half load.	Retention time	Engine speed of 1600rpm at 3/4 load.	Retention time	Engine speed of 1600rpm at full load.
		29.24	Dimethyl undecane				
						29.34	Naphthalene
		29.52	Dichloromethyl benzene			29.53	Dichloromethyl benzene
		30.49	Trimethyl Dodecane	30.5	Trimethyl Dodecane	30.5	Trimethyl Dodecane
		31.03	Tridecane	31.03	Tridecane	31.03	Tridecane
						31.6	Tetrahydromethyl naphthalene
		31.69	Methyl naphthalene	31.7	Methyl naphthalene	31.7	Methyl naphthalene
		32.07	Methyl naphthalene	32.09	Methyl naphthalene	32.09	Methyl naphthalene
		32.44		32.47			
		32.82	Butadecane	32.82	Butadecane	32.82	Butadecane
				33.7	Dimethylnaphthalene		
		33.84	Unknown	33.87	Unknown	33.87	Unknown
		34.42	Pentadecane	34.43	Pentadecane	34.43	Pentadecane
		35.85	Hexadecane	35.88	Hexadecane		
		36.52	Unknown	36.54	Unknown		
		37.19	Heptadecane	37.2	Heptadecane		
				37.28	Unknown		
		38.54	Octadecane	38.55	Octadecane		
		38.72	Unknown				
				40.04	Nonadecane		

The compounds listed in Table 2.5 were identified by retention time (where standards were available) and/or spectral data library matches. An initial look at the compounds released from the diesel engine at the three speeds identifies several compounds including hexane, benzene, ethyl benzene and xylene isomers. Other compounds identified included thiophene, pyridine, various branched alkanes, alkyl benzenes, alkyl naphthalenes in addition to an envelope of alkane compounds from C11 (undecane) to C19 (Nonadecane). The variation of these combustion volatiles compared to their rated power was not investigated.

It can be seen from these results that the dominant family of compounds are the straight chained alkanes, from C11 to C19. These are the main constituent of diesel fuel, with the alkane fraction extending from at least C10 to C27 (GC/MS chromatogram of alkane standard: Figure 2.7, and fractionated diesel fuel: Figure 2.8). Therefore, these alkanes are released from the exhaust of the engine in the gaseous phase either as un-combusted or partially combusted material.

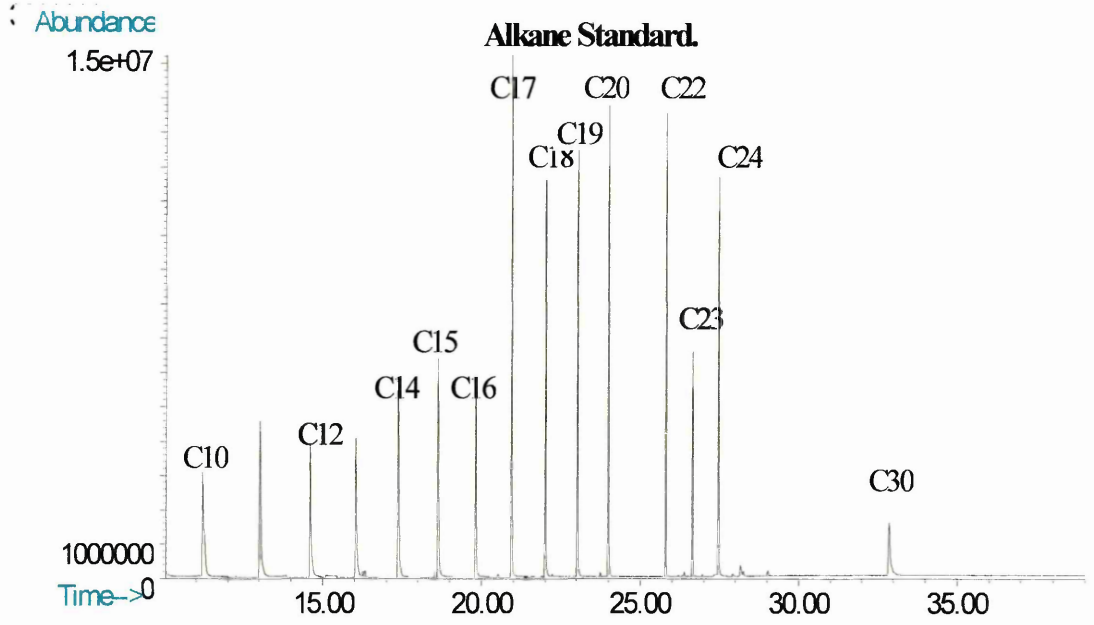


Figure 2.7: Alkane Standard Containing C10-C20, C22-C24 and C30.

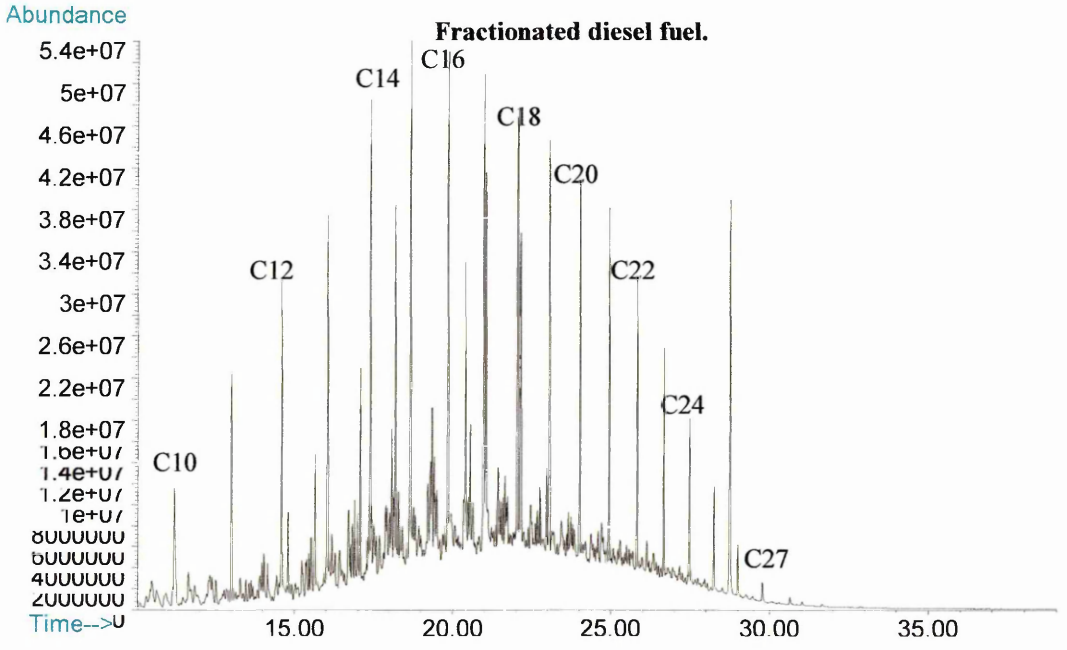


Figure 2.8: Fractionated Diesel Fuel, Identifying the Major Alkane Envelope Typical in Diesel Fuel.

Even though this thermal desorption analysis (Figure 2.6) was not quantitative it can be inferred that as the carbon length increases from decane (C10), the size of the peak diminishes. This suggests that the quantity of the alkane reduces with increasing length from decane (C10). This is expected, since as the volatility of alkanes decreases with increasing chain length, and the larger alkanes are more likely to be found associated with particulate material.

A compound in the gaseous phase unique to diesel emissions was not identified. The volatile compounds released by diesel engines are almost entirely aliphatic in nature. These are likely to be released from other anthropogenic sources (such as petrol engines) in a similar, if not larger quantity. These results are comparable to those obtained from volatile compounds in roadside water (58), in which it was also not possible to identify a potential anthropogenic volatiles marker compound.

However, some interesting compounds were identified in samples from this phase. These included thiophene, pyridine (also identified as present in ETS (7)) and volatile PAH. The presence of benzene, toluene and the xylene isomers is also of interest, as they have been identified as being in both indoor and outdoor environments. Quantitative analysis of these compounds as well as others were undertaken in the field sampling (see Section 3.5.2).

Environmental Tobacco Smoke (ETS).

The ETS ATD/GC/MS chromatogram (Figure 2.9) looks very different to that obtained from the diesel samples. There is no alkane envelope which is so dominant in the diesel chromatogram. Table 2.6 lists the presence of a number of compounds found in the ETS chromatograms, these include: benzene, toluene and the xylene isomers, all of which were present in diesel emissions. However, there are a large number of compounds that were not seen in the diesel samples. Nicotine is a major peak along with heterocyclic compounds including furans, pyrroles and pyridine derivatives. Oxygenated species are also present, including various aldehydes and ketones. Naphthalene is the only PAH seen in the ETS chromatogram.

These results compare well with volatile compounds identified in literature by thermal desorption or analogous methods. However, it was noted by Thompson et al (18) that up to 10% of the adsorbed nicotine stayed on the Tenax (p-2,6-diphenyl phenylene oxide) resin. Hence, nicotine is not suitable as a volatile tracer molecule. Other volatile tracer molecules discussed in the literature include 3-ethenyl pyridine, pyrrole, and pyridine (20). Pyridine was immediately rejected as it had been identified in the diesel emissions (See Section 2.2.6.1-Diesel). 3-ethenyl pyridine and pyrrole were positively identified as being present in the standard ETS atmosphere samples. 3-ethenyl pyridine had also been used as a volatile tracer molecule in previous studies (59). However, the concentration range which was available from the sampling procedures only allowed detection of 3-ethenyl pyridine in two of the nine smoking environments (see Section 3.6.1.1). Pyrrole was found in six of the nine environments (see Section 3.6.1.1), and was found to have a lower limit of detection than 3-ethenyl pyridine. These practical reasons led to the use of pyrrole as the volatile organic marker compound for ETS since it had a quantifiable concentration in more of the field samples than 3-ethenyl pyridine and no evidence of any problems in its recovery from tenax had been found in the literature.

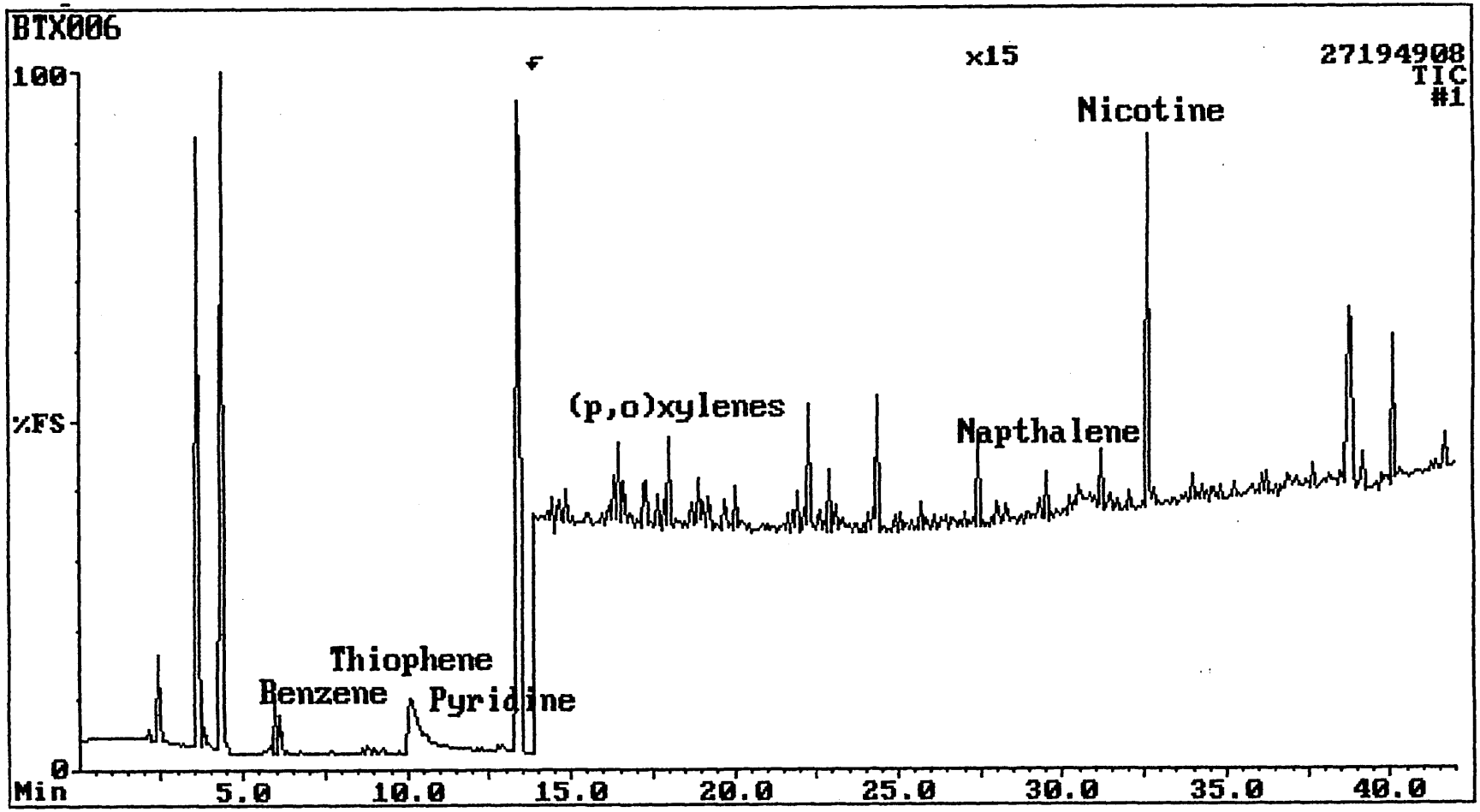


Figure 2.9: An ATD/GC/MS Chromatogram of Volatiles Sampled in Environmental Tobacco Smoke (ETS).

Table 2.6: Volatile Organic Compounds from a Smokers Environment (ATD-GC/MS)

Retention time	Standard	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	4 Cigarettes smoked in a closed environment and passively sampled
		2.4	Water	2.4	Water	2.4	Water
				3.62	Acetonitrile	3.62	Acetonitrile
				3.81	Pentandiene		
4.35	Dichloromethane	4.35	Dichloromethane	4.35	Dichloromethane	4.35	Dichloromethane
6	Hexane	5.98	Hexane	5.98	Hexane	5.98	Hexane
		6.08	Butanone	6.1	Butanone	6.1	Butanone
				6.28	Methyl Furan		
						7.26	Methyl Propanitrile
						7.48	Hexyne
						7.88	Hexatriene
						8.28	Butanal
8.61	Benzene	8.61	Benzene	8.61	Benzene	8.61	Benzene
				8.78	Hydroxy propanone		
		8.97	Thiophene	8.97	Thiophene		
9.68	1,2 dimethyl cyclopentane						
						9.72	Diethyl cyclobutane
		9.73	Trifluoroacetamide				
10.05	Heptane						
						10.1	Butandione
						10.58	Dimethyl Furan
						12.25	Methyl Pyrrole
		12.6	Pyridine	12.6	Pyridine		
				12.88	Pyrrole	12.86	Pyrrole
13.37	Toluene	13.4	Toluene	13.4	Toluene	13.38	Toluene

Retention time	Standard	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	4 Cigarettes smoked in a closed environment and passively sampled
		14.27	Octene			14.27	Octene
		16.32	Bromo Pentane				
		16.43	Furancarboxaldehyde	16.43	Furancarboxaldehyde	16.43	Furancarboxaldehyde
		16.6	Unknown	16.6	Unknown	16.58	Unknown
						17.02	Methyl Pyrrole
		17.27	Furanmethanol	17.27	Furanmethanol	17.25	Furanmethanol
17.65	Ethyl Benzene	17.65	Ethyl Benzene	17.67	Ethyl Benzene	17.65	Ethyl Benzene
		17.85	Ethandiol Diacetate	17.83	Ethandiol Diacetate	17.85	Ethandiol Diacetate
17.97	(p.m) Xylene	17.97	(p.m) Xylene	17.97	(p.m) Xylene	17.97	(p.m) Xylene
		18.62	Nonene			18.62	Nonene
						18.93	Ethenyl Benzene
19.03	(m) Xylene	19.03	(m) Xylene	19.03	(m) Xylene		
		19.22	Cyclohexanone	19.21	Cyclohexanone	19.22	Cyclohexanone
		20.03	Dihydrofuranone	20.03	Dihydrofuranone	20.03	Dihydrofuranone
20.32	Isopropylbenzene	21.8	Ethyl methyl benzene			21.8	Ethyl methyl benzene
		22.18	Ethenyl benzene			22.18	Ethenyl benzene
		22.25	Phenol	22.25	Phenol	22.25	Phenol
		22.92	Decane	22.91	Decane		
23.97	Dichlorobenzene						
		24.38	Trimethyl bicyclo heptene	24.38	Trimethyl bicyclo heptene	24.38	Trimethyl bicyclo heptene
				25.68	Methyl phenol		
		27.47	Unknown	27.47	Unknown		
		28.04	Unknown				
		29.32	Naphthalene	29.32	Naphthalene	29.32	Naphthalene

Retention time	Standard	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	2 Cigarettes smoked in a closed environment and passively sampled	Retention time	4 Cigarettes smoked in a closed environment and passively sampled
		29.52	Dichloro methoxy benzene	29.52	Dichloro methoxy benzene	29.52	Dichloro methoxy benzene
		31.24	Unknown				
		32.6	Methyl pyrolidinyl pyridine	32.6	Methyl pyrolidinyl pyridine	32.6	Methyl pyrolidinyl pyridine
		38.8	Degradation	38.8	Degradation	38.8	Degradation

ETS apportionment.

In order to use pyrrole for "apportionment" work it is necessary to know the following: the ratio of the concentration of pyrrole to the organic compound of interest, in ETS; the concentration of pyrrole in the atmosphere in question and the concentration of the organic compound in the atmosphere. With these values the percentage contribution from ETS to the total concentration of a compound in the atmosphere can be determined. In this thesis I am going to describe such work as "apportionment". Work of this type has been published by other authors (20,59).

Samples of standard ETS atmospheres were obtained from the smoke generating system described in Section 2.2.1.2 with low flow pumps (50ml/min) using tenax and carboxen tubes in series (see Section 2.2.2.2). Quantitative analysis by ATD/GC/MS produced the concentrations of the listed volatile compounds shown in Table 2.7. The ratio of the volatile to pyrrole was then obtained. This ratio A, multiplied by the concentration of pyrrole in a sample gave that concentration of the volatile released by ETS in that atmosphere.

A = ratio of volatile to pyrrole compound under investigation from standard atmosphere.
B = Pyrrole concentration in sample under investigation.
C = Concentration of volatile compound due to ETS in the sample under investigation.
D = Total concentration of volatile compound in sample under investigation.

$$A \times B\mu g/m^3 = C\ \mu g/m^3$$

$$\% \text{ apportionment} = (C/D) \times 100.$$

Table 2.7: Concentrations (μg/m^3) and Ratio Values (compared to pyrrole) for Selected Volatile Organic Compounds, (N=2) Identified in a Standard ETS Atmosphere

	Standard ETS atmosphere		
Compounds	μg/m^3	Std. Dev.	Ratio
Pyrrole	113.8	7.6	1.0
Benzene	374.6	19.8	3.29±0.05
Toluene	3773.65	65.66	33.14±1.77
O-xylene	37.8	7.3	0.33±0.04
P + M-xylene	85.0	6.8	0.75±0.06
ethyl benzene	79.5	8.9	0.70±0.08
1,4 dichlorobenzene	0.0	0	0.0

These ratios are used in, Section 3.6.1.1 to provide percentage apportionment values for the above volatile compounds for ETS in smokers atmospheres.

2.2.6.2 Semi-volatiles.

Diesel.

The chromatogram seen in Figure 2.10 is a typical chromatogram for diesel exhaust semi volatile emissions obtained in this work. These compounds were sampled directly behind the glass fibre filter paper onto XAD-4 resin tubes. This sampling was undertaken to identify if any other compounds could be found in the gaseous phase which were not sampled by the thermal desorption system, due to their lower volatility. We can see that there are a few such compounds but they are not major constituents of the gaseous polluting diesel emissions. The identification of an envelope of alkanes from tridecane (C13) to tricosane (C23) shows that even these longer chain alkanes are not entirely associated with the particulate material. In addition to the straight chained alkanes, there are a number of other compounds, including branched alkanes and cyclohexyl derivatives. Positive identification of these aliphatic alkanes was achieved by using standards and obtaining retention times, as the mass spectra are often very similar for alkanes. Thus it can seen that no specific diesel marker was immediately apparent in this phase.

However, an interesting feature of the resin samples is the identification of two methylnaphthalene ($M^{+\bullet}$=142) compounds by ion extraction (Figure 2.11) while no naphthalene ($M^{+\bullet}$=128) (Figure 2.12) itself was identified. This is not consistent with the literature, where naphthalene and its two methyl derivatives are observed in diesel emissions (60). The difference is probably due to the samples being reduced to dryness, so loss of the naphthalene is likely to have occurred.

PAH are released from most anthropogenic sources during incomplete combustion or pyrolysis of coke (61), petrol (61,62), diesel (61) and wood (61). Since not all of these sources were available for analysis, naphthalene and its alkyl derivatives could not be selected as appropriate marker compounds. However, naphthalene is identified in all the previously stated samples (61). No tracer was found sufficiently unique for diesel emissions in the gaseous phase.

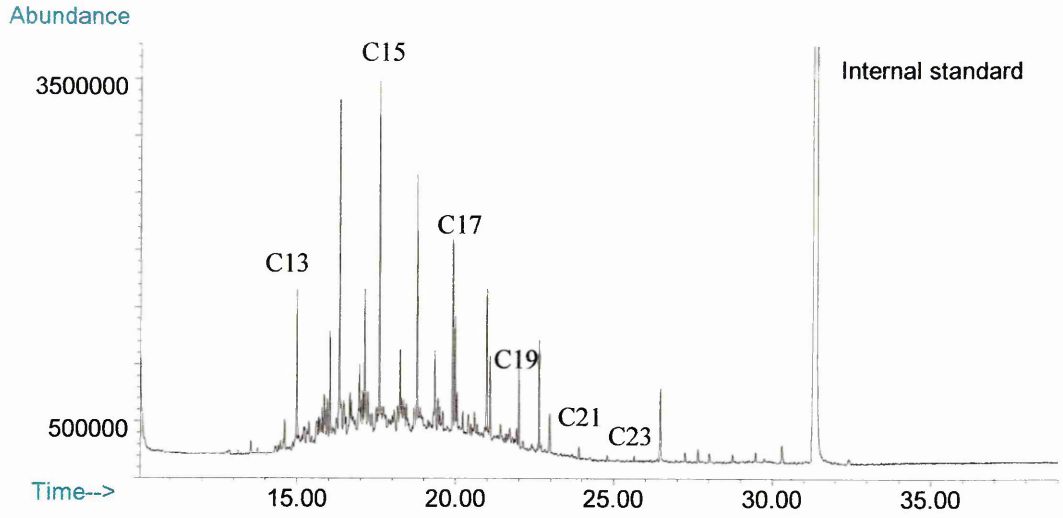


Figure 2.10: Semi-volatiles (sampled on XAD-4 resin) Chromatogram of Typical Diesel Emissions.

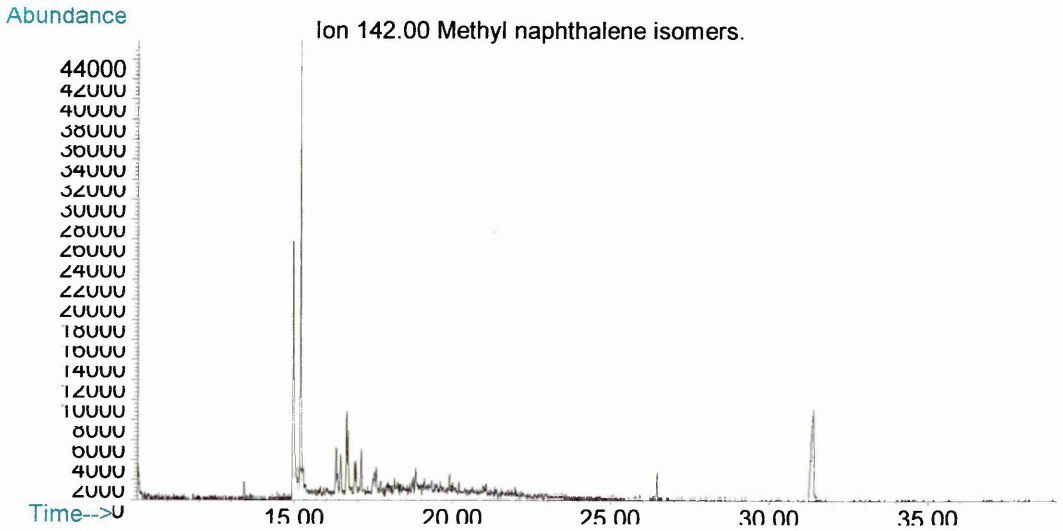


Figure 2.11: Molecular Ion Extraction for Methyl Naphthalene Compounds.

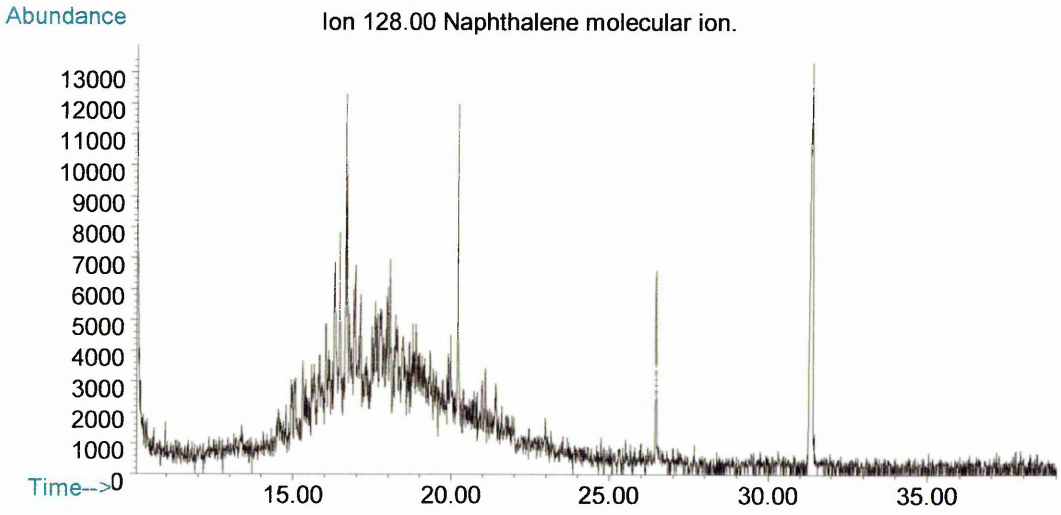


Figure 2.12: Molecular Ion Extraction for Naphthalene.

Environmental Tobacco Smoke (ETS).

All compounds were identified by MS library matches only.

Table 2.8: Compounds Identified in the Gaseous Phase of ETS Sampled onto XAD-4 Resin.

Tr	Resin extract from XAD-4
10.91	Phenol
11.78	Limonene
13	Benzoic acid methyl ester
13.84	Unknown
14.17	Naphthalene derivative
14.5	Naphthalene
14.66	Phenol, 2-(1methylethyl-
15.64	Ethanone 1(4ethylphenyl)-
15.94	1H Inden-1-one 2,3 dihydro
16.44	Phthalic Anhydride
17.14	Nicotine
17.55	1,1 Biphenyl, 2 methyl
18.59	Unknown
20.44	Unknown
20.56	Unknown
20.96	Heptadecane
22.27	Unknown
22.45	Unknown
22.84	Phthalate
23.78	Phthalate
27.53	hexanedioic acid dioctyl ester
28.75	Phthalate

It can be seen from Table 2.8 that few compounds in the dichloromethane extract from gaseous ETS could be identified by GC/MS. Nicotine is the major gaseous tracer molecule used for ETS determination. However, due to its inconsistent phase distribution (see Section 2.1.2), it is a poor ETS marker. Two compounds of similar structure to nicotine, i.e. myosmine and nicotyrine, were identified as other possible marker compounds. However, the concentration of these compounds in this phase are often low, and a large sample is needed, for identification/quantification to be possible. Naphthalene was also identified as being present in gaseous ETS.

ETS sampled onto XAD-4 resin was also analysed for polycyclic aromatic hydrocarbons (PAH) by GC/MS-SIM, to identify any possible specific PAH or PAH ratios. An example of a chromatogram of the 16 EPA PAH can be seen in Figure 2.13. Quantitation was achieved using D10-Anthracene as the internal standard. By extracting the relevant ions, accurate integration was possible, even though D10-anthracene co-elutes with phenanthrene and anthracene. The reconstructed ion chromatograms (Figure 2.14) show complete separation of the three compounds and accurate quantitation. The quantitative results can be seen in Table 2.9. Quantitative PAH analysis was not possible for the diesel semi-volatile emissions, as the flow rates throughout the dilution tunnel were not routinely measured.

Table 2.9: Quantitative Analysis of ETS Sampled onto XAD-4 Resin (N=2) from a Standard ETS Atmosphere.

Basildon sample	Vapour ETS	
Concentration	Mean (ng/m^3)	Std Dev.
Naphthalene	16389.3	549.1
Acenaphthylene	167.9	7.3
Acenaphthene	146.0	5.6
Fluorene	182.4	17.1
Phenanthrene	362.5	38.6
Anthracene	0.0	0.0
Fluoranthene	0.0	0.0
Pyrene	0.0	0.0
B.(a)anthracene	0.0	0.0
Chrysene	0.0	0.0
B.(b)fluoranthene	0.0	0.0
B.(k)fluoranthene	0.0	0.0
B(a)Pyrene	0.0	0.0
B(g,h,i)Perylene	0.0	0.0
Dib(a,h)Anthracene	0.0	0.0
Indeno(1,2,3,c-d)pyrene	0.0	0.0

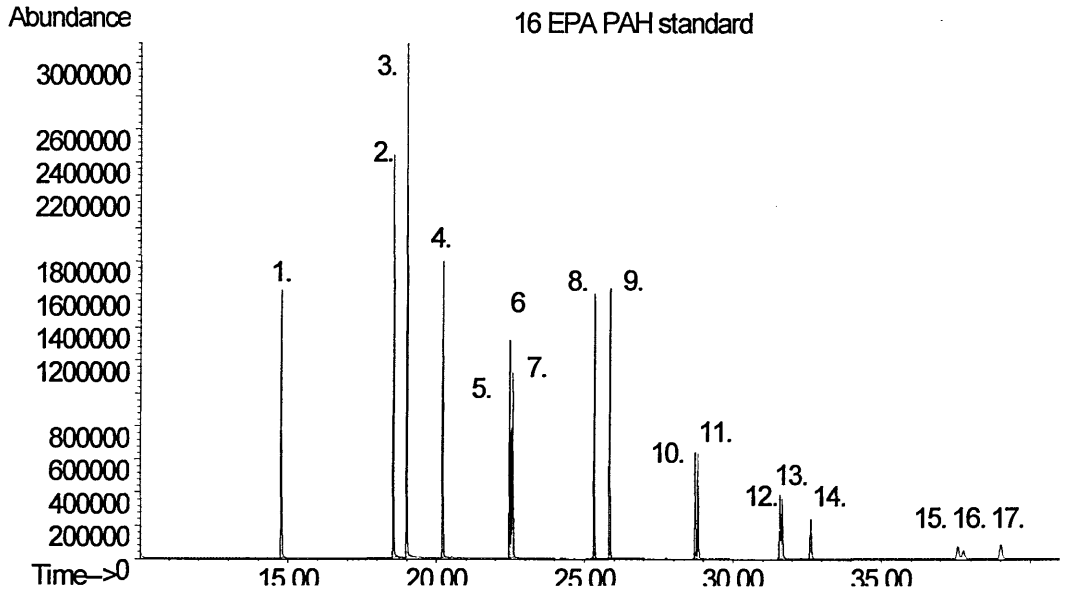


Figure 2.13: Total Selective Ion Chromatogram of 16 EPA PAH with D10 Anthracene Internal Standard. 1. Naphthalene, 2. Acenaphthylene, 3. Acenaphthene, 4. Fluorene, 5. Phenanthrene, 6.D10 anthracene, 7. Anthracene, 8. Fluoranthene, 9. Pyrene, 10. Benzo(a)anthracene, 11. Chrysene, 12. Benzo(b)fluoranthene, 13. Benzo(k)fluoranthene, 14. Benzo(a)pyrene, 15. Benzo(g,h,i)perylene, 16. Dibenzo(a,h)anthracene, 17. Indeno(1,2,3,c-d)pyrene.

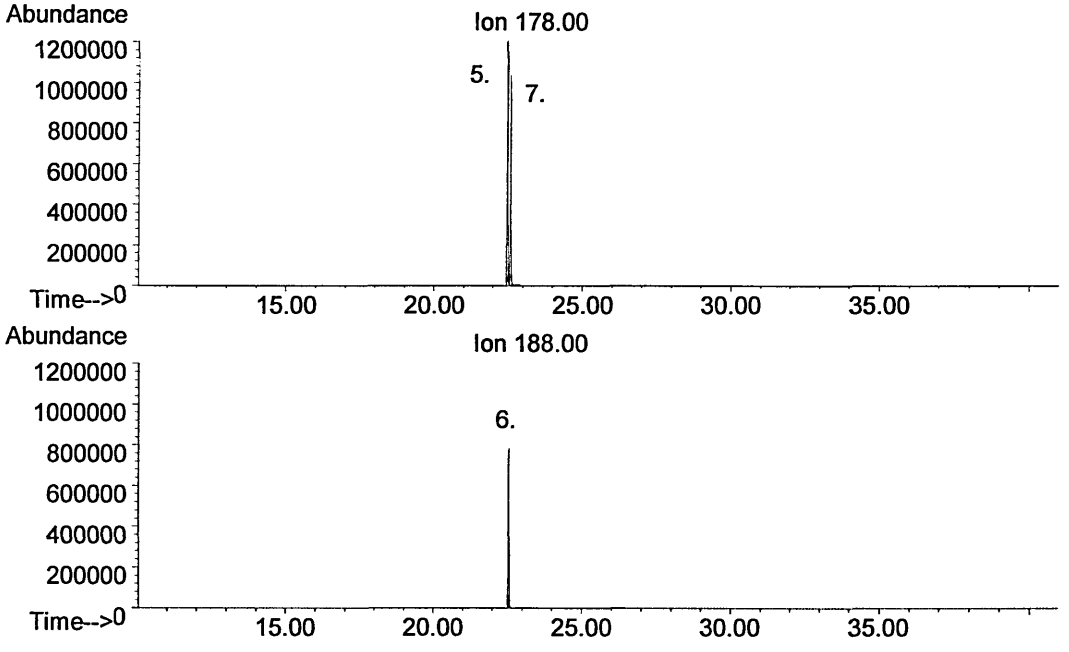


Figure 2.14: Reconstructed Ion Chromatograms of m/z 178 for Phenanthrene (5) and Anthracene (7) and m/z 188 for D10-Anthracene (6).

Salomaa et al (63) reported that increased levels of 34 polycyclic aromatic compounds were seen in samples taken from rooms in which smoking had occurred. They found that a large proportion of the three ringed PAH studied were found in the vapour phase, with little associated with particulate material. This was true to an extent with the samples taken from the smoking environment in our study, with the majority of the three ring PAH compounds being found in the vapour phase. However, we found that there was also an appreciable amount of these PAH associated with the particulate material (see Section 2.2.6.3). They also identified fluoranthene and pyrene in the vapour phase (63) however, we found that all of the fluoranthene and pyrene was associated with the particulate fraction in the ETS atmospheric samples.

Table 2.10: Comparison of Quantitative Data from PAH Analysis with Literature Values.

		Vapour ETS	Vapour ETS from Salomaa et al (63)	Ratio of PAH conc. to fluorene conc.	Ratio of PAH conc. to fluorene conc. from Salomaa (63)
Concentration		ng/m^3	ng/m^3		
Naphthalene		16389.39	-	89.81	-
Acenaphthylene		167.94	162.8	.915	2.78
Acenaphthene		146.02	33.1	0.800	.565
Fluorene		182.49	58.6	1	1
Phenanthrene		362.55	124.4	1.987	2.12
Anthracene		0.00	21.7	-	0.37
Fluoranthene		0.00	15.6	-	0.27
Pyrene		0.00	6.6	-	0.11

Comparison of the ratios of the concentration of each PAH to fluorene concentration, seems to yield little similarity between the two sets of data. There may be several reasons for this; a different brand of cigarettes were used by Salomaa et al, the number of cigarettes smoked was different and also the sampling procedure. However, the concentration ranges are similar (ng/m^3). Little other quantitative data on PAH in ETS has been reported and therefore further comparisons were not possible.

2.2.6.3 Particulate associated organic compounds.

Possible marker compounds for diesel.

The residue extracted from the diesel particulate emissions were fractionated using an amino/alumina separation system (see Section 2.2.4.1). This was originally devised for the pre-concentration of nitrated PAH compounds adsorbed to tree bark (64). A fractionation step was necessary due to the large amount of compounds released from the diesel exhaust, including alkanes, PAH and heterocyclic compounds.

Nitrated PAH

Nitrated PAH compounds have been identified as possible diesel markers because of nitration processes that occur in the engine and exhaust system. In these processes an electrophilic aromatic substitution reaction occurs, which produces the most resonantly stable isomer (See Section 4.2.3.2). Nitrated PAH compounds can also be produced in the atmosphere, but the route of formation is different, producing different isomers for several nitrated PAH compounds. (see Section 4.2.3.3). Many of these compounds are found almost entirely associated with particulate material. Particulate material is produced in a far greater quantity in diesel engines along with a higher proportion of NO_x compared to petrol driven vehicles. These facts, along with the ability to detect these compounds (as they are produced in trace amounts compared to many other compounds), seemed to make them ideal as a marker for diesel emissions.

Separation and detection was completed using Gas chromatography/ Mass spectrometry using negative ion chemical ionisation working in selected ion monitoring mode.

Seven Nitrated PAH were quantitatively analysed, using their ($M^{-\bullet}$) (Figures 2.15 and Figure 2.16). These ions are the most abundant ion since chemical ionisation is a soft ionisation technique. Table 2.11 shows the quantities of each identified PAH by both GC/NICIMS (SIM) and GC/ECD. However, the GC/ECD results are in reality only semi-quantitative due to interfering peaks.

Table 2.11: Quantitative Analysis of Diesel Particulates for Selective Nitrated PAH.

Compound	M/Z of $M^{-\bullet}$ ion.	Diesel Particulates NICIMS (SIM) µg/g	Diesel Particulates GC/ECD µg/g
1-Nitronaphthalene	173	1.64	2.5
Internal Standard	188	-	-
4-Nitrobiphenyl	199	6.14	13.19
5-Nitroacenaphthene	199	2.48	12.43
2-Nitrofluorene	211	N.D.	N.D.
9-Nitroanthracene	223	4.13	9.79
3-Nitrofluoranthene	247	Trace	Obscured
1-Nitropyrene	247	21.73	18.39

N.D. None determined.

Trace. Peak present but below limit of detection.

Obscured. The relevant peak was obscured beneath a large contamination peak.

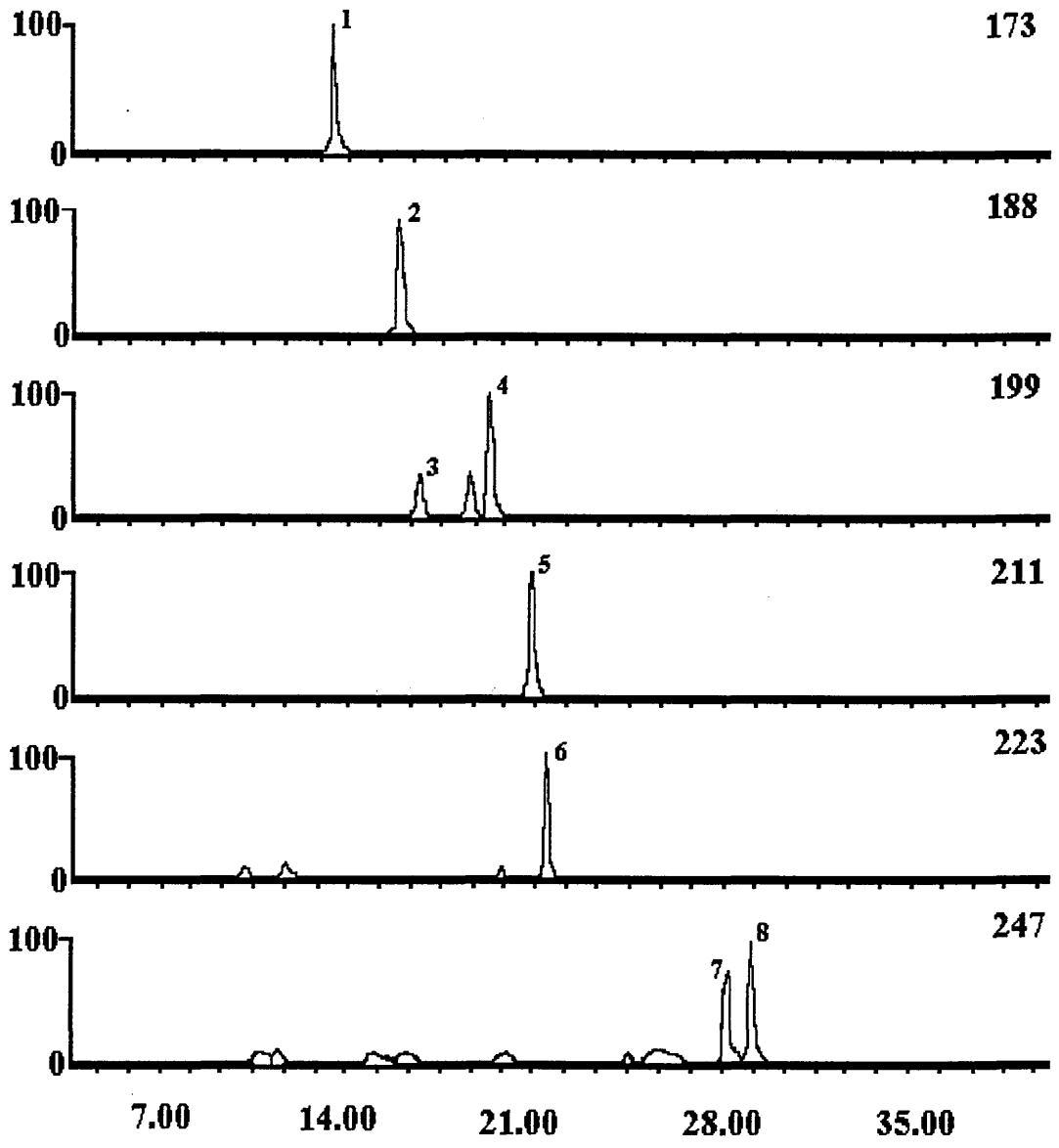


Figure 2.15: GC-NICI-SIM Chromatograms of a Standard Containing Seven Nitrated PAH and an Internal Standard: 1. 1-Nitronaphthalene, 2. Internal Standard, 3. 4-Nitrobiphenyl, 4. 5-Nitroacenaphthene, 5. 2-Nitrofluorene, 6. 9-Nitroanthracene, 7. 3-Nitrofluoranthene, 8. 1-Nitropyrene.

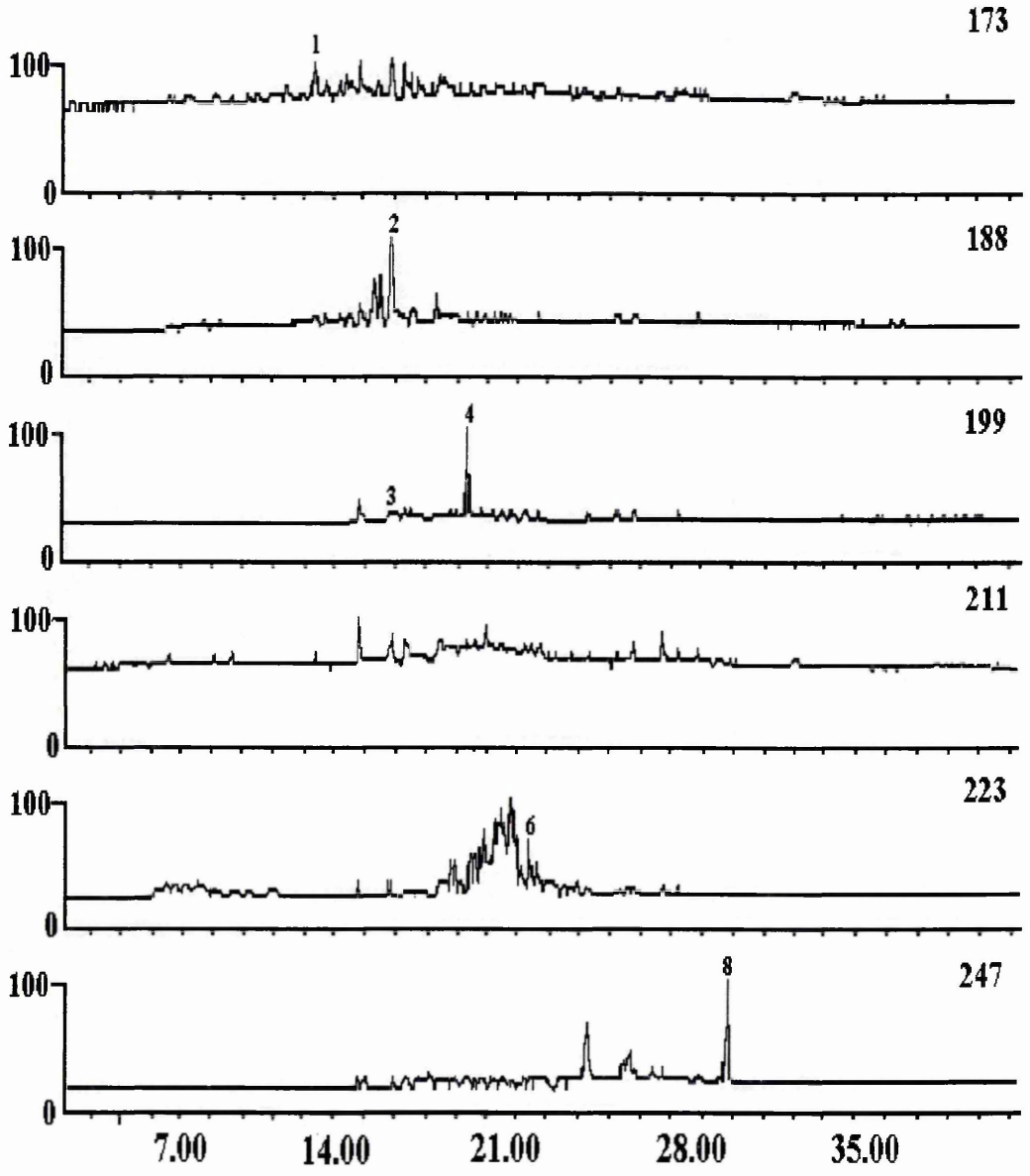


Figure 2.16: GC-NICI-SIM Chromatograms of Diesel Particulates After Fractionation Identifying 1. 1-Nitronaphthalene, 2. Internal Standard, 3. 4-Nitrobiphenyl, 4. 5-Nitroacenaphthene, 6. 9-Nitroanthracene, 8. 1-Nitropyrene.

Of the seven nitrated PAH that were determined, five were quantifiable by both methods. 1-Nitropyrene was found in the largest amounts by both methods, at approximately 20ng/g of particulate material. This corresponds very well with published quantitative values for 1-Nitropyrene in diesel particulate reference material 1650. The quantitative value for 1-nitropyrene quoted by the Laboratory of Government Chemists, (LGC) (65) for the reference material is 19±2 μg/g of diesel particulate exhaust material. Thus a sensitive and selective robust method had been developed for the determination of 1-Nitropyrene in atmospheric particulate samples. Using 1-nitropyrene as a diesel particulate marker compound, a percentage attribution of diesel emissions could be determined for any sample.

However, the atmospheric samples that were to be taken for the field analysis were for 12 hours, at a flow rate of 1l/min (see Section 3.3). This produced samples of particulate material of between 7.33 and 155.3μg (see Section 3.5.1). Even if all this material was due to diesel particulates, the total quantity of 1-nitropyrene would be approximately 150-3100pg. This is the total amount of 1-nitropyrene in the sample, which would be diluted in 100μl of solvent. Therefore the quantity injected on column would be 1.5-31pg, with the limit of detection for 1-nitropyrene being seldom better than 100pg, it can be clearly seen that the concentration of 1-nitropyrene in diesel particulates is beyond our limit of detection from the size of sample taken.

Unfortunately the sample size could not be increased since the flow rate effected the size of particulate material sampled onto the filter paper. With the sampling system in place, the pumps were unable to achieve a flow rate of above 1.3l/min. Therefore, 1-nitropyrene could not be used directly as a marker compound in this study. However there are a great number of compounds released in the exhaust emissions of diesel engines, and with the use of GC/MS and GC/AED it was hoped that other specific compounds could be identified and used instead.

The fractionated samples that were analysed by the GC/AED gave an indication of the elemental content of the compounds released by the diesel engine. The wavelengths used to detect carbon and hydrogen produced almost identical chromatograms to that obtained from GC/MS. The wavelengths for the analysis of chlorine and bromine gave no response. We concluded that there were no chlorine or bromine containing compounds released by the diesel engine that were associated with the particulate material. The sulphur and nitrogen wavelengths were of more interest, with peaks visible in several of the fractions. However, due to the inherent insensitivity of the nitrogen line, the few small peaks observed were not investigated any further.

The sulphur wavelength (Figure 2.17) showed that a number of compounds containing sulphur were released by the diesel engine, and associated with the particulate material. The sulphur content was also found to be almost entirely contained in one fraction. As thiophene had also been identified in the volatile GC/ATD/MS analysis it was decided to look for larger analogues of this sulphur heterocycle including benzothiophene and dibenzothiophene. No benzothiophenes or alkyl derivatives were identified in any of the diesel fractions. Such compounds have been identified in petrol prior to combustion, so it was decided that they would not therefore be specific to diesel (66). However dibenzothiophene (67) in addition to a range of alkyl derivatives (68) and benzonaphthothiophene type compounds (69) have been found in diesel fuel. Dibenzothiophene (Figure 2.18) along with some of its alkyl derivatives (i.e. methyl (C1), dimethyl and ethyl (C2) etc.(Figure 2.19) were subsequently identified in the 5% DCM fraction by library spectral matching.

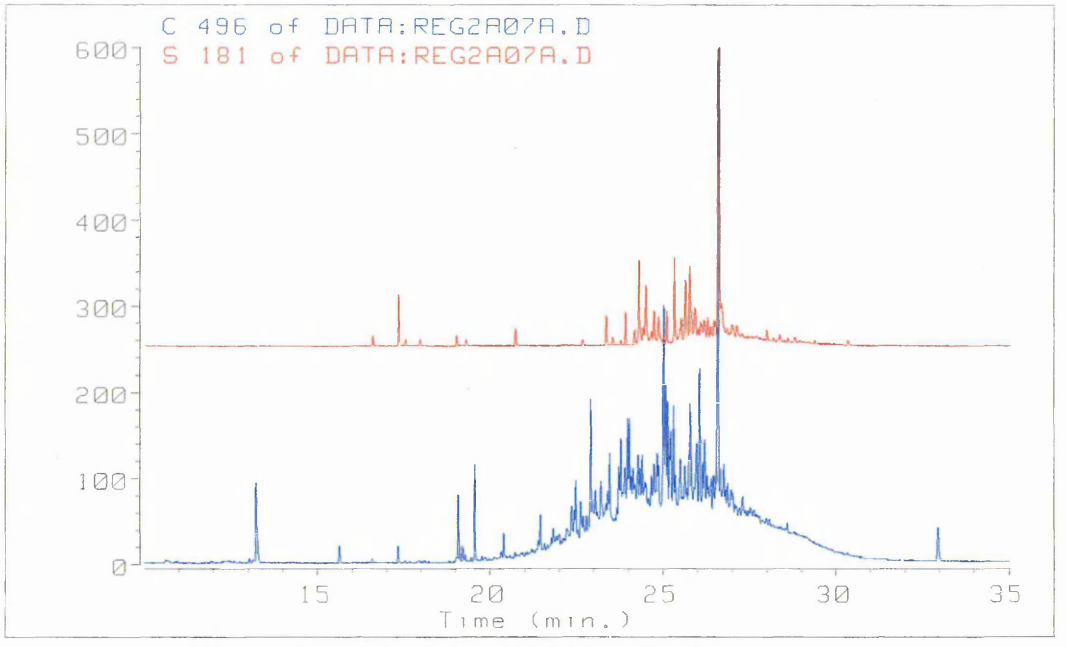


Figure 2.17: Carbon and Sulphur Lines From an AED of the Analysis of Fractionated Particulate Material.

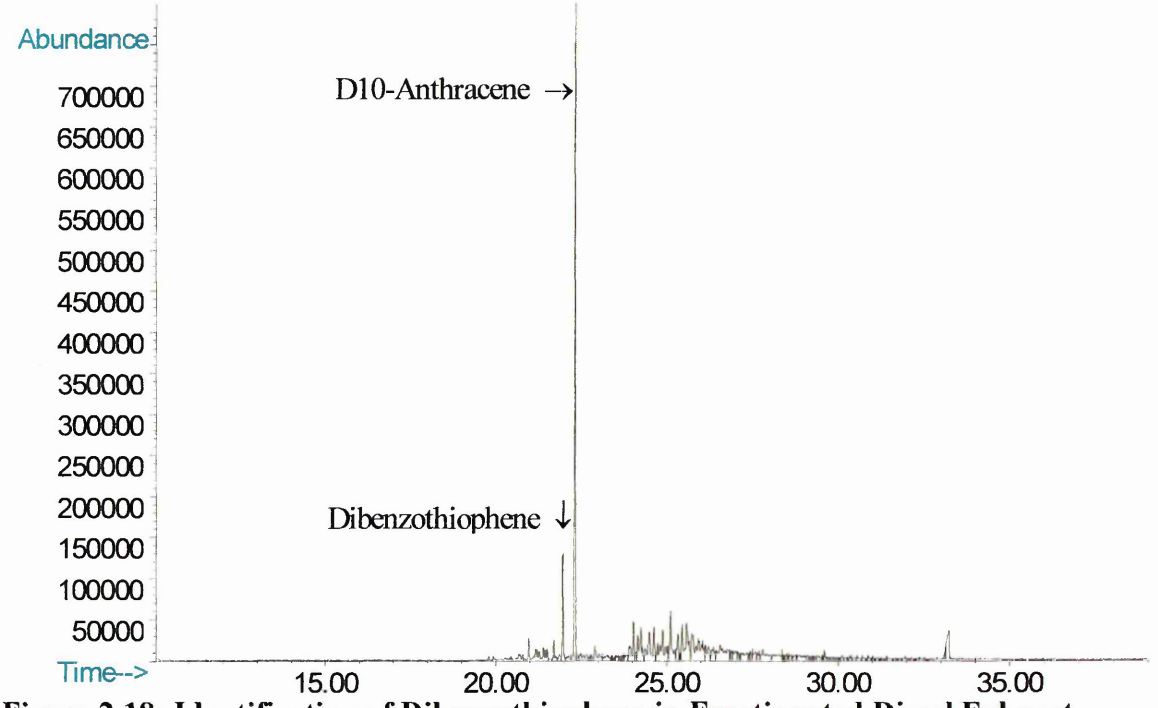


Figure 2.18: Identification of Dibenzothiophene in Fractionated Diesel Exhaust Emissions by GC/MS.

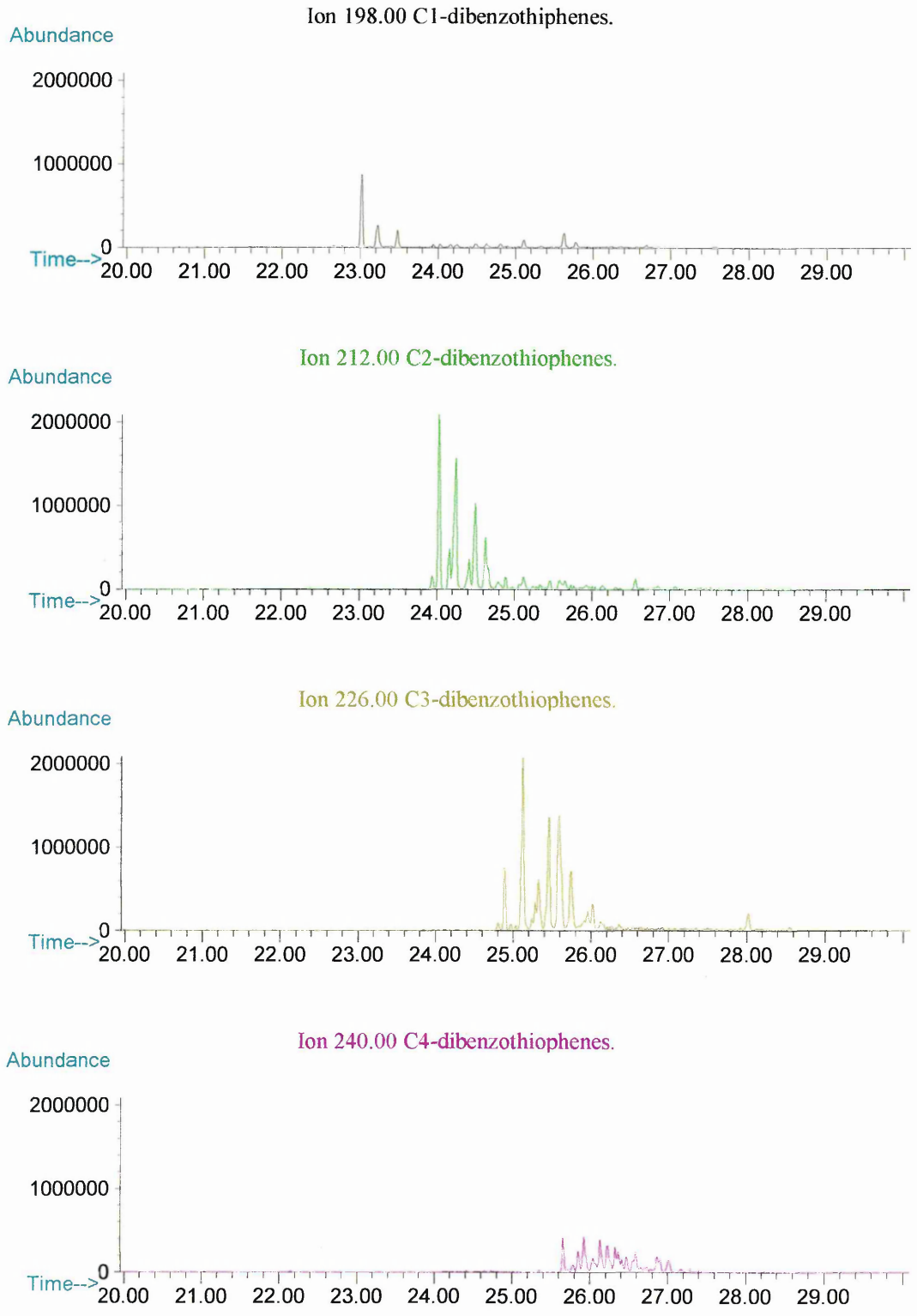


Figure 2.19: Reconstructed Ion Chromatograms for C1, C2, C3 and C4 Dibenzothiophenes in Fractionated Diesel Emissions.

The alklylated dibenzothiophene compounds, specifically C2 and C3 derivatives, were released in quantifiable amounts, so identification of one of these C2 or C3 dibenzothiophene derivatives would possibly lead to a satisfactory marker compound for diesel. The quantity identified in the exhaust emissions is comparable to that found in the fuel prior to combustion, indicating that these compounds undergo little chemical conversion/reaction during combustion (70). However, standards of these compounds are not commercially available. The synthesis of dibenzothiophene compounds was outside the scope of this work. A German company (Agentur für Sensor-Technologie GmbH Nottulner Landweg 90, D-48161 Münster, Germany) was able to supply one C2 dibenzothiophene, (no C3 alkyl derivatives were available). The compound obtained was 2,8-dibenzothiophene. Another set of diesel exhaust samples were taken, fractionated and analysed by GC/MS for C2-dibenzothiophene isomers (Figure 2.20). When the standard was run on the GC/MSD (Figure 2.21) a peak in the same area as all the C2 dibenzothiophene compounds in diesel emissions was observed. However, close inspection of the chromatogram indicated that none of the C2 alkyl dibenzothiphenes released in diesel particulate emissions were 2,8-dimethyldibenzothiophene.

Due to time restrictions it was decided that the identification of a marker compound specific to diesel emissions and found at the necessary concentration was unlikely. It was also observed that a reduction in the sulphur content of diesel fuel, (EEC regulations (71) from 0.2% by weight to 0.05% from 1/10/96) would reduce the concentration of sulphur compounds released by diesel engines. A thiophene type compound became less attractive as a marker due to this reduction.

Use of an n-alkane.

It was therefore decided that an abundant compound found in diesel emissions should be used for the initial identification of the diesel polluting contribution. The value obtained could then be corrected by obtaining a ratio of the general compound to 1-nitropyrene in a large air sample to correct for the contribution from non diesel sources.

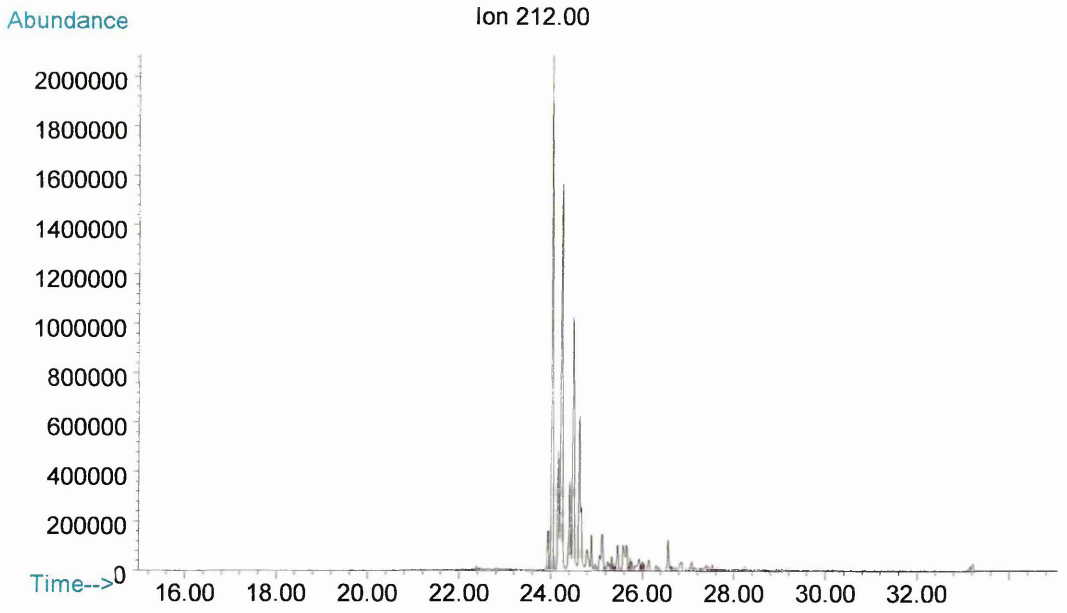


Figure 2.20: Reconstructed Ion Chromatogram for (C2) Dibenzothiophenes from Fractionated Diesel Emissions.

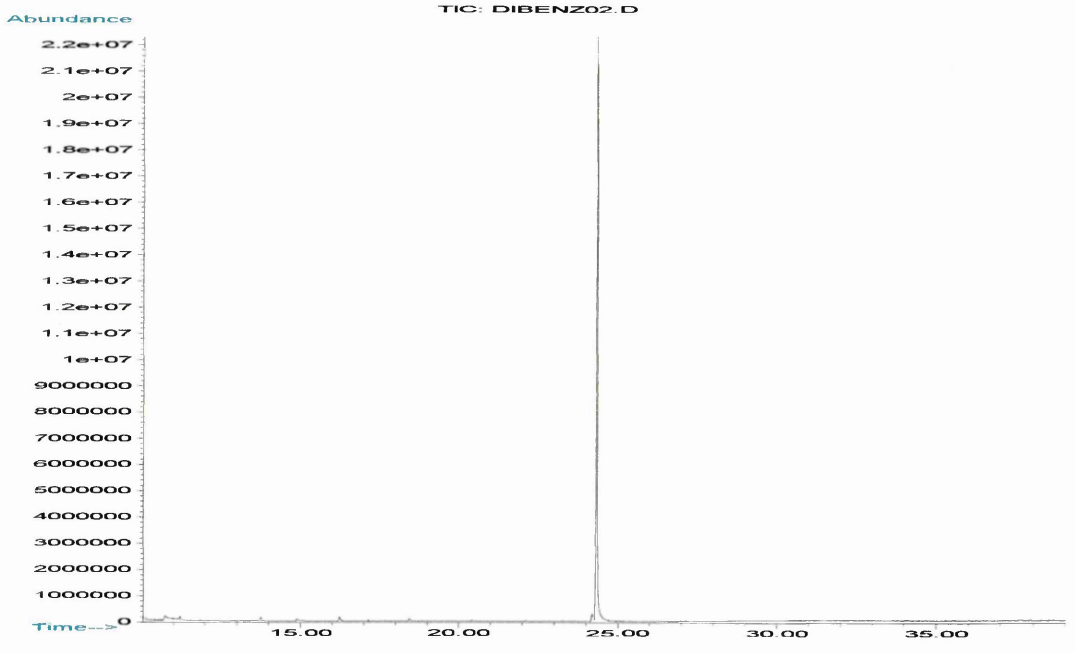


Figure 2.21: 2,8 Dibenzothiophene Standard.

The greatest quantity of organic material emitted by a diesel engine are the aliphatic alkanes. Up to 60% of the elutable (material that will pass through/fractionate on a GC column) organic material released in diesel particulates emissions are aliphatic alkanes (72) this is markedly different to non catalytic and catalytic petrol engines which contained 61% PAH and 53% n-alkanoic acids respectively (72).

The fractionation system discussed earlier was used to remove the majority of the non-polar alkane material, so that identification of other compounds released in lower quantities could be identified. Vehicle fuel, be it petrol or diesel, is mainly aliphatic alkanes. However, petrol is a lower boiling point fraction compared to diesel.

A typical alkane envelope of diesel fuel prior to combustion has been displayed in Section 2.2.6.1 (Figure 2.8) with identification of alkanes ranging from C10 (decane) to C27 (Heptacosane). Analysis of particulate associated alkanes (Figure 2.22) and those found partially in the vapour phase (see Section 2.2.6.2, Figure 2.10) shows that ≥C21 alkanes are found to associate almost entirely with the particulate material. Aliphatic alkanes (C16-C25) were also identified in roadside water extracts from a major road in Britain (58). It was therefore decided that C24 would be used as an anthropogenic emissions marker as it is likely to be released in larger quantities in diesel emissions than from any other anthropogenic combustion source and is found to associate almost entirely with the particulate material (73). The over-estimation of diesel contribution given by using C24 could be corrected by measuring the overestimation for large volume air samples (by comparison with 1-nitropyrene values) and subsequent data from smaller volume samples adjusted using the correction factor determined.

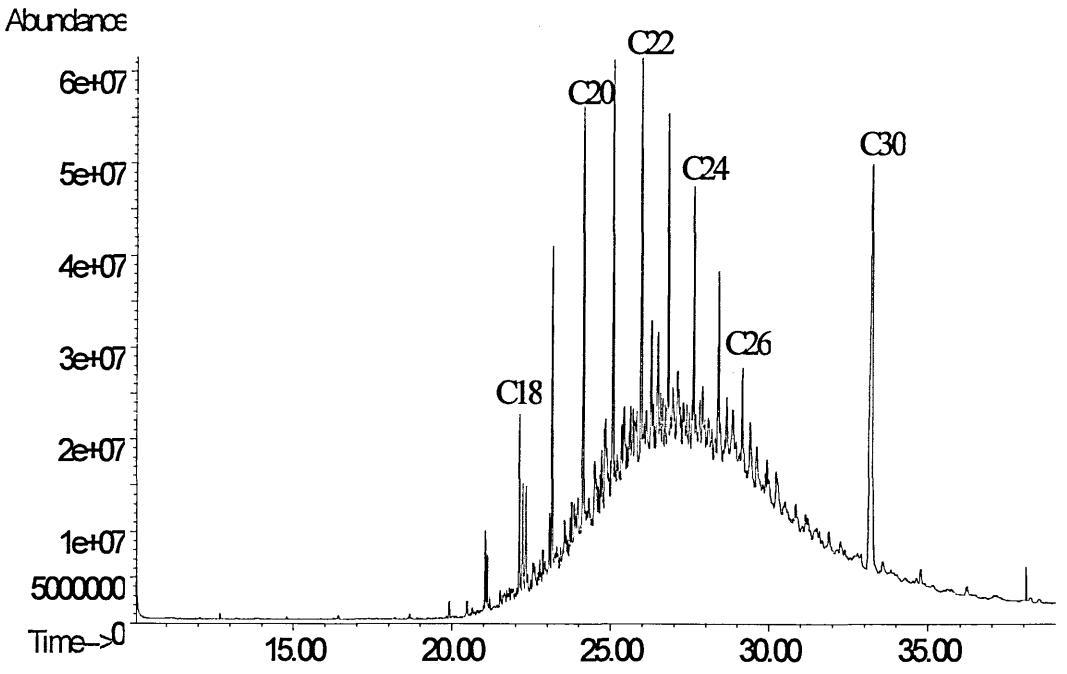


Figure 2.22: Particulate Associated Diesel Emissions Extract.

Quantification of C24 (Tetracosane).

Table 2.12 shows the amount of C24 and 1-nitropyrene measured in diesel particulates from a test engine run at three engine speeds. Each engine speed (stated in revolutions per minute - RPM) was calculated from three different rated powers (also known as load), these were 1/2, 3/4 and full rated power, samples were taken in duplicate. These concentrations were averaged to produce the value seen in the table.

Table 2.12: The Average Concentrations of C24 (Tetracosane) and 1-Nitropyrene Released in Diesel Emissions (2x3 rated power for each engine speed).

Engine speed (RPM) and rated power	Tetracosane (C24) (μg/g)	1--Nitropyrene (μg/g)
1300/averaged rated power	626.0 ±82.5	17.3
1600/averaged rated power	332.2 ±43.1	22.9
2500/averaged rated power	359.1 ±54.1	24.8
Mean	**439.1 ±59.9**	**21.7**

Due to the nature of the calculated mean (an average concentration of C24 and 1-Nitropyrene for diesel emissions from a range of engine conditions), the standard

deviation identified is purely an error parameter associated with instrumental variation (produced from the duplicate injections of the diesel samples). The values are used in the calculations associated with apportionment of diesel emissions in field environments discussed later in this thesis (See Section 3.6.2.1).

Table 2.13: Concentration of C24 (Tetracosane) and 1-Nitropyrene in a Sheffield City Centre Large Volume Sample (n=3).

	Mean (μg/g)	Std. Dev.
Tetracosane (C24)	470.7	57.4
1-Nitropyrene	13.7	1.6

The quantitative values for tetracosane and 1-nitropyrene determined in the large volume urban air sample (Table 2.13) provide several points of interest. Assuming 1-nitropyrene is released in only diesel emissions, and using the value of 20ng/g of 1-nitropyrene in diesel particulates determined earlier, 63% of the total particulate material ≤5μm is from diesel engines. This seems a perfectly reasonable value for particulate emissions released by diesel engines in the city centre of a large city in England, These results do confirm that 1-nitropyrene would be an interesting marker compound for diesel particulate emissions, and should be investigated further.

The value for tetracosane on the other hand, is quite high compared to the value obtained from the test diesel engine. This may be due to a number of factors including that the test engine was a LGV engine which is unlikely to produce an accurate representative average emission value for all of the various types of diesel engines that were commercially available. The emission rates of particulate and associated organic compounds from diesel engines can vary due to engine parameters including size, type, design, operating times and control systems. Other possible sources of C24 which may also add to the high value obtained for the atmospheric sample include HGV diesel engines (72), petrol engines (both catalysed/non catalysed) (72) and biological emissions (74). However, using these data a correction value for diesel particulate measurements based on the use of C24 can be calculated. In the control samples 21.7μg/g of 1-nitropyrene correlated to 439.1μg/g of C24. For the large volume air sample the

13.7μg/g of 1-nitropyrene should have given a value of 277.6μg/g of C24 for purely diesel particulates, however, 470.7μg/g were detected. Hence the correction factor required is 0.59.

Environmental Tobacco Smoke.

Four methods for the identification of ETS contribution to an atmosphere were investigated. These included:-

1. Total UV absorption.
2. Total fluorescence.
3. Solanesol determination.
4. Scopoletin determination.

Publications in the literature have used a ratio of concentration of ETS (obtained from one of the four methods stated above) associated with a gram of particulate ETS (22). The ratios for each method can be used to identify the quantity of sampled particulate material that has been released by ETS, identified by the four different methods. The original ratio is obtained from samples taken from an enclosed ETS environment where 100% of the particulate material is assumed to be from ETS. The particulate ratios for the four methods from our work (and published values in the literature), are given in Table 2.14:-

Table 2.14: ETS Quantitation Methods Ratio Values Determined in This Study (N=2) and Published in Literature.

Method	Ratio	Published ratio (22)	Published ratio (75)
Total UV absorption	5.3 ±0.45	8.2	8.0
Total fluorescence	28.7 ±3.3	45	33.6
Solanesol	53.7 ±4.8	43	
Scopoletin	203.0 ±10.1	-	

These compare favourably with the values obtained by our research on Rothmans cigarettes, and are equivalent to the ratio values obtained independently by Rothmans International (76). Variation between the two sets of ratios occurs because the samples were taken from slightly different standard smoking environments. The published data (22) sampled an ETS atmosphere from people smoking in a closed environment, while the samples taken at Rothmans International came from a closed environment in which a

smoking machine was used to produce ETS. It has been noted that variation in ratios are obtained when these different methods of standard ETS formation are used (76). The standard deviation values associated with instrumental variation are used throughout the apportionment data produced in Section 3.6.2.2.

Solanesol was found to contribute approximately 2% of the total ETS from the closed environments, while scopoletin contributed 0.32% of the total mass of ETS. This explains the order of magnitude difference seen in the ratio values. The determination of scopoletin was not a problem due to the inherent increased sensitivity obtained from using the fluorescence detection system.

Polycyclic Aromatic Hydrocarbons (PAH) analysis.

Both particulate associated diesel emissions and ETS were analysed by GC/MS-SIM for their PAH content. Table 2.15 shows the concentration of the PAH compounds.

Table 2.15: Quantitative Analysis of 16 PAH Compounds in both Particulate Diesel and ETS Emissions, from controlled sampling apparatus (n=2 for ETS analysis, while n=3 for diesel emissions).

Basildon sample	ETS particulates Conc ng/m^3	ETS particulates Conc µg/g	ETS particulates Std. Dev.	Diesel particulates Conc µg/g	Diesel particulates Std. Dev.	SRM 1650 (2) Conc µg/g
Naphthalene	372.4	92.9	17.8	0.0	0.0	**
Acenaphthylene	8.3	2.1	0.9	0.0	0.0	**
Acenaphthene	43.4	10.8	2.9	0.0	0.0	**
Fluorene	84.0	21.0	5.6	0.0	0.0	**
Phenanthrene	175.8	43.9	8.5	23.4	16.6	71
Anthracene	10.5	2.6	0.6	0.6	1.0	**
Fluoranthene	58.7	14.7	3.3	25.2	12.1	51±4
Pyrene	87.3	21.8	4.1	53.2	27.9	48±4
B.(a)anthracene	53.1	13.2	2.0	16.0	4.9	6.5±1.1
Chrysene	138.0	34.4	5.9	41.4	18.8	22
B.(b)fluoranthene	0.0	0.0	0.0	1.2	2.1	**
B.(k)fluoranthene	0.0	0.0	0.0	17.0	13.1	2.1
B(a)Pyrene	0.0	0.0	0.0	0.0	0.0	1.2±0.3
B(g,h,i)Perylene	0.0	0.0	0.0	0.0	0.0	2.4±0.6
Dib(a,h)Anthracene	0.0	0.0	0.0	0.0	0.0	**
Indeno(1,2,3,c-d)pyrene	0.0	0.0	0.0	0.0	0.0	2.3

The PAH concentration of particulate associated compounds is displayed in both ng/m^3 and μg/g concentrations for the ETS samples. The diesel samples are displayed only as μg/g as the flow rates through the dilution tunnel were not accurately noted during sampling. This is slightly problematic as PAH concentrations in diesel emissions are mainly published as ng/m^3 (61).

Recently it has been reported that lower molecular weight PAH compounds are found mainly in the vapour phase, while higher molecular mass PAH are adsorbed to particulate material (77). This partitioning has been shown to be dependant upon ambient temperature (which directly relates to the individual PAH vapour pressure) and total suspended particulate (available surface area) concentrations (78).

Diesel

Historically, major sources of PAH in both the vapour and particulate phases were stationary, with emissions being produced from heating of individual households and power generation. However, more recently, PAH from mobile sources (cars and lorries) have increased (79), especially in the urban and sub urban areas. It has been published that 60-95% of most particulate associated PAH in Paris (80) and 88% of ambient benzo(a)pyrene in Britain are released from vehicles (81).

PAH can be produced in three ways from vehicular emissions, these include:-

1. Synthesis from simpler molecules in the fuel (particularly aromatics) such as ethyl benzene and xylenes as these have been identified as better pre-cursors than benzene (82,83).
2. Emissions of PAH already present in the fuel (77,84).
3. Pyrolysis of lubrication oil (77,84) or diesel fuel (85).

Emissions of Polycyclic Aromatic Compounds (PAC = PAH in addition to derivatives and nitrogen and sulphur heterocyclic compounds) from diesel engines have been shown to vary with both speed and load. Low speeds and low loads were the criteria under which the largest quantity of three and four ringed PAC were emitted (67). This suggests

that the main source of PAC is directly from the fuel, as has been previously suggested (70,84,86), and that at the higher engine temperatures (observed during higher loads) the combustion efficiencies of the PAC increases. The optimum speed for the highest combustion efficiency of PAC occurs at medium speeds, when the swirl characteristics, combustion timing and temperature are all at their optimum. Low speeds are less efficient, due to low swirl and low chamber temperatures whilst high speeds lead to over swirl and reduced combustion time in the chamber (67). This produces larger quantities of PAC in the engine emissions.

Comparing the concentration of particulate associated PAH determined in diesel particulates, with values reported in literature (Table 2.15 (65)), it can be seen that there are significant quantities of phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(k)fluoranthene associated with the diesel particulates. Phenanthrene and pyrene are both found at significant concentrations in average diesel fuel. The accuracy of the measurements in the two sets of data is a little questionable in terms of direct comparison. However, considering that the source (i.e. engine type and size), engine conditions (speed and load), sampling method, sample preparation, and analysis were different for each data set, the variations are perhaps not surprising.

Many of these PAH have previously been identified in diesel exhaust particulates including pyrene, fluoranthene, and phenanthrene (62,70,87). Several publications also identified other PAH including chrysene, anthracene, benzo(a)anthracene, benzo(b) and benzo(k)fluoranthene (60,88). The data given in these publications are unfortunately quoted in $\mu g/m^3$ or as percentages, while our quantitation is in $\mu g/g$ of particulate material. Direct comparison of the data is therefore not possible. However, the compounds identified are comparable to those observed in similar emissions described in the literature which is encouraging since the profiles of PAH compounds in diesel are known to vary considerably depending upon the source of the crude oil (70).

Environmental Tobacco Smoke.

No PAH compounds larger than the four ringed chrysene were quantifiable in the ETS samples. However, this does not mean that the compounds were not released, as several

have been identified by the use of HPLC with a fluorescence detector (89). They are simply below the limit of detection of the GC/MS-SIM detection technique that was employed.

Few studies were found in the literature which compared the concentration of PAH in the vapour phase to that associated with the particulates emitted in ETS. However, a comparison with the studies available, did indicate several interesting trends.

Many of the volatile PAH identified in the vapour phase were also identified adsorbed to particulate material. As expected, the concentrations of naphthalene, acenaphthylene, acenaphthene, fluorene and phenanthrene were all higher in the vapour phase than associated with particulate material. The more labile particulate associated PAH identified in Table 2.15 (phenanthrene to chrysene) have also been identified in ETS (90,91), after pre concentration and fractionation. The concentrations of these PAH in the publication are however measured in ng/cigarette, making it difficult to directly compare this with the ng/m^3 calculations used in our study. However, a qualitative comparison shows that all the PAH identified by our GC/MS-SIM method are also present in ETS from the independent study.

Salomaa et al (63) were the only group to measure PAH in ng/m^3. The quantities they detected were a lot lower, but they observed the same compounds as those reported here. The variation in concentration could be due to differences in the sampling, preparation or analysis of the samples, as their sample were taken from more of a "field" site (i.e. a smokers room) while our samples are totally of ETS taken from a specifically set method for ETS atmospheric determination.

2.2.6.4 Elemental Analysis of particulate material.

Diesel.

The data shown in Table 2.16 indicates elevated levels of several elements in diesel exhaust particulate emissions. These include large quantities (mg/g) of sodium and

potassium in addition to significant quantities (μg/g) of silicon, manganese, iron, nickel, copper, bromide, molybdenum, silver, tin, iodide and lead.

Few studies could be found in literature, that identified the elemental composition of diesel particulate exhaust emissions. Various studies have been conducted on elements that are found in larger concentrations around areas of anthropogenic use, for example roads. Elevated levels of Mn, Fe, Ni, Cu, Br, Mo, Cd, Cr, Zn and Pb are all associated with roads and road verges (58,92). A number of these element are released from abrasion of other parts of road vehicles such as Cd, from plated components and tyre rubber attrition, Zn from tyre rubber and Cu from brake linings (58). Therefore, Cu could not be used as a tracer element for diesel emissions due to abrasion sources causing an overestimation of diesel contribution.

Lead emissions are often associated with older leaded petrol powered vehicles as tetra ethyl lead was used as an anti-knock agent in leaded petrol. The introduction of unleaded petrol and the reduction in the lead content in leaded petrol from 0.4g/l to 0.15g/l has produced a decline in atmospheric lead since 1986 (4,93,94). Our results show that lead is also released in significant quantities in diesel emissions.

Mo, Ni, Mn and Ag have all been identified as being released in anthropogenic emissions including coal (95), while Br has been identified in petrol emissions (96). These elements are therefore not totally specific to diesel emissions. Marine or soil suspended particulates contain amongst other elements, Na, Cl, Si, K and Fe, all of which are found in diesel emissions and would hence not be specific.

From the list of elements identified in diesel emissions, the only ones left are Sn and I. Sn is a component of various types of bearing and roller type engine material (97). The elemental contribution is therefore unlikely to be solely from the fuel during combustion but from engine attrition associated with vehicles in general and not specifically diesel engines. Iodine (I) is therefore the only element found at a relatively high concentration in diesel emissions that could be used as a possible diesel marker. However, there is no clarification of this from the literature, therefore it was decided not to use it as a marker for diesel fuel.

Table 2.16: Average Metal Concentrations (μg/g) of Elements Found in Diesel Engine Particulate Exhaust Emissions.

	Lithium	Beryllium	Boron	Sodium	Magnesium	Aluminium	Silicon	Potassium	Calcium
Diesel emissions	-	-	-	128534.7	-	-	36.418	25599.829	-

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Diesel emissions	-	-	0.257	-	2.035	449.871	0.268	2.785	58.912	-

	Gallium	Germanium	Arsenic	Selenium	Bromine	Rubidium	Strontium	Yttrium	Zirconium	Niobium
Diesel emissions	-	0.004	-	-	12.961	-	-	-	-	0.024

	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony
Diesel emissions	1.157	0.004	0.0578	0.0021	-	2.464	-	0.027	3.074	-

	Tellurium	Iodine	Cesium	Barium	Lanthanum	Cerium	Praseodymium	Neodynium	Samarium	Europium
Diesel emissions	-	5.677	-	-	-	-	-	-	0.039	-

	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	Hafnium	Tantalum	Tungsten
Diesel emissions	-	-	-	0.001	-	0.001	-	0.001	-	-	0.071

	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Thorium	Uranium
Diesel emissions	0.028	-	-	-	-	0.614	-	3.363	0.0503	-	-

Environmental Tobacco Smoke (ETS).

The results for the elemental analysis of ETS can be seen in Table 2.17 (μg/g) and Table 2.18. The following elements were found to be released at elevated concentrations (μg/g) in ETS, boron, sodium and barium. Elements found at lower (ng/g) concentrations in ETS included titanium, gallium, arsenic, rubidium, niobium, silver, neodymium, samarium, europium, dysprosium, iridium, platinum, mercury, thallium and bismuth.

However, the important result obtained from this analysis was the absence of cadmium in the ETS samples. Cadmium has been proposed as a possible elemental tracer for ETS by Wu et al (24). Our analysis of small amounts of ETS particulates from a standard smoking environment indicated that the method we used was unable to measure cadmium in ETS. Hence cadmium could not be used in this study as an ETS particulate tracer.

Of the elements identified in this study, only arsenic, and sodium (51,98) have been identified in ETS previously. Sodium is fairly ubiquitous throughout the atmosphere, leaving arsenic as the only possible ETS elemental marker detected. It has also been found in ETS by others (99) in concentrations of up to $5ng/m^3$. Our ETS samples produced a concentration of $9ng/m^3$. This is higher than the values in the other studies but this would be expected as the amount of ETS in the control room was very high.

Summary.

The elemental analysis of particulate emissions from diesel and ETS did identify trace elemental markers. Iodine was identified specifically in diesel particulates and arsenic was identified specifically in particulate ETS. These conclusions are tentative as iodine has not previously been described in diesel emissions and only a few ETS studies have detected arsenic.

Table 2.17: Average Metal Concentrations (μg/g) of Elements Found in Fresh Filter sampled Environmental Tobacco Smoke.

		Lithium	Beryllium	Boron	Sodium	Magnesium	Aluminium	Silicon	Potassium	Calcium
ETS		-	-	6000.15	7050.176	-	-	-	-	-
	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
ETS	-	120.003	-	-	-	-	-	-	-	-
	Gallium	Germanium	Arsenic	Selenium	Bromine	Rubidium	Strontium	Yttrium	Zirconium	Niobium
ETS	195.005	-	2.700	-	-	19.500	-	-	-	16.500
	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony
ETS	-	-	-	-	-	360.009	-	-	-	-
	Tellurium	Iodine	Cesium	Barium	Lanthanum	Cerium	Praseodymium	Neodymium	Samarium	Europium
ETS	-	-	-	1800.045	-	-	-	0.900	5.400	1.500
	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	Hafnium	Tantalum	Tungsten
ETS	-	-	2.850	-	-	-	-	-	-	-	-
	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Thorium	Uranium
ETS	-	-	3.450	2.550	-	3.450	6.450	-	10.350	-	-

Table 2.18: Average Metal Concentrations (ng/m^3) of Elements Found in Fresh Filter sampled Environmental Tobacco Smoke.

		Lithium	Beryllium	Boron	Sodium	Magnesium	Aluminium	Silicon	Potassium	Calcium
ETS		-	-	20000	23500	-	-	-	-	-
	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
ETS	-	400	-	-	-	-	-	-	-	-
	Gallium	Germanium	Arsenic	Selenium	Bromine	Rubidium	Strontium	Yttrium	Zirconium	Niobium
ETS	650	-	9	-	-	65	-	-	-	55
	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony
ETS	-	-	-	-	-	1200	-	-	-	-
	Tellurium	Iodine	Cesium	Barium	Lanthanum	Cerium	Praseodymium	Neodymium	Samarium	Europium
ETS	-	-	-	6000	-	-	-	3	18	5
	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	Hafnium	Tantalum	Tungsten
ETS	-	-	9.5	-	-	-	-	-	-	-	-
	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Thorium	Uranium
ETS	-	-	11.5	8.5	-	11.5	21.5	-	34.5	-	-

2.3 Conclusion.

The object of the work described in this chapter was to identify possible vapour and particulate associated markers for diesel emissions and ETS. These compounds could then be used to give a percentage apportionment of pollutants to be for "real" samples.

The following marker compounds were identified :-

Diesel.

No volatile tracer molecule was identified for diesel emissions.

Particulate associated apportionment will be achieved using C24 (tetracosane) as the marker compound in the atmospheric sample and the over-estimation will be corrected by using the ratio of C24 to 1-nitropyrene calculated from the analysis of large volume air samples.

ETS.

Pyrrole was identified as a possible marker compound for ETS and will be used to apportion percentage contributions of volatile ETS compounds to each environment sampled.

For particulate apportionment, two tracer methods have been used, total UV and total fluorescence. Two specific ETS tracer molecules have been investigated, these are Solanesol and Scopoletin. The over-estimation of the total UV and total fluorescence methods can thus be investigated along with the identification of the most accurate particulate ETS tracer compound. Arsenic will be investigated as a possible ETS elemental marker.

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3. ATMOSPHERIC SAMPLING.

3.1 Introduction.

After the identification of the marker compounds/elements for diesel and ETS, a sampling regime of atmospheric samples was undertaken to check the validity of the marker compounds. Additional analytical methods were incorporated into this field study (i.e. nicotine determination, total UV and fluorescence in addition to PAH and elemental analysis). Sites which exhibited elevated concentrations of vehicular emissions and/or ETS were needed.

3.2 Sites.

After examining previous studies, it was decided that the following sites would be investigated with a sampling system in both their indoor and outdoor environments:-

1. Four smokers homes.
2. Four non-smokers houses.
3. Four smokers offices.
4. Four non-smokers offices.

Other sites that were investigated included :-

5. Eight roadside samples within the city of Sheffield.
6. Two samples in the countryside outside the city of Sheffield.

All the houses were situated in residential areas around the city of Sheffield. Samples were taken from houses during either a Saturday or Sunday when the occupants were present in the house and emissions due to the presence of people were at their highest. All the office samples were taken from one building situated in the city centre of Sheffield. The samples were taken during the week so the occupants would once again be present in the office for the maximum amount of time. Roadside samples were either

taken from the city centre (adjacent to a large bus and train station), or along major roads that radiated from the city centre. Countryside samples were obtained from areas of the Peak district, away from roads, to try and obtain control samples.

These sample sites were deemed to give the maximum amount of information about the two specific sources under investigation, i.e. diesel emissions and ETS. By taking both indoor and outdoor samples from the various houses/offices, diffusion of sources from one context to the other could also be investigated.

3.3 Sampling.

Indoor sampling devices were housed in a converted briefcase to reduce the noise of the pumps and prevent tampering once the system was installed. The outside sampling apparatus was housed in a wooden box designed to look like a large bird box which could be attached to the side of a building by a number of methods. The box was lockable to prevent tampering and vandalism during the twelve hour sampling period.

Samples taken from each indoor and outdoor site included:-

1. Two filter samples for the collection of particulate material of $\leq 5\mu m$ using the aluminium size specific head described in Section 2.2.2.2. The particulate material was collected on PTFE coated filter papers of diameter 37mm (Supelco, Dorset, England). Situated directly behind each filter head was an XAD-4 resin tube (SKC Ltd, Dorset England), attached to the filter head by brass 1/4 inch tube fitting with rubber o-ring. Each resin tube was attached to a pump (SKC Ltd, Dorset England) by a length of tubing. The two pumps sampled at a flow rate of 1l/min.

2. Volatile samples were taken using a two stage thermal desorption tube system, with the first tube containing 0.16g of Tenax (mesh 60/80 (Supelco, Dorset, England). and the second tube containing 0.18g of carboxen 569 (mesh 20/45 (Supelco, Dorset, England). The two tubes were attached using a brass 1/4 inch tube fitting with rubber o-ring. A piece of rubber tubing attached the metal sampling tubes to the low flow pump. The summation of the concentrations from the two tubes produced the total

concentration of the volatile pollutants. The pumps used were low flow (SKC Ltd, Dorset England) pumps, sampling at a flow rate of 50ml/min. Two volatile pump systems were used from every indoor and outdoor site, so a second set of samples were available if the inherent "one shot" thermal desorption system failed at any time.

All pumps were converted to run on batteries as the pumps needed to continue sampling for a long period of time on external battery supplies since various sites had no accessible electricity sockets. All pumps were converted and loaned to us by Rothmans International (Basildon, Essex, England).

Immediately after sampling all tubes were separated, labelled and capped, while all filter samples were weighed and stored in amber screw topped vials. All samples were stored in a fridge (<5°C) prior to pre-treatment and analysis.

3.4 Sample Extraction and Analysis.

The following pre-treatment procedures were carried out.

1. All Filter samples were weighed to identify the mass of particulate material ≤5μm in diameter, that was sampled on each filter paper.

2a. All filter 1 samples from both indoor and outdoor contexts were placed in 7ml amber vials and extracted with 4mls of dichloromethane (containing 0.01% triethylamine to ensure nicotine extraction (1)) for 30 minutes in an ultrasonic bath. The sample was then reduced to 100μl after addition of quinoline (Aldrich, Poole, Dorset, UK) and D10 anthracene (Supelco, Dorset England) as internal standards. Nicotine, tetracosane (C24) and PAH quantitation was carried out using GC/MS as described in section 2.2.5.2.

2b. All filter 2 samples were cut in half using a ceramic GC capillary column cutter. This was done to reduce elemental contamination. Half the filter was placed in a 7ml screw topped amber vial and extracted into 4mls of methanol (warmed to 40°C). The resulting extract was analysed by HPLC for total UV, total fluorescence, Solanesol, and

Scopoletin (Section 2.2.5.2). The second half of filter 2 was wet ashed in nitric acid. Analysis for elemental/inorganic content was completed using ICP/MS (Section 2.2.5.2).

3. Of the two XAD-4 resin tubes taken from each site, one was sent to Rothmans International for nicotine quantitation, while the resin from the other was extracted with 4mls of dichloromethane (containing 0.01% of triethylamine (1), after it had been removed from the tube and placed into an amber vial. The glass tube which had contained the resin during sampling was also washed through with dichloromethane (containing 0.01% triethylamine (1)) and the washings were added to the resin, to ensure all nicotine was extracted. Nicotine and PAH quantitation was completed using GC/MS (see Section 2.2.5.2).

The thermal desorption tubes were analysed using ATD/GC/MS as described in Section 2.2.5.1. without pre-treatment.

3.5 Results.

A small questionnaire was devised to identify if there was likely to be any confounding factors that may have effected the results obtained from the house sites under investigation. The questions and answers are listed in Table 3.1.

The questionnaire identified that all the dwellings used gas for heating and that a range of gas and electric stoves were used for cooking. An additional fact obtained from the questionnaire was that one non smoking household also had a cat as a pet.

Table 3.1: Results of the Questionnaires Given to the Members of the Households Sampled During this Study.

	Smokers houses					Non-Smokers houses			
	House 1	House 2	House 3	House 4	House 5	House 1	House 2	House 3	House 4
How many people live in the house	1	2	2	2	4	4	2	2	2
How many occupants smoke?	1	2	1	2	1	0	0	0	0
How is the house heated?	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Is your cooker gas or electric?	Gas/electric	Electric	Gas	Gas	Electric	Gas	Gas	Electric	Gas
Have you any pets?	0	0	0	0	0	0	0	0	1 Cat
Approx. how many cigarettes smoked during sampling?	10	13	11	15	11	0	0	0	0
Approx. how many smoked a day?	15-20	15-20 (each)	20	25-30	10-15	-	-	-	-

3.5.1 Particulate gravimetric quantitation.

The mass of particulate material obtained in all the contexts can be seen in Table 3.2. The colour of the filter was also noted for each sample. Filter samples taken from houses/offices in which smoking had occurred often exhibited an orange/brown colouration (Figure 3.1), while samples taken from non smoking houses/offices or outdoor samples were grey in colour (Figure 3.2). There is no colour identified on the blank filters (Figure 3.3) which were simply left in the filter head sampler with no flow. This was done to identify any contamination from the filter head itself.

The weather was also noted when the samples were taken, as removal of particulate material was thought to occur (wet deposition see Section 1.2.1.2) during wet days reducing the quantity of particulates identified on the outdoor filter. The average mass of filters 1 and 2 from each sample context was calculated and the highest, lowest and average values are shown graphically in Figure 3.4. From this we can clearly see differences in the quantities obtained from various contexts.

Table 3.2: Quantitative Gravimetric Results of Particulate Material (≤5μm) in both Indoor and Outdoor Samples from the Sites Under Examination. Weather Conditions and the Colour of the Filter Paper was also Noted.

Location	Filter colour.	Weather	Indoor		Filter colour.	Outdoor	
			PM mass (<5um)	PM mass (<5um)		PM mass (<5um)	PM mass (<5um)
Non smokers houses	Indoor		Filter 1 (ug)	Filter 2 (ug)	Outdoor	Filter 1 (ug)	Filter 2 (ug)
House 1	Faint grey	No rain	41.33	33.33	Faint grey	36.67	26.67
House 2	Faint orange	No rain	90.67	88.00	Faint grey	18.67	22.67
House 3	No discolouration	No rain	12.33	19.00	Faint discolour	10.67	16.00
House 4	Faint grey	No rain	18.33	28.33	Faint grey	21.00	28.00
Average			**40.67**	**42.17**		**21.75**	**23.33**
Smokers houses							
House 1	Faint orange/brown	Rain	81.67	80.67	Grey	45.67	47.33
House 2	Faint orange/brown	No rain	70.33	66.67	Faint grey	16.33	34.00
House 3	Orange/brown	No rain	78.67	100.33	Faint grey	61.33	51.00
House 4	Dark orange/brown	Rain	150.00	155.33	Faint grey	28.67	39.33
House 5	Faint orange/brown	No rain	27.33	34.00	Faint discolour	17.67	20.33
Average			**81.60**	**87.40**		**33.93**	**38.40**
Non smokers offices							
Office 1	Faint grey	No rain	14.00	17.33	Faint grey	26.00	26.33
Office 2	Grey	No rain	42.67	38.67	Faint grey	41.67	57.67
Office 3	Faint grey	Rain	20.67	18.67	Faint grey	21.33	23.67
Office 4	Grey	Rain	17.33	15.33	Faint grey	18.33	17.67
Average			**23.67**	**22.50**		**26.83**	**31.33**

Smokers offices							
Office 1	Orange/brown	No rain	64.33	70.33	Grey	22.33	17.67
Office 2	Faint orange/brown	No rain	29.33	28.00	Grey	14.00	34.00
Office 3	Faint orange/brown	Rain	31.33	30.67	Faint grey	8.33	14.00
Office 4	Orange/brown	Rain	53.67	56.67	Grey	7.33	13.00
Average			**44.67**	**46.42**		**13.00**	**19.67**
Roadside samples							
Roadside sample 1	N/A	Rain	N/A	N/A	Faint grey	8.33	5.67
Roadside sample 2	N/A	No rain	N/A	N/A	Grey	15.00	20.67
Roadside sample 3	N/A	Rain	N/A	N/A	Grey	20.33	25.00
Roadside sample 4	N/A	No rain	N/A	N/A	Grey	31.33	41.00
Roadside sample 5	N/A	No rain	N/A	N/A	Faint grey	16.33	17.67
Roadside sample 6	N/A	Rain	N/A	N/A	Faint grey	17.33	16.00
Roadside sample 7	N/A	Rain	N/A	N/A	Grey	37.00	36.00
Roadside sample 8	N/A	No rain	N/A	N/A	Faint grey	28.00	32.33
Average			**N/A**	**N/A**		**21.71**	**24.29**
Countryside samples							
Countryside sample 1	N/A	No rain	N/A	N/A	No discolouration	35.000	32.67
Countryside sample 2	N/A	Rain	N/A	N/A	Faint light grey	39.667	45.67
Average			**N/A**	**N/A**		**37.333**	**39.17**

Key. N/A not applicable as there is no indoor sample associated with roadside or countryside samples.

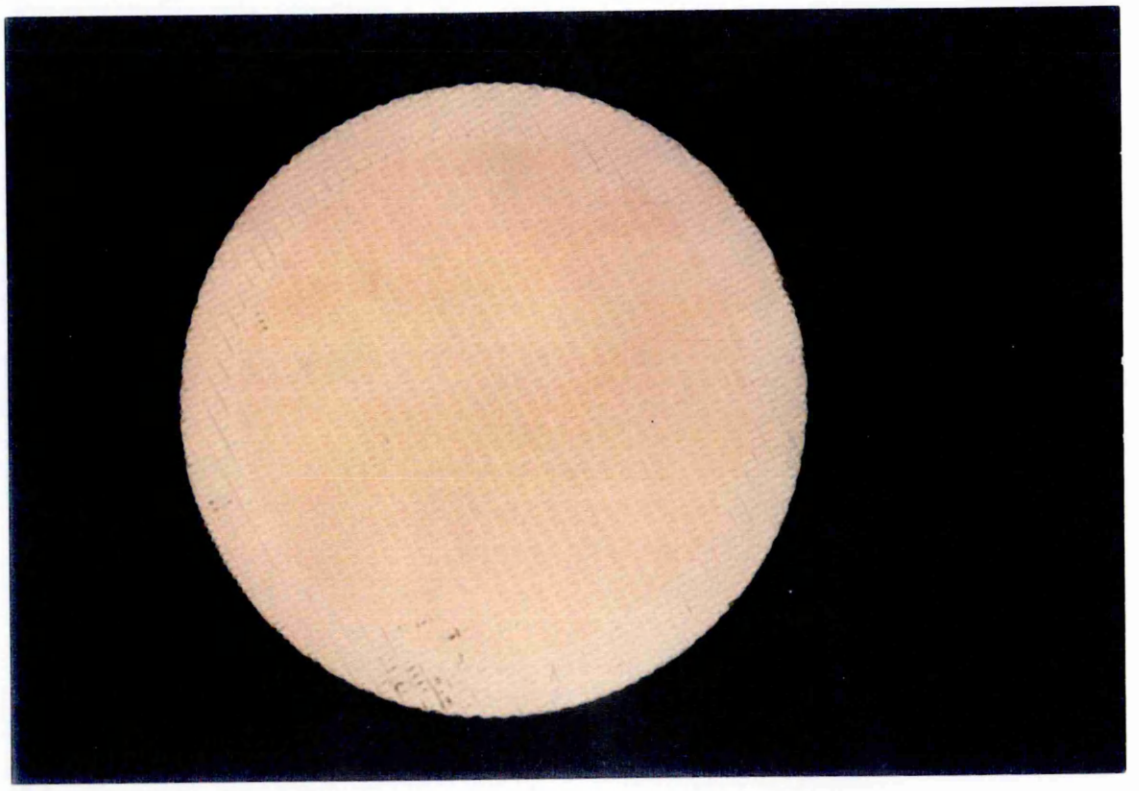

Figure 3.1: Filter Sample Taken From a Smokers Environment, Displaying an Orange/Brown Colouration.

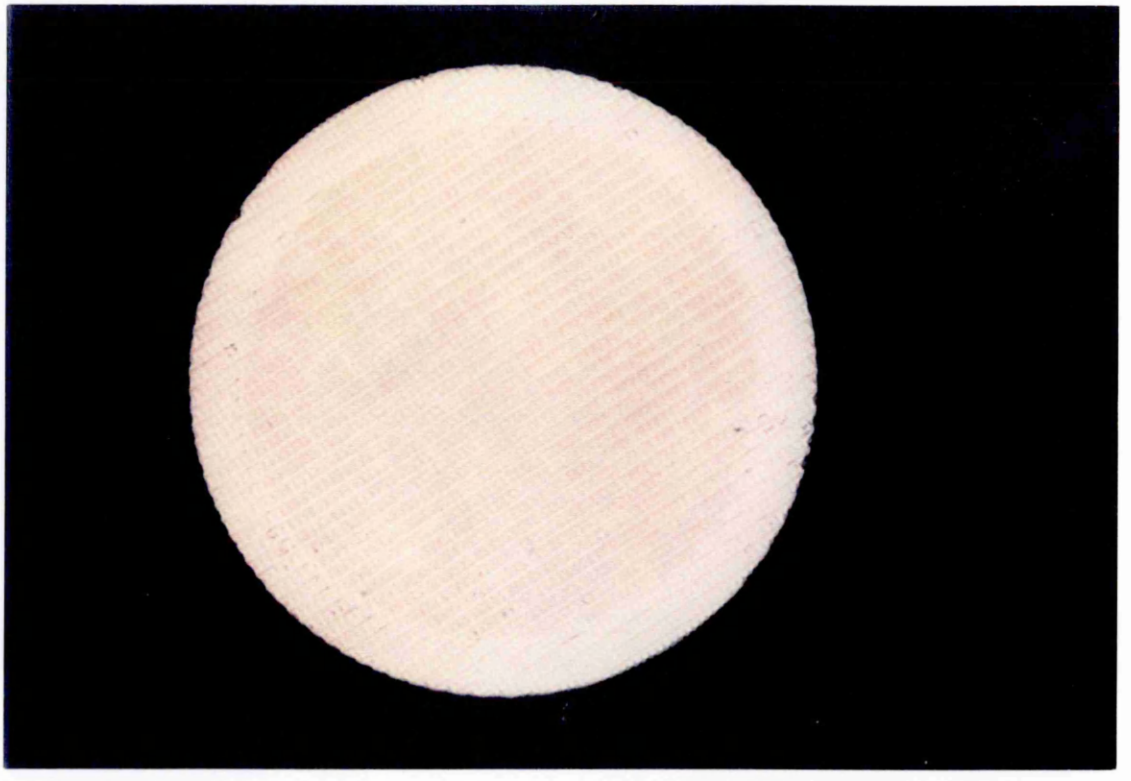

Figure 3.2: Filter Sample Taken From Other Contexts (i.e. Not a Smokers Environment), Displaying a Grey Discolouration.

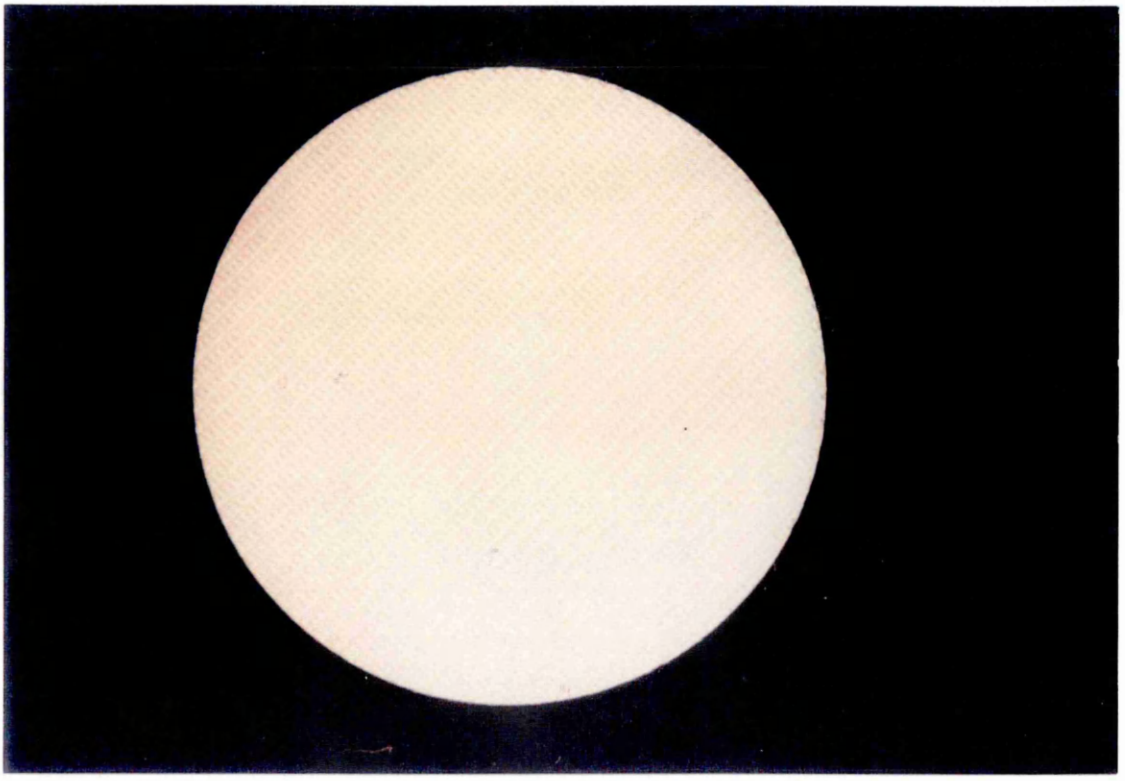

Figure 3.3: Blank Filter Displaying No Discolouration.

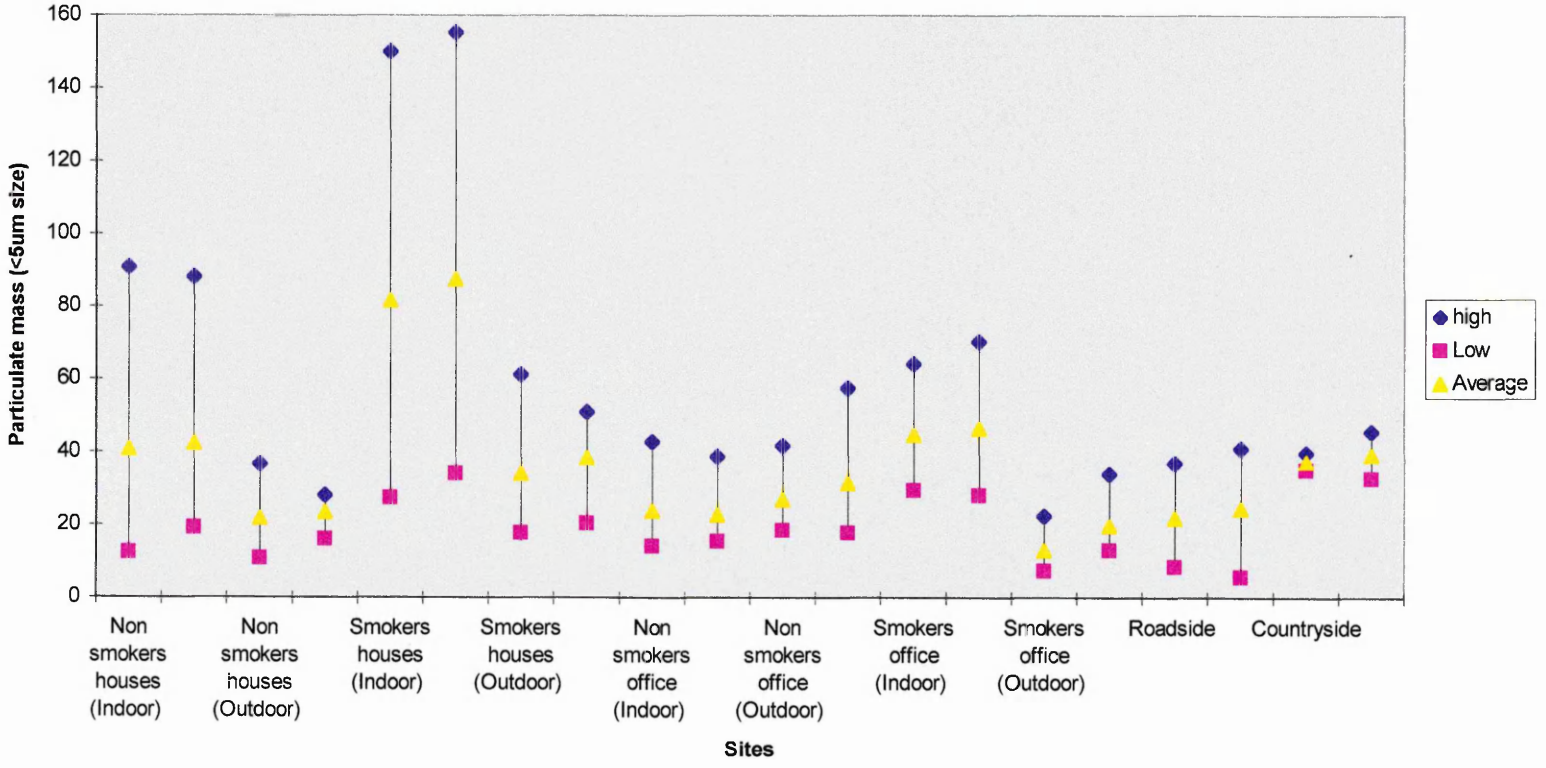

Figure 3.4: Chart to show the Highest, Lowest and Average Atmospheric Particulate Material Mass (<5um size) from All Duplicate Samples from the Sites Investigated.

It can be seen from Figure 3.4 that the smokers houses contained the highest average quantity of particulate material (≤5μm) with an average value of above 80μg (range 27.33-155.33μg). Smokers office values were also fairly high with an average value of around 45μg (28-70.33μg), identifying ETS as a source of particulate material <5μm. However, non smokers house average values were not far from this with an average of around 41μg (12.33-90.67μg). This value is perhaps artificially high due to one of the non smokers houses (house 2) burning incense during the sampling period causing an increase in particulate material and producing a faint orange colour on the filter paper.

The mean values from this study (84.5μg/m^3 and 41.4μg/m^3 for smokers and non-smokers houses respectively), are slightly higher than RSP levels determined in other publications. For smokers homes, levels of 88.81μg/m^3 (2), 74μg/m^3 (3), 44.6μg/m^3 (4), and 44.1ug/m^3 (5) have been reported, while non smokers homes contained mean levels of 27.62μg/m^3 (2), 28μg/m^3 (3), 18.1μg/m^3 (4), and 15.2μg/m^3 (5) for RSP. Our slightly higher values are expected since those published in literature were for personnel samplers while our study used static sampling. This can cause increases in concentration due to constant exposure to smokers material in smokers environments while no exposure to low levels occurs owing to the lack of movement of the sampling system.

All the other sites including all outdoor contexts have a similar average particulate mass value from between 16μg for outside the smokers offices to 38μg for the countryside samples. The presence of a cat as a pet in one of the non smokers houses had little effect on the particulate quantity. Particulate material (≤5μm) can therefore be seen to be fairly ubiquitous throughout the environment, with elevated levels being most prominent in indoor environments in which smoking had occurred. However, other sources can also produce elevated quantities of particulate material as seen in non-smokers houses and also the countryside samples (possibly pollen).

3.5.2 Volatiles.

A number of the "common" volatile organic compounds detected by GC/ATD/MS were quantified. These included benzene, toluene, ortho, meta and para-xylene, ethyl benzene and para-dichlorbenzene. In addition 3-ethenylpyridine and pyrrole were also quantified for use as specific volatile marker compounds for ETS. Benzene was the only compound besides the two ETS marker compounds that has been shown to have a significant correlation with ETS in the literature (3,6).

No suitable volatile marker compound for diesel emissions could be identified for quantitative determinations. However, many of the previously stated volatile compounds are released in anthropogenic emissions including diesel. The removal of organo-lead compounds (used as anti-knock agents) due to their toxicity, lead to an increase in the aromatic content in unleaded fuel. This has produced fuels in some developing countries with an aromatic content of 40-50% (7).

Emissions of benzene, toluene and xylene isomers in unleaded petrol emissions have increased accordingly (7). It was calculated in 1994 that approximately 78% of total outdoor benzene emissions were from petrol engine exhausts (8). With the introduction of catalytic converters as standard engine additions, and anti-emission devices associated with the petrol tank during filling, this quantity, and the overall quantity of benzene should begin to fall. However, this will take time so benzene will still be present in the atmosphere from these sources for the foreseeable future.

Figures 3.5-3.10 show the levels of a range of VOC determined at each of the sampling sites. The mean concentration of the volatiles in each context is given in Table 3.3. The raw data for individual concentrations in each sample, used for the figures of the volatile compounds are given in Appendix A Tables A1-A6.

Table 3.3: Average Concentration of the Volatile Organic Compounds Investigated in the Various Field Sample Contexts.

Indoors	Number of	Particulates	Benzene	Toluene	O-xylene	P+M-xylene	Ethyl benzene	p-dichlorobenzene
Location.	samples.	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
Non smokers house	4	41.4	4.9	59.8	2.3	1.3	5.0	1.0
Smokers house	5	84.5	6.5	62.8	3.3	3.3	2.1	1.9
Non smokers office	4	23.1	5.3	145.9	2.1	2.6	2.8	4
Smokers office	4	45.5	8.3	25.7	2.0	2.4	2.2	4.4
Roadside	8	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Countryside	2	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Outdoors	Number of	Particulates	Benzene	Toluene	O-xylene	P+M-xylene	Ethyl benzene	p-dichlorobenzene
Location.	samples.	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$
Non smokers house	4	22.5	3.2	18.7	1.2	0.5	1.7	0.1
Smokers house	5	36.2	4.1	26.4	1.3	1.7	1.2	0
Non smokers office	4	29.1	4.7	174.0	3.2	3.4	2.2	1.8
Smokers office	4	16.3	3.5	29.0	2.2	2.0	1.8	0.5
Roadside	8	23	4.9	62.2	3.3	2.6	3.0	0
Countryside	2	38.3	2.7	33.1	0.7	1.0	2.2	0

Key. N/A. Not Applicable as roadside and countryside samples only taken outside.

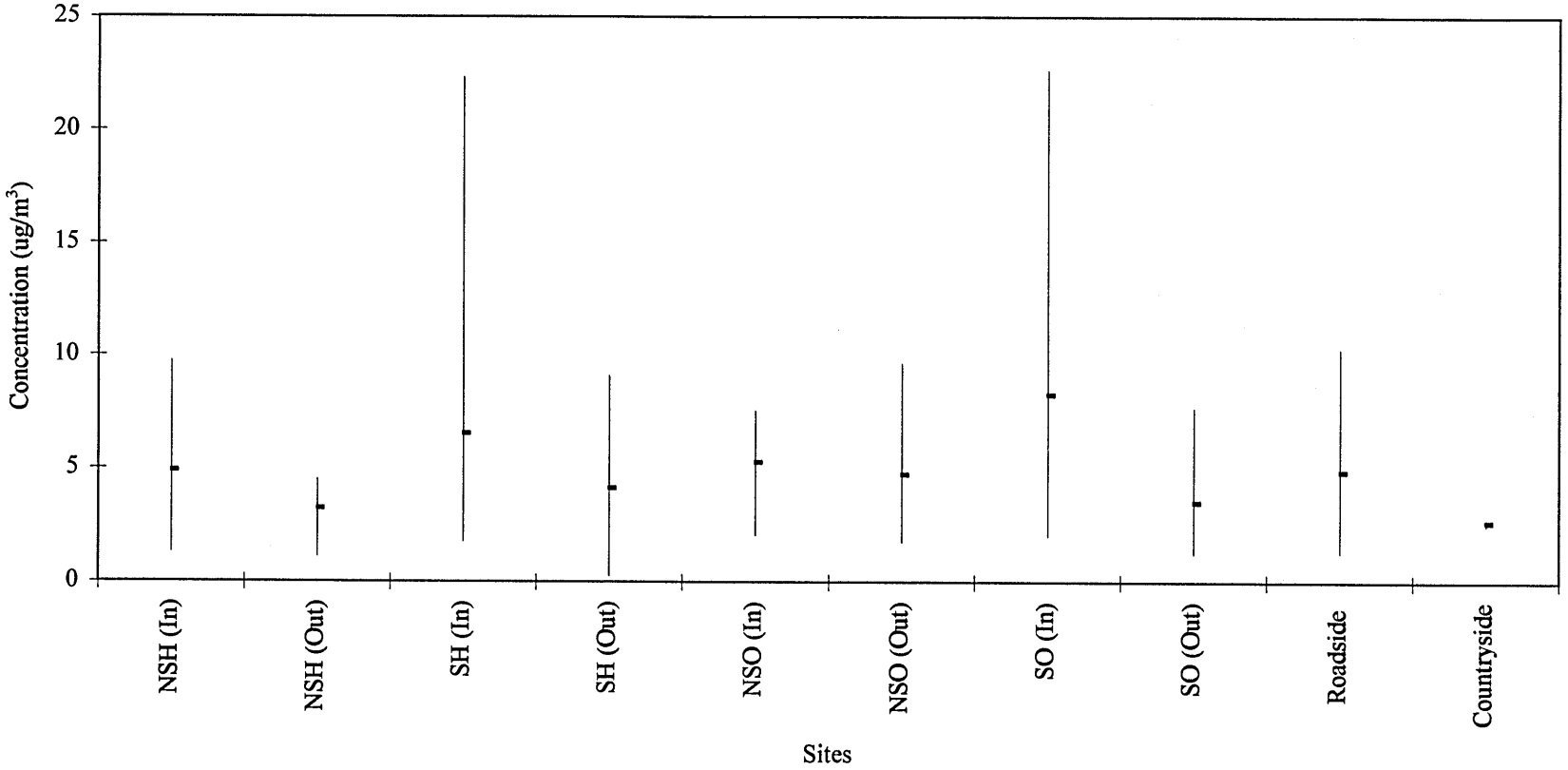

Figure 3.5: Chart Identifying the Highest, Lowest and Average Concentration of Benzene in All the Atmospheric Contexts.

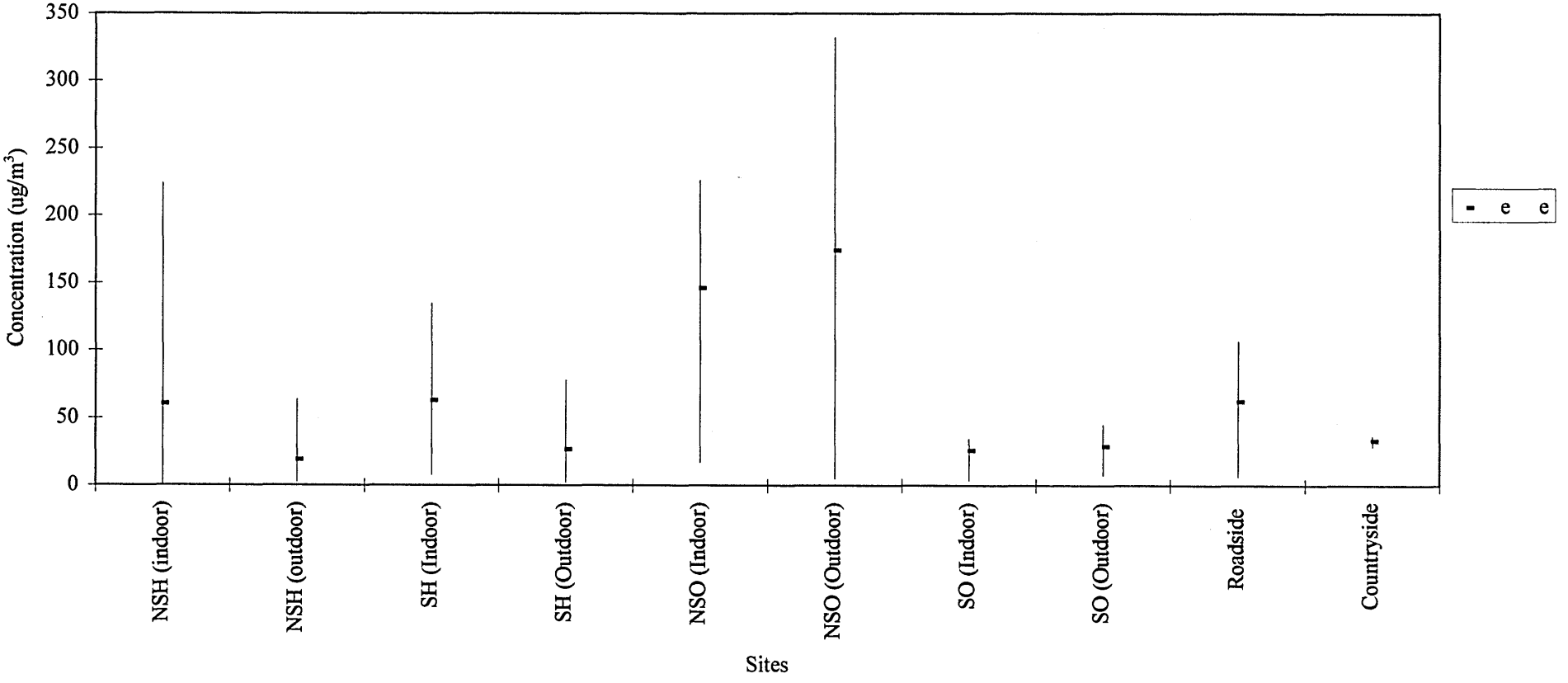

Figure 3.6: Chart Identifying the Highest, Lowest and Average Concentration of Toluene in All the Atmospheric Contexts.

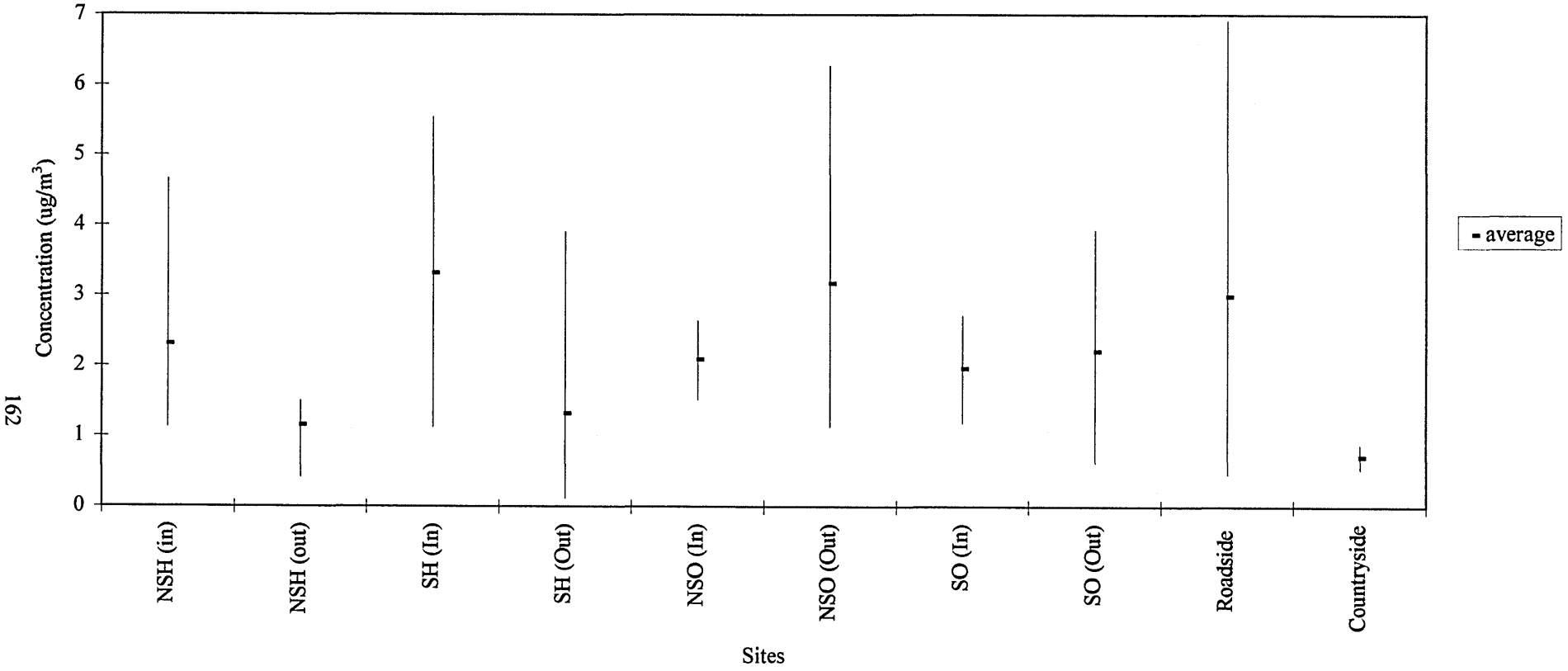

Figure 3.7: Chart to Identify the Highest, Lowest and Average Concentration of Ortho-xylene in All Atmospheric Contexts.

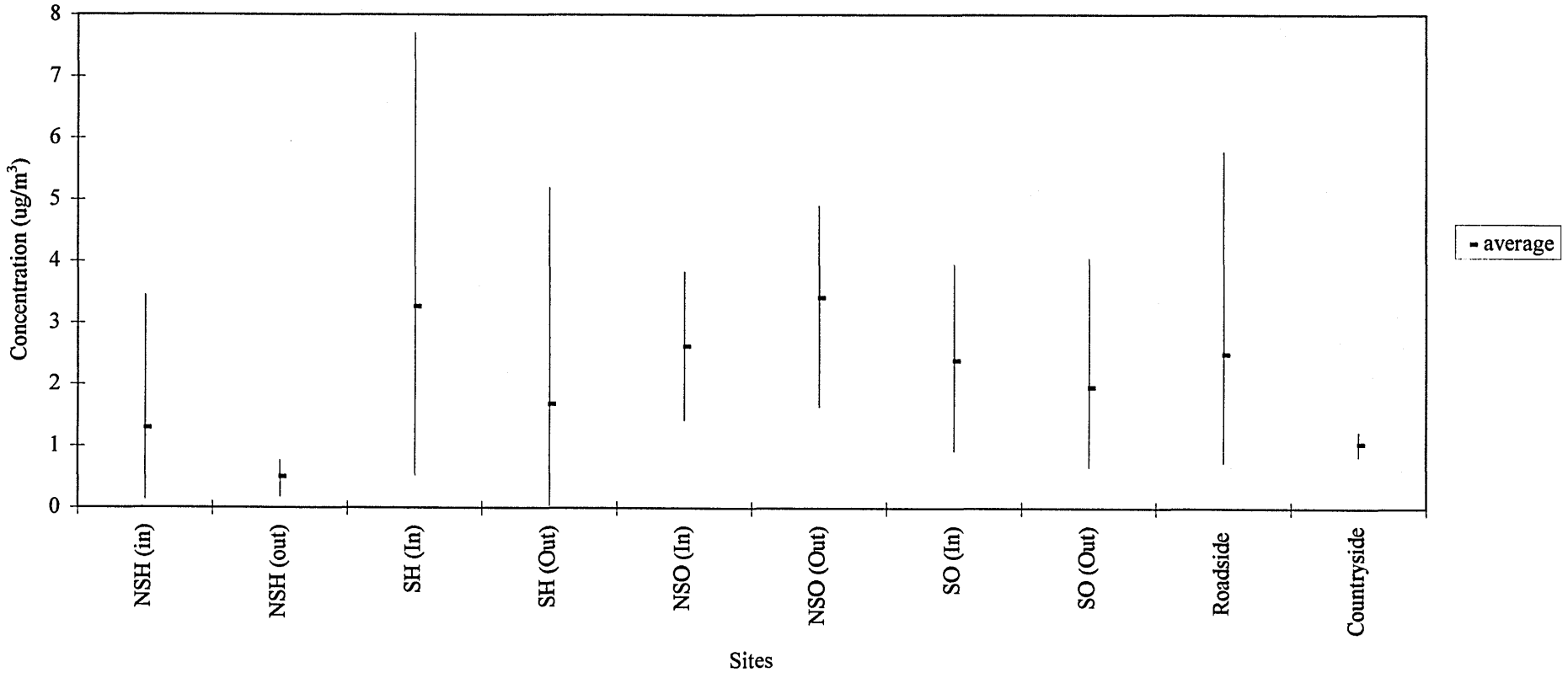

Figure 3.8: Chart to Identify the Highest, Lowest and Average Concentrations of Para and Meta-xylenes in All Atmospheric Contexts.

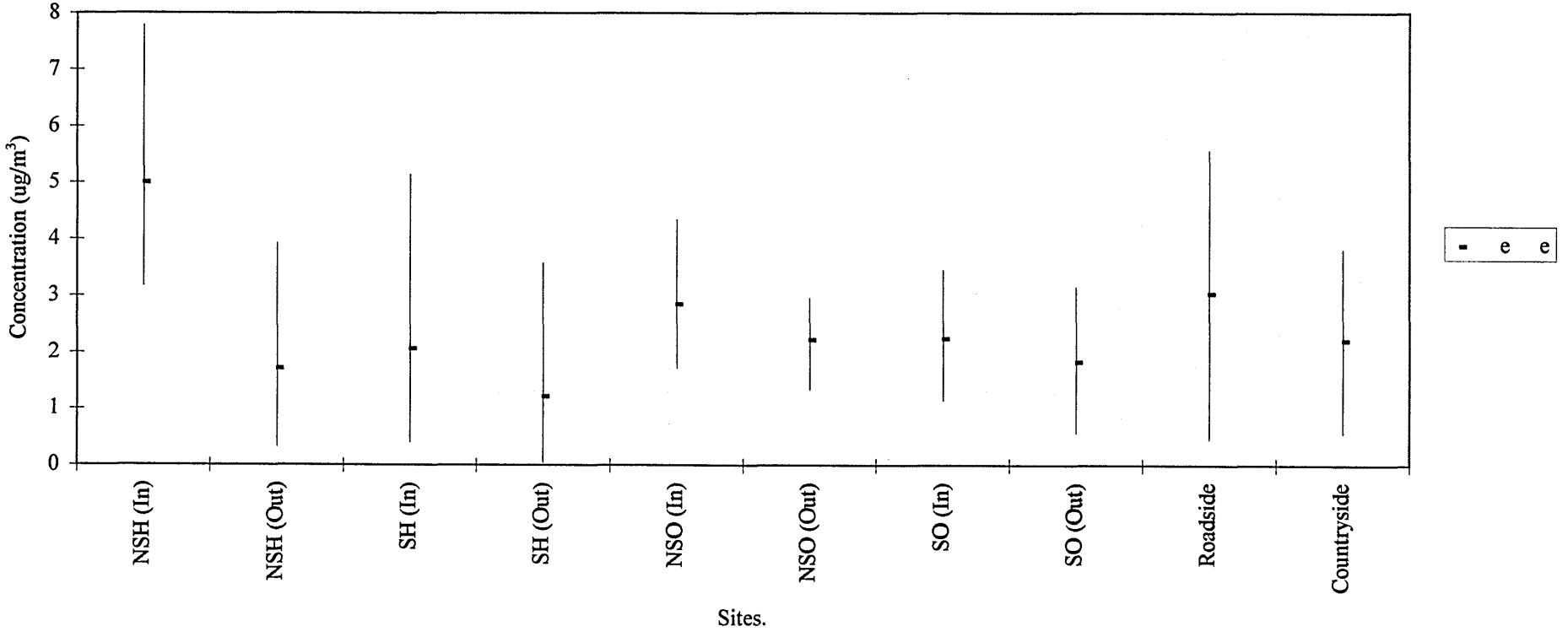

Figure 3.9: Chart to Identify the Highest, Lowest and Average Concentrations of Ethyl Benzene in All Atmospheric Contexts.

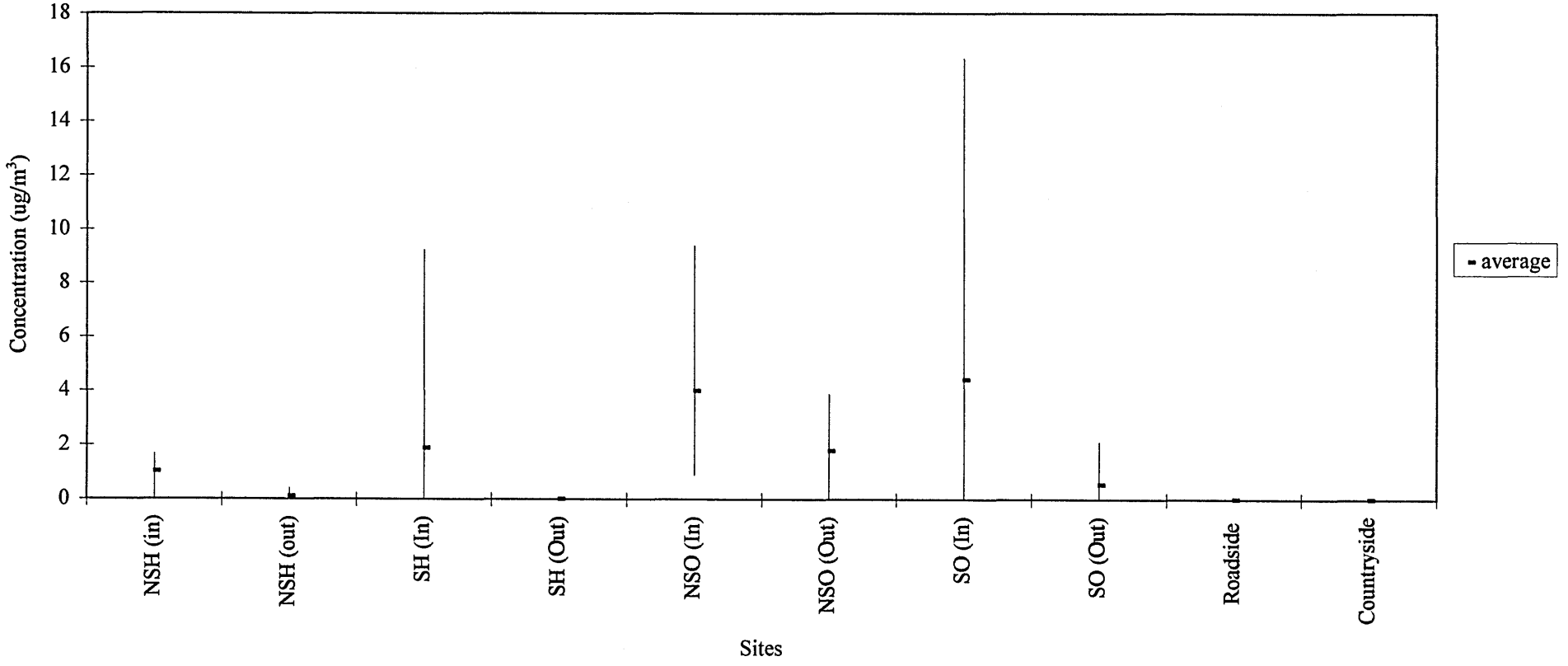

Figure 3.10: Chart to Identify the Highest, Lowest and Average Concentration of Para-dichlorobenzene in All Atmospheric Contexts.

It can be seen from the average quantitative values for benzene (Table 3.3) and on the accompanying graph (Figure 3.5) that a far wider range of concentrations were obtained in both the smokers environments compared to the other contexts. The average benzene concentrations (6.5μg/m^3 and 8.3μg/m^3 in the smokers houses and offices respectively) are higher than the average concentrations identified in all the other indoor and outdoor sites (range from 2.7-5.3μg/m^3). We can therefore propose that ETS is likely to contribute to the concentration of benzene, this has also been noted in the literature (6) and was observed in the ETS standard samples studied in this thesis (see Section 2.2.6.1). There also appears to be a number of other sources of benzene in both indoor and outdoor environments, as the city roadside and indoor non smokers concentrations are all above the level found in the countryside samples. Benzene has been identified in diesel emissions (see Section 2.2.6.1).

Accumulation of benzene is apparent in indoor samples as nearly all indoor sites have slightly elevated quantities of benzene compared to outdoor samples. With few exceptions, this is consistent for all the volatile compounds when the concentrations in the indoor and outdoor environments are studied (Table 3.3). It has been reported that benzene concentrations are often between 2-5 times higher in indoor samples with a benzene source (ETS or an attached garage) compared to outdoor samples (10,11). This trend can also be seen for benzene in other studies (12,13), that have identified similar concentrations of benzene to those determined in this study. They found statistical significance between having a smoker in an indoor environment and elevated benzene concentrations. In addition, an increase in benzene in dwellings which had an attached garage that were in use was found (11,12). The identification of attached garages was not taken into consideration in this study.

The position of the sample in a city was also described as having an effect on the concentration of benzene both indoors and outdoors. Higher concentrations are often found in urban areas where there is a large contribution from combustion emissions. These can also penetrate indoor environments raising the level of benzene in that sample (7). This is not clearly seen in the samples taken in this field study. However the highest concentration of benzene outdoors is associated with roadside samples, many of which were obtained from urban sites.

The toluene results, (Table 3.3 and Figure 3.6) show that levels are not only elevated in smokers environments. Major elevated levels are identified in the non-smoking offices, (both indoors and outdoors) this could be due to several of the offices having been recently furnished with new desks and cupboard equipment. Toluene has been identified in emissions from various building materials, solvents and adhesives (7). The reason for the large variation in toluene outside the non-smokers offices is unknown, perhaps diffusion from the indoor environments is occurring.

If we look at the concentration of toluene in samples other than the office samples, elevated levels are seen in the indoor samples (59.8μg/m^3 and 62.8μg/m^3 in non smokers and smokers houses respectively) with a possible slight increase due to ETS. These concentrations are two-three times higher than those in the outdoor samples (18.7-33.1μg/m^3), except for the roadside samples which have a comparable concentration to toluene concentrations indoors (62.2μg/m^3). Therefore we can conclude that toluene has major indoor sources (furnishings, paints etc.) and an outdoor source which could possibly be vehicular emissions, as identified by others (13).

The xylene isomers Table 3.3, Figure 3.7 and 3.8 seem to be at lower levels in outdoor residential and countryside outdoor air, (non-smokers/smokers houses) while higher average concentrations were found in all indoor environments and urban outdoor samples (outdoor office samples and roadside samples).

Ortho-xylenes mean levels are elevated in smokers houses and offices in addition to roadside samples. We can therefore identify that ortho-xylene is released by unknown indoor source(s), as well as ETS (see Section 2.2.5.1), while the elevated outdoor concentrations are possibly due to traffic emissions (13) and have been observed in the standard diesel samples (see Section 2.2.5.1).

The interpretation of meta + para-xylene data is not so simple with mean concentrations higher in indoor smokers environments, but also high in the non smokers offices, both indoor and outdoor. Such levels could be caused by ETS in the smokers environments (see Section 2.2.5.1) (2) while the non smokers sources could include indoor furnishings

in addition to the diffusion of these volatiles from outdoor traffic emitting sources, i.e. diesel.

Ethyl benzene, Table 3.3, Figure 3.9, seems fairly evenly distributed throughout the different sample sites with little dependence upon ETS or traffic. A higher concentration is seen in the non-smokers house, the reason for this is not known. However the source seems fairly ubiquitous as it is high in all of the non smokers house samples. Levels are universally higher in indoor and urban outdoor (offices) samples i.e. similar to the pattern identified by the xylene isomers. The indoor levels could be due to the same unknown indoor sources such as furnishings while the elevated levels seen in urban areas and roadside samples are once again likely to be due to traffic emissions (see Section 2.2.5.1), (13).

Para-dichlorbenzene, Table 3.3, Figure 3.10, is seen to be present in all the office samples, both for smokers and non-smokers. This is probably because the building from which the samples were taken had toilets on each floor, which were cleaned daily. The use of toilet cleaner is fairly liberal so the quantity sampled is more likely be due to the positioning of the offices in relation to the toilets. Quantities of para-dichlorobenzene were detected in several of the smokers and non-smokers houses, once again the quantity measured is likely to be due to the distance from the source (i.e. bathroom) that the sampling took place. Smaller quantities of para-dichlorobenzene were observed in outdoor samples, identifying the possibility of diffusion from the indoor source to the outdoor environment. This hypothesis is further supported by the lack of para-dichlorobenzene in samples taken away from dwellings (i.e. roadside and countryside samples).

It can be seen that for nearly every determined organic compound, that the indoor levels measured were higher than the corresponding outdoor concentration (o-xylene office samples and p+m-xylene in non-smokers offices excepted, Table 3.3) this has been observed in the literature (14). This shows that there is likely to be an accumulation of organic compounds and other pollutant material in indoor environments from furnishings, human activity and combustion sources (both indoor and outdoor diffusing in (7,14)). This could be due to pre-concentration effects through poor

ventilation/diffusion into the outdoor atmosphere. ETS is likely to contribute in part to the benzene concentration in smokers environments (15) however, there is only a small contribution (not significant (2)) to ethyl benzene and xylene isomer concentrations from ETS (15) in indoor smokers sites.

Vapour Phase Nicotine.

Two vapour phase nicotine samples were taken from each sample site, one was sent to Rothmans International for extraction and analysis while the second sample was extracted and analysed in house. The quantitative results are displayed in Table A8 (Appendix A). These show that nicotine is found specifically in samples where smoking has taken place. However, the precision of the results from the two different laboratories are very poor. In fact there is no consistency between the results at all. The reason for this is not known as the only difference observed between the methods employed for extraction and analysis was that our laboratory used an ultra-sonic bath for extraction while the Rothmans Laboratory (Basildon, Essex) used a wrist shaking extraction procedure. The Basildon results seem to be far more consistent than those carried out in our laboratory. However, neither set of results are consistent with the pattern of data observed in the ETS associated particulate methods.

Figure 3.11 shows the quantitative results for vapour phase nicotine, ETS particulate analysis by RSP, solanesol and scopoletin. Assuming that the quantity of vapour phase emissions will be directly related to the quantity of particulate ETS released we would assume that the pattern of emissions from vapour phase nicotine and the particulate marker compounds would be similar. Figure 3.11 shows this not to be the case with the set of samples analysed in Sheffield being low in nicotine and not following the pattern at all. This shows either poor sensitivity for nicotine analysis or poor extraction. The set of samples analysed in Basildon contained quantities of nicotine but the pattern of nicotine concentration does not follow the pattern of RSP, solanesol and scopoletin (the pattern from total UV and fluorescence also follow that of the other three particulate methods (not shown of this figure)). These data seem to be more confusing since the nicotine results determined by ATD/GC/MS do seem to follow the pattern identified by the particulate marker methods (see later in this section).

Such results support the idea of nicotine being a poor ETS marker, due to the difficulty in obtaining an accurate sample. Vapour phase nicotine is rapidly removed from the environment (20) either due to degradation (21), or adsorption to particulate material and surfaces (16). Work by Nelson (22) discussed the variation of marker compounds ratios with time. He identified nicotine as a poor vapour phase marker due to the variation in its concentration with time. 3-ethenylpyridine was suggested as a better vapour phase ETS marker compound due to its greater stability over longer sampling periods.

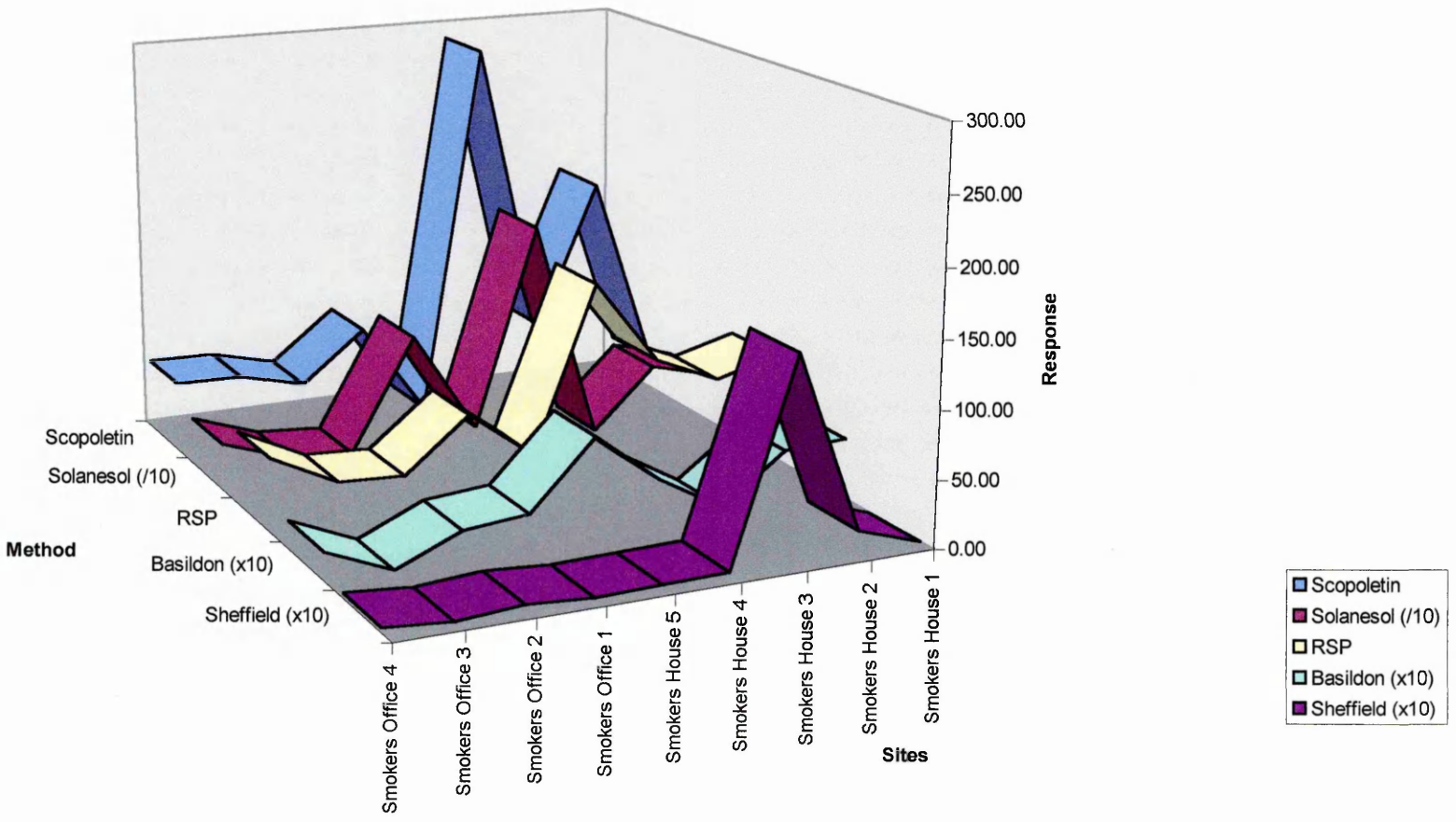

Figure 3.11: A Chart to Compare the Vapour Phase Nicotine Determination Methods with Other Particulate Methods for ETS Analysis.

XAD-4 resin tubes have been tested in a comparison study of several methods analysing for the accurate determination of both vapour and particulate phase nicotine (23,24). It was found that in some cases, the results were low, but this was attributed to a leak in the sampling system. However the results were relatively consistent, and the extraction efficiency of the nicotine from the resin (ethyl acetate with 0.01% triethylamine rather than dichloromethane) was determined to be 100%. The reasons for the poor vapour phase results obtained in this study are therefore unknown.

Nicotine concentrations were also determined in the vapour phase by thermal desorption GC/MS as inconsistent results were obtained from the XAD-4 resin and nicotine adsorbed to particulate material (Sections 3.5.2 and 3.6.2.2). The data obtained can be seen in Table A9 (appendix A). They are displayed graphically in Figure 3.12 where the pattern of concentration is compared with that of other ETS methods (these other methods are discussed fully in Section 3.6.2.2). Here the trends observed by the other particulate ETS measurement methods is followed to some extent, with house 4 showing the highest vapour phase nicotine (also identified by the other particulate methods as the sample containing most ETS). There was a low concentration (0$\mu g/m^3$ for nicotine) in house 3, increasing to (6.09$\mu g/m^3$) in house 2. Once again some of the samples were below the limit of detection (three office samples and one house sample) making the pattern harder to follow, but a consistent pattern of variation was observable from all methods, including the nicotine data.

Analysis of vapour phase nicotine by thermal desorption-GC/MS has been reported to be fairly efficient, with a collection efficiency of 88% (23) and quantitative. Thompson et al (25) found total desorption of nicotine did not occur from the tenax resin, with up to 10% of the nicotine staying on the tube. However, he noted that the addition of triethylamine increased the desorption of nicotine from the tube. (This technique was not employed in this study). Concentrations of 0.5-37.2$\mu g/m^3$ for vapour phase nicotine have been reported in literature (25). These compare well with our results of 0-20.95$\mu g/m^3$. However, thermal desorption is seldom used for the determination of vapour phase nicotine. This could be due to the low flows associated with thermal desorption collection (in our case 50ml/min) while filter and XAD-4 resin sampling systems can sample at a much faster flow (in our case 1l/min). The larger volume sampled and the

apparent efficiency and ease of extraction from the XAD-4 resin make this a more attractive method for vapour phase nicotine analysis.

We found therefore that thermal desorption was a more consistent method of vapour phase nicotine analysis compared to the XAD-4 resin tubes. The accepted method for vapour phase nicotine analysis is however, the XAD-4 sorbent method with solvent extraction (containing 0.01% triethylamine). This method (1) has been subjected to collaborative trials (26) and is accepted as a general method by The Association of Official Chemists (27), The American Society of Testing and Materials (28) and the U.S. Environmental Protection Agency (29).

However it should be noted that even though nicotine is specific to ETS, that there are real problems in using it as a marker compound. These are its inconsistency of distribution between the vapour and condensed phase (due to desorption and re-adsorption to surface/particles) and the rapid removal of vapour phase nicotine (20,24,25,28). This makes it a poor marker for vapour phase and particulate associated ETS, as we observed.

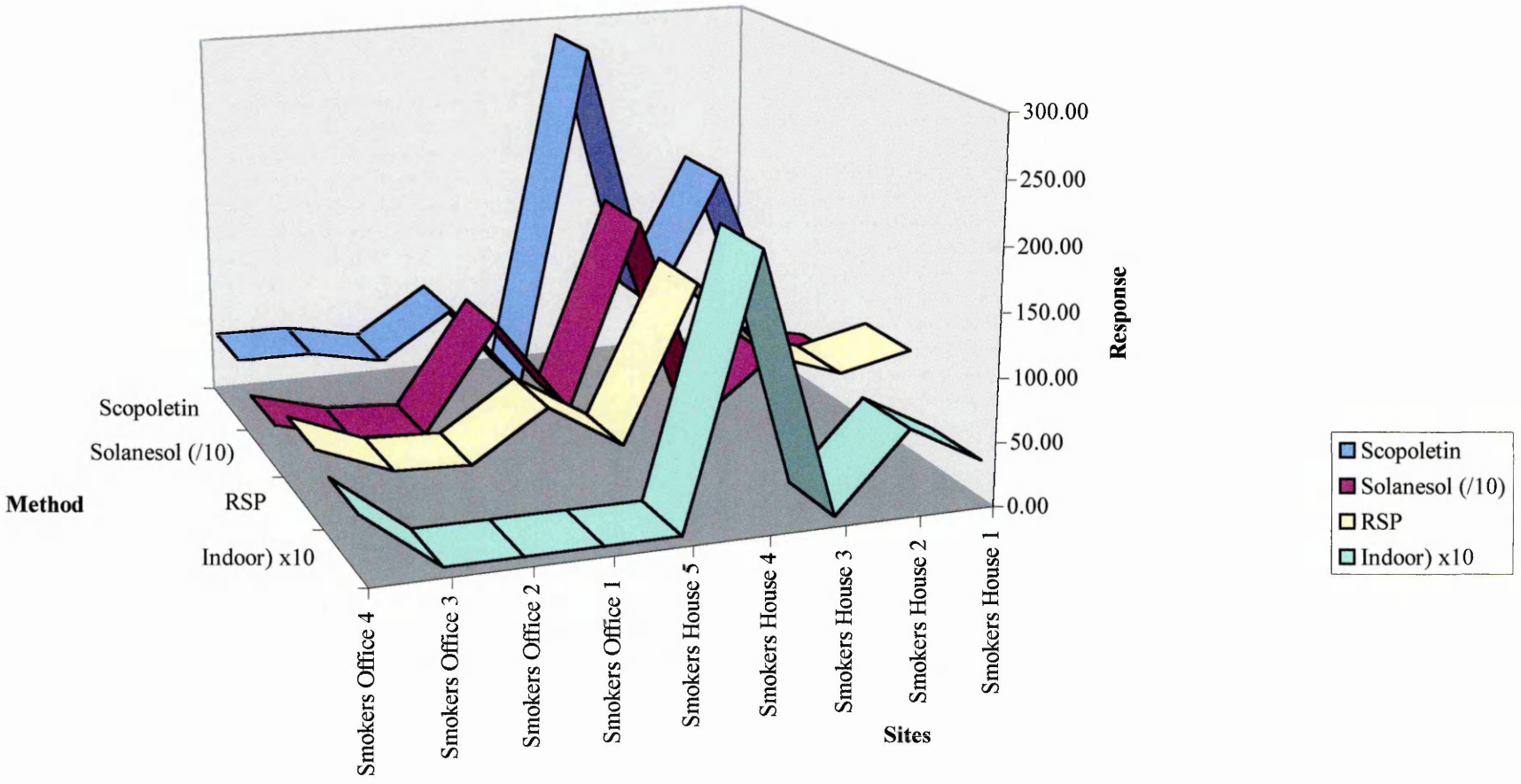

Figure 3.12: Comparrison of Thermal Desorption Determination of Nicotine with Other ETS Methods.

3.5.3 Particulates

Results for the concentrations of the various analytes under investigation from the sampled field sites can be seen in Appendix A.

Table A10 Particulate associated tetracosane (C24).

Table A11 Particulate associated nicotine.

Table A12 Particulate associated UV absorbent material.

Table A13 Particulate associated fluorescent material.

Table A14 Particulate associated solanesol.

Table A15 Particulate associated scopoletin.

The majority of the particulate associated analysis is discussed in terms of percentage contribution to a site after statistical manipulation these can be seen in section 3.6. As these statistical results are based upon one point analysis the section 3.6 (Statistical analysis of the field study results) is a discussion section in which the results are compared with literature and used to provide a basis on which further work can be constructed.

3.5.4 Polycyclic Aromatic Hydrocarbons (PAH).

PAH are a family of benzenoid compounds, with structures consisting of two or more benzene rings fused at the ortho position in such a way that each pair shares two carbons. systems, producing a range of compounds. Some of these compounds have been identified as being possibly toxic, with individual PAH being described as possible mutagens, carcinogens, co-carcinogens or pre-carcinogen agents. Their toxic activity can depend upon factors including chemical structure, absorption by the body tissue, cellular transport, storage and metabolism (30).

The mean concentrations of the 16 EPA PAH (vapour phase and particulate associated), from all the various field contexts are displayed in Tables 3.4-3.6. Due to the insensitivity of the analytical method to some of the PAH under investigation, no compound eluting after chrysene, (the larger, labile five ringed PAH) were identified, and will not be

discussed in the following section. This does not mean that they are not present, but simply that they were below the limit of detection by GC/MS/SIM.

Table 3.4: Identification of 16 US EPA PAH (Vapour and Particulate Associated) Identified in the Indoor and Outdoor Environments of Sub-Urban Smokers and Non Smokers Houses.

	Mean Non smokers house					Mean Smokers houses.			
	Indoor		Outdoor			Indoor		Outdoor	
	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3		Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3
Naphthalene	N.Q.	N.Q.	N.Q.	N.Q.		N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene	0.10	1.45	0.00	4.87		3.59	25.98	2.31	2.89
Acenaphthene	0.96	86.21	0.42	354.44		1.96	38.66	2.26	21.67
Fluorene	1.65	662.75	28.91	174.74		1.79	1731.04	51.05	26.71
Phenanthrene	9.11	51.27	35.16	884.63		8.91	109.54	6.84	55.41
Anthracene	0.22	0.14	0.00	4.66		0.00	0.00	0.60	0.00
Fluoranthene	1.40	2.52	0.18	10.17		3.80	3.96	0.93	3.83
Pyrene	1.66	1.29	2.03	3.61		3.29	2.11	0.75	1.41
B.(a)anthracene	0.19	0.00	0.00	0.00		0.00	0.00	0.00	0.00
Chrysene	0.45	0.00	0.00	0.00		1.67	0.00	0.48	0.00
B.(b)fluoranthene	0	0	0	0		0	0	0	0
B.(k)fluoranthene	0	0	0	0		0	0	0	0
B(a)Pyrene	0	0	0	0		0	0	0	0
B(g,h,i)Perylene	0	0	0	0		0	0	0	0
Dib(a,h)Anthracene	0	0	0	0		0	0	0	0
Indeno(1,2,3,c-d)pyrene	0	0	0	0		0	0	0	0

Table 3.5: Identification of 16 US EPA PAH (Vapour and Particulate Associated) Identified in the Indoor and Outdoor Environments of Urban Smokers and Non Smokers Offices.

	Non smokers offices (mean).					Smokers office			
	Indoor		Outdoor			Indoor		Outdoor	
	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3		Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3
Naphthalene	N.Q.	N.Q.	N.Q.	N.Q.		N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene	1.04	25.86	0.81	24.64		0.08	54.37	0.07	2.36
Acenaphthene	0.69	410.23	0.74	40.05		0.40	150.40	0.52	11.04
Fluorene	0.00	197.85	1.48	4.84		77.71	3269.34	1.02	3.45
Phenanthrene	29.40	670.28	19.21	306.91		10.04	85.53	2.70	19.99
Anthracene	11.97	189.45	6.28	104.54		0.28	1.78	0.10	0.00
Fluoranthene	1.18	2.62	3.04	1.94		0.55	4.46	0.30	1.17
Pyrene	6.58	1.81	2.51	1.76		1.39	3.13	0.30	0.00
B.(a)anthracene	2.73	2.45	0.00	0.00		0.00	0.00	0.00	0.00
Chrysene	51.54	2.59	0.00	0.00		0.28	0.00	0.00	0.00
B.(b)fluoranthene	0	0	0	0		0	0	0	0
B.(k)fluoranthene	0	0	0	0		0	0	0	0
B(a)Pyrene	0	0	0	0		0	0	0	0
B(g,h,i)Perylene	0	0	0	0		0	0	0	0
Dib(a,h)Anthracene	0	0	0	0		0	0	0	0
Indeno(1,2,3,c-d)pyrene	0	0	0	0		0	0	0	0

Table 3.6: Identification of 16 US EPA PAH (Vapour and Particulate Associated) Identified in Roadside and Countryside Samples.

	Roadside			Countryside	
	Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3		Filter 1 Conc ng/m^3	Resin tube Conc ng/m^3
Naphthalene	N.Q.	N.Q.		N.Q.	N.Q.
Acenaphthylene	3.23	5.41		3.26	6.52
Acenaphthene	4.60	43.60		11.57	13.41
Fluorene	0.49	4.65		0.00	0.00
Phenanthrene	12.12	51.62		10.41	77.42
Anthracene	9.91	10.79		0.00	0.00
Fluoranthene	8.56	1.35		11.29	0.00
Pyrene	6.68	0.93		6.16	0.00
B.(a)anthracene	0.00	0.00		0	0
Chrysene	0.23	0.00		0	0
B.(b)fluoranthene	0	0		0	0
B.(k)fluoranthene	0	0		0	0
B(a)Pyrene	0	0		0	0
B(g,h,i)Perylene	0	0		0	0
Dib(a,h)Anthracene	0	0		0	0
Indeno(1,2,3,c-d)pyrene	0	0		0	0

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

The following section will discuss the PAH profiles obtained from the various contexts and identify any similarities/trends that can be identified with indoor/outdoor, diesel/ETS emissions.

Initial trends that are readily identifiable include the phase distribution of the PAH investigated. Phase distribution of these compounds is dependant not only upon the physical conditions present in the atmosphere (ambient temperature and pressure), but also on the particular characteristics of the compound. The smaller PAH (2 ringed naphthalene to 3 ringed anthracene/phenanthrene) are found predominantly in the gas phase compared to the larger four ringed PAH molecules (discussed further in this section) which seem to be associated with both particulate material and the gas phase. The distribution of these smaller PAH compounds has been shown to be difficult to accurately quantify as particulate associated 3-4 ringed PAH have been shown to vapourise into the vapour phase from the particulate material sampled on filters (49).

Diesel.

To try and clarify the PAH emitted in specific contexts (i.e. indoor and outdoor), all outdoor contexts were separated into vapour phase and particulate associated, Table 3.7 and 3.8 (in addition, the particulate associated PAH identified in diesel emissions are also shown in Table 3.8). The vapour phase PAH (acenaphthylene-anthracene) in Table 3.7 are found in higher concentrations than the concentration associated with particulate material. In fact, in some of the samples, quantities of several hundred ng/m^3 are identified. These contexts (non smokers offices and non smokers houses) could be high due to point sources associated with one or more of the sampling sites. The majority of the vapour phase PAH have concentrations of between $0\text{-}80ng/m^3$ which is consistent with literature published in this area (50-52) during sampling that occurred during the colder, winter months. The sum total of the individual PAH is also very similar to results obtained from the Toxic Organic Micropollutants Survey (TOMPs) in the UK, conducted at Warren Springs for the Department of the Environment (52-54). Please note that uncombusted fuel was not analysed directly for PAH due to the complex nature of the sample and the difficulty associated with fractionation of the fuel.

Table 3.7: Vapour Phase PAH Quantified in all Outdoor Contexts.

		Roadside Resin tube Conc ng/m^3	NS office Resin tube Conc ng/m^3	S office Resin tube Conc ng/m^3	NS house Resin tube Conc ng/m^3	S house Resin tube Conc ng/m^3	Countryside Resin tube Conc ng/m^3
Naphthalene		N.Q.	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene		5.41	24.64	2.36	4.87	2.89	6.52
Acenaphthene		43.60	40.05	11.04	354.44	21.67	13.41
Fluorene		4.65	4.84	3.45	174.74	26.71	0.00
Phenanthrene		51.62	306.91	19.99	884.63	55.41	77.42
Anthracene		10.79	104.54	0.00	4.66	0.00	0.00
Fluoranthene		1.35	1.94	1.17	10.17	3.83	0.00
Pyrene		0.93	1.76	0.00	3.61	1.41	0.00
B.(a)anthracene		0.00	0.00	0.00	0.00	0.00	0
Chrysene		0.00	0.00	0.00	0.00	0.00	0
B.(b)fluoranthene		0	0	0	0	0	0
B.(k)fluoranthene		0	0	0	0	0	0
B(a)Pyrene		0	0	0	0	0	0
B(g,h,i)Perylene		0	0	0	0	0	0
Dib(a,h)Anthracene		0	0	0	0	0	0
Indeno(1,2,3,c-d)pyrene		0	0	0	0	0	0

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

Table 3.8: Identification of all PAH Associated to Particulate Material Quantified in all Outdoor Contexts.

	Diesel Average Conc μg/g	Roadside Filter 1 Conc ng/m^3	NS office Filter 1 Conc ng/m^3	S office Filter 1 Conc ng/m^3	NS house Filter 1 Conc ng/m^3	S house Filter 1 Conc ng/m^3	Countryside Filter 1 Conc ng/m^3
Naphthalene	0.00	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene	0.00	3.23	0.81	0.07	0.00	2.31	3.26
Acenaphthene	0.00	4.60	0.74	0.52	0.42	2.26	11.57
Fluorene	0.00	0.49	1.48	1.02	28.91	51.05	0.00
Phenanthrene	23.38	12.12	19.21	2.70	35.16	6.84	10.41
Anthracene	0.59	9.91	6.28	0.10	0.00	0.60	0.00
Fluoranthene	25.24	8.56	3.04	0.30	0.18	0.93	11.29
Pyrene	53.22	6.68	2.51	0.30	2.03	0.75	6.16
B.(a)anthracene	15.97	0.00	0.00	0.00	0.00	0.00	0
Chrysene	41.40	0.23	0.00	0.00	0.00	0.48	0
B.(b)fluoranthene	1.20	0	0	0	0	0	0
B.(k)fluoranthene	16.98	0	0	0	0	0	0
B(a)Pyrene	0.00	0	0	0	0	0	0
B(g,h,i)Perylene	0.00	0	0	0	0	0	0
Dib(a,h)Anthracene	0.00	0	0	0	0	0	0
Indeno(1,2,3,c-d)pyrene	0.00	0	0	0	0	0	0

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

The phase distribution of each PAH in the vapour phase compared to the PAH associated to the particulate material was determined (Table 3.9).

Table 3.9: The Mean Percentage of each PAH Found in the Vapour Phase from all Outdoor Samples.

PAH.	% vapour
Naphthalene	N.Q.
Acenaphthylene	79.8
Acenaphthene	88.0
Fluorene	72.9
Phenanthrene	89.4
Anthracene	82.2
Fluoranthene	62.2
Pyrene	45.7

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

The above Table 3.9 shows that more than 72.9% and often more than 80% of 2-3 ringed PAH are found in the vapour phase. This compares favourably with the literature where Benner et al (55) found 88% and 86% of phenanthrene and anthracene in the vapour phase. Our percentage values were 89% and 82% respectively. They also identified that approximately half the quantity of fluoranthene and pyrene (45% and 49%) was in the vapour phase. Our study identified 62% and 45% for fluoranthene and pyrene to be in the vapour phase. This similarity in phase distribution shows that the two methods of sampling are comparable (they used a high volume sampler with a polyurethane foam plug after the filter to collect vapour phase compounds (55)), for sampling PAH from both the vapour and particulate associated phases.

Such distribution is dependant upon ambient temperature and humidity during the time of sampling. It has been clearly identified that a larger concentration of PAH (both vapour phase and particulate associated) are found in the colder winter months compared to the summer months (50,51,53). The main reasons for this could include the reduced photochemical reactions that can occur. An increase in emissions from various sources

due to increased energy (for heat and light) and transport (increase in urban congestion and "cold start" emissions (53)). Weather effects can also cause an increase in localised pollution due to unfavourable dispersion conditions.

Other factors which can effect the phase distribution of PAH include the individual compounds vapour pressure in addition to the type of surface available for adsorption (carbonaceous particles from diesel engines provide a better surface than mineral based gasoline particles (56)).

However, these quantitative results and phase distribution values do compare with phase distribution results published by Halsall (52) for PAH concentrations in the UK. They identified that 80% of pyrene was in the vapour phase throughout the year. The reasons for phase distribution differences between our results and those published by Halsall (52) are unknown.

Outdoor particulate associated PAH (shown in Table 3.8) do display a number of trends which possibly identify compounds that are associated with anthropogenic emissions (specifically vehicular) as these are found in higher concentrations around the city centre and the major roads used for sampling. Examples of these are fluoranthene and pyrene which are found in higher concentrations in the roadside samples (8.56ng/m^3 and 6.68ng/m^3 respectively). These concentrations of fluoranthene and pyrene are also towards the lower end of the concentration range (identified by Benner (55)), and lower than their mean concentrations (20ng/m^3 and 27ng/m^3 (55)). This is to be expected as our samples, taken in Sheffield were in the open air and not in an enclosed tunnel (55).

Some of the outdoor urban office samples had elevated concentrations for fluoranthene and pyrene (3.04ng/m^3 and 2.51ng/m^3 respectively), compared to suburban house samples (0.6ng/m^3 and 0.93ng/m^3). However, the concentration of these two PAH in the countryside samples are high (11.29ng/m^3 and 6.16ng/m^3). The reason or possible point sources of these elevated concentrations could not be identified.

The quantitative PAH results for particulate diesel emissions, displayed in Table 3.8 show that fluoranthene and pyrene are present at quite high concentrations along with

benzo(a)anthracene and chrysene (which were unfortunately not quantified on a regular basis in the field samples). The levels of fluoranthene were approximately half those of pyrene in the diesel emissions, yet fluoranthene was found in higher concentrations than pyrene in the field samples. This could be due to a number of additional fluoranthene sources increasing the levels in the atmosphere, or a variation in emissions from different engines (diesel or petrol). The type/variation of the fuel content and the way in which the vehicles are run/serviced could produce a highly varied quantity of the two PAH molecules. Variation in PAH composition of exhaust emissions is described by Nielsen (57), where he states that a variation in combustion temperature (low, producing alkylated PAH and high producing unsubstituted PAH) can cause emission differences. He identified that diesel emissions produced a higher quantity of alkylated PAH compounds, specifically methyl phenanthrenes (observed by Douce et al (58), and Jensen et al (59)) compared to petrol engines which produced a larger proportion of unsubstituted PAH. Pyrene could also be more susceptible to reaction/degradation once released into the atmosphere.

It has also been suggested (55) that certain PAH are found at higher concentrations in certain anthropogenic emissions compared to others. For example, methyl and dimethyl phenanthrenes in addition to pyrene are associated with diesel emissions (this was supported by field samples in a road tunnel which found high levels of methyl phenanthrenes in the air sampled mainly from diesel vehicles (55)). Conversely, fluoranthene was found associated more with petrol emissions (55). This could explain why the particulate associated diesel emissions contained a larger quantity of pyrene to fluoranthene, while the field samples (specifically the roadside samples) gave a higher concentration of fluoranthene to pyrene associated to particulate material.

Summary.

As lead compounds have been reduced in petrol engines over the last decade, other compounds have been added to maintain the anti-knock parameters associated with organo-lead compounds. PAH have been such compounds (60), and as previously discussed one source of PAH from anthropogenic emissions includes uncombusted material directly from the fuel (50,61). PAH emissions from petrol engines (specifically

2-4 ringed PAH) are therefore likely to increase along with emissions from an increasing diesel powered sector, as diesel contains a higher proportion of total PAH (containing higher concentrations of larger PAH, >3 ringed) in the fuel compared to petrol fuels (62).

The use of PAH for source apportionment studies is difficult as many of the PAH are released in varying concentrations by a number of sources. However, PAH in conjunction with other emissions including inorganics (51) and alkanes (63) could be used with statistical multivariate techniques to identify source apportionment of up to eight sources in one sample (51,63). In addition, the use of source "fingerprints" have been discussed where all quantified PAH are ratioed to one PAH (often benzo (e or a) pyrene) (50). Unfortunately, an inadequate database of source fingerprints (often due to the wide and varied emission concentrations emitted from similar engine types/sources because of age, construction, manner of use etc.) has made this type of source apportionment difficult to accurately interpret (50).

Environmental Tobacco Smoke (ETS).

To try and identify ETS specific PAH all indoor samples, tables for vapour phase, (Table 3.10) and particulate associated, (Table 3.11) PAH were constructed. In addition to the average concentration found in the various contexts, quantitative samples from ETS atmospheres were also included in both tables.

The only vapour phase PAH quantified in the ETS atmospheric samples were acenaphthylene, acenaphthene, fluorene and phenanthrene (Table 3.10). All these PAH were observed in the different contexts with elevated concentrations of fluorene seen specifically in the smokers contexts (3269ng/m^3 and 1731ng/m^3 in smokers offices and houses respectively compared to 197ng/m^3 and 662 ng/m^3 in non smokers offices and houses). This would suggest that fluorene was a major constituent of ETS, which is not apparent in the ETS atmospheric samples (fluorene concentration of 182ng/m^3). The reasons for these major differences include differences in fluorene contribution between cigarette type/brand, (our standard atmospheres used Rothmans International cigarettes). Perhaps fluorene is an unreactive gaseous phase compound (as many vapour phase ETS

compounds have a longer atmospheric residence time compared to the particulate material due to rapid adsorption of particles to surfaces). However, fluorene in ETS has been shown to have a half life of 3.4 hours (under static conditions (64)), accumulation due to slow continuous emissions and slow removal is therefore unlikely. Few of the other vapour phase PAH show an increase due to smokers contexts therefore the fluorene concentrations could be due to other unidentified sources present at the sites. Perhaps from a method/oderant used to disperse/mask the smell of ETS.

The high mean concentrations of the vapour phase PAH in the non smokers offices made it difficult to identify any further increases in PAH concentration due to ETS. However, our results were similar in concentration to those reported in the literature from smokers and non smokers homes (65), with slight increases in the concentration of acenaphthylene, phenanthrene, fluoranthene and pyrene in smokers compared to non smokers houses. Higher concentrations and statistical significance of additional vapour phase acenaphthylene, phenanthrene and anthracene was identified by Chuang (66), in homes containing various heating and cooking systems. They identified pyrene and phenanthrene as possible marker compounds for ETS (66).

Table 3.10: Vapour phase PAH Quantified in all Indoor Contexts.

	ETS Resin tube Conc ng/m^3	NS office Resin tube Conc ng/m^3	S office Resin tube Conc ng/m^3	NS house Resin tube Conc ng/m^3	S house Resin tube Conc ng/m^3
Naphthalene	N.Q.	N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene	167.94	25.86	54.37	1.45	25.98
Acenaphthene	146.02	410.23	150.40	86.21	38.66
Fluorene	182.49	197.85	3269.34	662.75	1731.04
Phenanthrene	362.55	670.28	85.53	51.27	109.54
Anthracene	0	189.45	1.78	0.14	0.00
Fluoranthene	0	2.62	4.46	2.52	3.96
Pyrene	0	1.81	3.13	1.29	2.11
B.(a)anthracene	0	2.45	0	0	0
Chrysene	0	2.59	0	0	0
B.(b)fluoranthene	0	0	0	0	0
B.(k)fluoranthene	0	0	0	0	0
B(a)Pyrene	0	0	0	0	0
B(g,h,i)Perylene	0	0	0	0	0
Dib(a,h)Anthracene	0	0	0	0	0
Indeno(1,2,3,c-d)pyrene	0	0	0	0	0

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

Table 3.11: Particulate Associated PAH Quantified in all Indoor Contexts.

	ETS Particulate Conc ng/m^3	NS office Filter 1 Conc ng/m^3	S office Filter 1 Conc ng/m^3	NS house Filter 1 Conc ng/m^3	S house Filter 1 Conc ng/m^3
Naphthalene	372.37	N.Q.	N.Q.	N.Q.	N.Q.
Acenaphthylene	8.34	1.04	0.08	0.10	3.59
Acenaphthene	43.35	0.69	0.40	0.96	1.96
Fluorene	83.93	0.00	77.71	1.65	1.79
Phenanthrene	175.77	29.40	10.04	9.11	8.91
Anthracene	10.55	11.97	0.28	0.22	0.00
Fluoranthene	58.73	1.18	0.55	1.40	3.80
Pyrene	87.29	6.58	1.39	1.66	3.29
B.(a)anthracene	53.10	2.73	0.00	0.19	0.00
Chrysene	138.02	51.54	0.28	0.45	1.67
B.(b)fluoranthene	0	0	0	0	0
B.(k)fluoranthene	0	0	0	0	0
B(a)Pyrene	0	0	0	0	0
B(g,h,i)Perylene	0	0	0	0	0
Dib(a,h)Anthracene	0	0	0	0	0
Indeno(1,2,3,c-d)pyrene	0	0	0	0	0

N.Q. Compound not quantified due to poor or inconsistent peak shape on many of the chromatograms.

Particulate associated PAH constituents identify concentrations of nearly all the same 3-4 ringed PAH compounds identified in the vapour phase. However, the phase distribution of these compounds was seen to be slightly different to those identified in outdoor environments. The phase distribution of PAH in indoor environments can be seen in Table 3.12.

Table 3.12: Identifying the Phase Distribution of Quantified PAH in Indoor Environments.

	% vapour
Naphthalene	N.Q.
Acenaphthylene	94.32
Acenaphthene	98.41
Fluorene	99.33
Phenanthrene	90.67
Anthracene	72.81
Fluoranthene	68.30
Pyrene	43.45
B.(a)anthracene	23.64
Chrysene	1.20

All but anthracene and pyrene (both found in slightly lower proportions) are found in higher proportions in the vapour phase in indoor environments compared to outdoor environments. This is probably to be expected due to the higher average ambient temperatures associated with indoor environments compared to outdoor environments during the autumnal months.

There are no particulate associated PAH that are found to be considerably higher in concentration in smokers environments compared to non smoking contexts. The ETS atmospheric samples identify that quantifiable amounts of fluorene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene and chrysene are released associated to particulate material during smoking. However ageing of these emissions rapidly removes them from the atmospheric environment either by rapid volatilisation of the more thermally volatile compounds (such as fluorene, phenanthrene etc.) or due to adsorption of the moist particulates to surfaces.

3.5.5 Elemental and Inorganic.

All the ashed samples from the field sites were analysed by ICP/MS, using indium as an internal standard (described in Section 2.2.5.2). The mean concentrations of a number of elements/inorganics can be seen in Table 3.13. No tracer element was identified specific to diesel emissions but several elements/inorganics were observed at higher concentrations. Arsenic was identified as possibly being specific to ETS. The two contexts where these sources are likely to be elevated will be identified and any correlations identified.

Diesel (Outdoor samples).

Many elements are identified as being associated with anthropogenic emissions (vehicular in particular). These include detection of elevated levels of manganese (Mn), Iron (Fe), nickel (Ni), copper (Cu), bromine (Br), molybdenum (Mo) and lead (Pb), in both our samples and in literature (67,68). The only possible element/inorganic identified in Section 2.2.6.4 to be specific to diesel emissions was iodine (I).

If we compare this knowledge with the field sample results (Table 3.13), a number of trends can be observed. Mn, Fe, Ni, Cu, Br, Mo, I and Pb are all present in the roadside samples at quite elevated concentrations. However, many of the elements can be seen to be elevated in other contexts as well, many of which you would not expect to be associated with vehicular emissions. Some of the elements, Fe and Ni specifically are quite elevated (422.2-1122.2ng/m^3 for Fe and 19.8-55.1ng/m^3 for Ni) compared to similar environmental results published in the literature (69) where cumulative totals (for <2.1μm and >2.1-10μm diameter particulates) are 301ng/m^3 and 4.8ng/m^3 for Fe and Ni respectively. These elements could be elevated due to the close proximity of the iron smelters and steel foundries that are still present in and around the Sheffield area. Some of the high indoor values could be associated with an internal point source, or due to one high result that could have been caused by a contaminated sample (such as non smokers offices mean value for Ni).

Table 3.13: Mean Concentration of Elements/Inorganics from all the Field Contexts (ng/m^3).

	Lithium	Berylium	Boron	Sodium	Magnesium	Aluminium	Silicon	Potassium	Calcium
Non smokers house average (indoor)	9.72	1.32	475.00	113.19	0.00	308.26	194.44	36.81	2715.97
Non smokers house average (outdoor)	65.97	0.00	604.17	815.97	125.00	81.04	288.19	0.00	2104.17
Smokers house average (indoor)	0.8	2.1	1455.0	2871.7	116.7	1333.3	4655.6	85.0	241.7
Smokers house average (outdoor)	4.9	1.5	1021.1	1782.2	12.7	253.1	943.3	0.0	54.1
Non Smokers office average (indoor)	14.5	12.1	5486.1	534.7	0.0	304.2	1354.2	0.0	463.2
Non Smokers office average (outdoor)	2.8	7.8	3055.6	66.0	0.0	70.6	826.4	0.0	284.7
Smokers office average (indoor)	2.4	2.8	1141.0	729.2	0.0	1701.4	939.6	97.9	133.3
Smokers office average (outdoor)	34.9	1.3	668.8	1090.3	122.2	57.6	354.2	41.0	694.4
Roadside average	35.1	0.2	2099.0	2897.2	296.4	428.1	1597.2	1531.6	2743.1
Countryside average	1.0	5.3	3097.2	3055.6	84.7	180.6	6722.2	0.0	0.0

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Non smokers house average (indoor)	0.1	3.8	2.0	1.8	7.5	847.2	0.4	41.3	11.0	30.6
Non smokers house average (outdoor)	0.1	1.5	2.3	0.0	10.6	451.4	2.7	3.7	0.0	34.0
Smokers house average (indoor)	0.0	5.8	2.7	342.8	15.1	1122.2	2.1	65.6	32.8	2.8
Smokers house average (outdoor)	0.2	3.0	0.6	1.9	7.8	37.8	30.0	2.2	2.0	0.0
Non Smokers office average (indoor)	0.2	1.7	0.7	35.4	27.0	159.0	3.6	236.1	0.3	9.3
Non Smokers office average (outdoor)	2.0	3.0	0.4	0.0	8.1	613.9	0.0	0.1	0.0	5.4
Smokers office average (indoor)	0.1	1.7	0.5	2.4	4.5	0.0	0.4	19.8	26.5	2.6
Smokers office average (outdoor)	0.1	3.2	0.7	4.1	4.4	118.1	0.4	8.4	5.7	7.6
Roadside average	0.5	27.2	9.7	22.7	44.8	422.2	5.8	55.1	25.7	25.0
Countryside average	0.0	1.7	0.6	22.2	0.4	0.0	0.0	3.8	2.6	0.0

	Gallium	Germanium	Arsenic	Selenium	Bromine	Rubidium	Strontium	Yttrium	Zirconium	Niobium
Non smokers house average (indoor)	0.1	0.0	0.0	0.0	24.3	0.3	11.9	0.0	4.9	1.2
Non smokers house average (outdoor)	0.1	0.0	0.0	0.0	0.0	0.3	7.9	0.0	22.9	0.8
Smokers house average (indoor)	1.4	0.1	0.3	0.0	27.8	0.2	19.2	0.0	12.0	1.0
Smokers house average (outdoor)	1.2	0.0	0.1	0.0	1.5	0.0	0.0	0.0	38.1	0.4
Non Smokers office average (indoor)	0.1	0.0	0.0	0.0	0.0	0.1	77.6	0.0	2.8	0.5
Non Smokers office average (outdoor)	0.2	0.0	0.0	0.0	0.0	0.1	0.1	0.0	12.2	0.6
Smokers office average (indoor)	0.8	0.0	0.6	1.1	0.0	0.3	0.1	0.0	7.4	4.8
Smokers office average (outdoor)	0.5	0.0	0.2	0.7	3.6	0.3	4.4	0.0	6.0	0.2
Roadside average	2.0	0.1	0.3	0.0	49.5	1.0	8.4	0.0	27.6	1.5
Countryside average	0.0	0.0	0.0	0.0	4.2	0.0	3.8	0.0	1.0	0.1

	Molyybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony
Non smokers house average (indoor)	0.0	0.0	0.0	0.1	0.0	0.0	15.7	I.S.	250.0	23.9
Non smokers house average (outdoor)	0.0	0.0	0.0	0.1	0.0	36.1	2.5	I.S.	0.0	44.4
Smokers house average (indoor)	64.9	0.0	0.0	0.0	0.1	8.9	0.7	I.S.	137.0	0.1
Smokers house average (outdoor)	15.6	0.0	0.0	0.0	0.0	1.6	20.2	I.S.	3.6	13.9
Non Smokers office average (indoor)	256.9	0.0	0.0	0.0	0.0	0.0	10.1	I.S.	118.1	16.7
Non Smokers office average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	11.6	I.S.	0.0	6.3
Smokers office average (indoor)	9.5	0.0	0.0	0.0	0.0	0.0	6.9	I.S.	16.5	2.6
Smokers office average (outdoor)	0.1	0.0	0.0	0.0	0.0	6.8	7.2	I.S.	197.8	9.6
Roadside average	16.9	0.0	0.0	0.1	0.0	2.0	3.2	I.S.	135.1	36.6
Countryside average	30.6	0.0	0.0	0.0	0.0	0.0	0.3	I.S.	0.0	0.0

	Tellurium	Iodine	Ceasium	Barium	Lanthanum	Cerium	Praseodymium	Neodynium	Samarium	Europium
Non smokers house average (indoor)	0.0	38.9	0.5	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Non smokers house average (outdoor)	0.0	47.9	0.8	1.7	0.8	0.0	0.0	0.0	0.0	0.0
Smokers house average (indoor)	0.0	18.4	0.2	17.1	0.2	0.0	0.1	0.2	0.0	0.0
Smokers house average (outdoor)	0.0	17.8	0.2	12.9	0.0	0.0	0.0	0.0	0.0	0.0
Non Smokers office average (indoor)	0.0	20.4	0.2	1.0	0.1	0.0	0.0	0.0	0.0	0.0
Non Smokers office average (outdoor)	0.0	27.9	0.2	1.3	0.4	0.0	0.0	0.0	0.0	0.0
Smokers office average (indoor)	0.0	20.3	0.1	1.1	0.0	0.0	0.0	0.0	0.0	0.0
Smokers office average (outdoor)	0.0	15.3	4.0	4.5	1.7	0.0	0.0	0.0	0.0	0.0
Roadside average	0.0	30.8	0.7	24.9	0.5	0.0	0.0	0.1	0.0	0.0
Countryside average	0.0	12.8	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0

	Gadolium	Terbium	Dysprosium	Holmium	Erbium	Thulim	Ytturbium	Lutetium	Hafnium	Tantalium	Tungsten
Non smokers house average (indoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Non smokers house average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	23.6
Smokers house average (indoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	33.9
Smokers house average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	17.2
Non Smokers office average (indoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Non Smokers office average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Smokers office average (indoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.4
Smokers office average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0
Roadside average	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0
Countryside average	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.3

	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Thorium	Uranium
Non smokers house average (indoor)	0.0	0.0	0.3	0.0	0.1	90.1	5.0	2.2	0.3	0.1	0.1
Non smokers house average (outdoor)	0.2	0.0	0.4	0.1	5.9	4696.5	0.0	81.5	0.9	0.3	0.6
Smokers house average (indoor)	0.0	0.0	0.0	0.0	0.0	4.7	0.1	15.6	0.0	0.0	0.0
Smokers house average (outdoor)	0.0	0.0	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.1
Non Smokers office average (indoor)	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0
Non Smokers office average (outdoor)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Smokers office average (indoor)	0.0	0.0	0.0	0.3	0.0	2.4	0.0	1.3	0.0	0.0	0.0
Smokers office average (outdoor)	0.0	0.0	0.0	0.3	0.0	2.5	0.0	0.4	0.2	0.0	0.1
Roadside average	0.0	0.1	0.2	0.9	0.0	21.4	0.1	48.2	0.7	0.3	0.3
Countryside average	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4

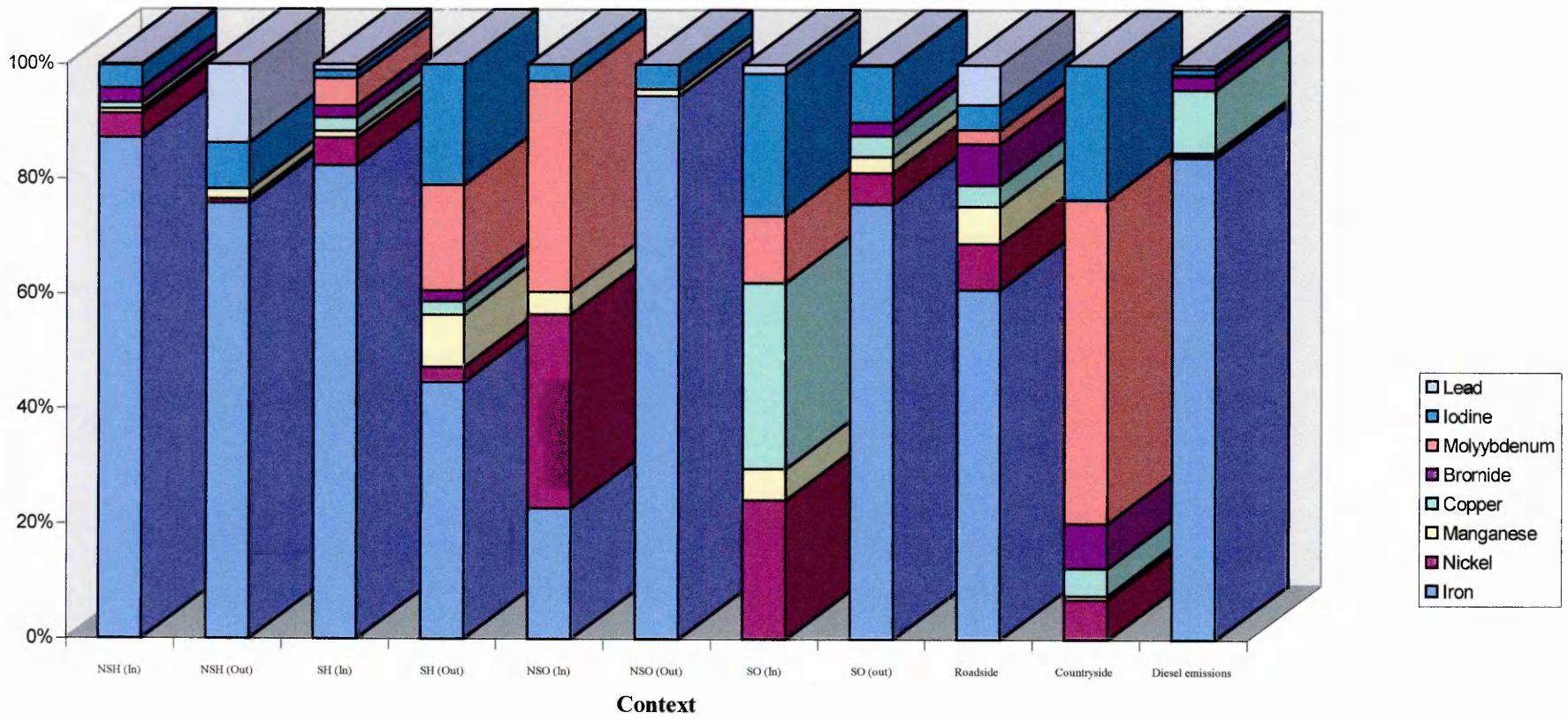

Figure 3.13: A Bar Graph to Identify the Major Elemental Constituents Present in Particulate material from All investigated Contexts, Compared to the Elements Identified in Diesel Emissions.

Figure 3.13 shows the major elemental constituents found in the field samples and diesel emissions. We can see that Fe is the major component of diesel emissions and this is also evident in many of field samples. The expected sites, roadside, and the urban outdoor samples (smokers and non smokers offices outdoor) show high levels of Fe. However, high levels of Fe are also seen in suburban area (smokers and non-smokers houses, both in and outdoors). The concentrations of Fe are in fact highest in the house samples, the reason for this was not identified. Iodine was also fairly ubiquitous throughout the sampled contexts removing its use as an individual tracer molecule for diesel emissions.

In fact many of the identified elements/inorganics are present in all the field samples in varying concentrations. For example, lead is found in all samples, but not necessarily higher in one context in comparison to another. It is present in the roadside samples, in some suburban samples (non-smokers house outdoors) and both the indoor smokers contexts (houses and offices). We can therefore conclude that elemental determination of diesel emissions (or even vehicular emissions) from elemental/inorganic concentrations will need extensive further work to identify possible unique tracer elements or elemental ratios for there contributions to be quantified. Work using Principal Component Factor Analysis (PCA) using SYSTAT software (70) has used similar data to identify sources of outdoor pollution. However, a larger number of samples (in excess of fifty, (51)) are needed for this type of analysis. Mathematical methods such as this are likely to be necessary to identify outdoor sources in the data obtained in this study.

ETS.

Elemental markers for the determination of ETS contribution to an atmosphere have been considered (71). Cadmium was identified as a possible elemental marker, due to its accumulation in the tobacco plant and also its accumulation in the ETS compared to its presence in the filter and ash (72). Cadmium was not identified in the ETS produced in our closed environment ETS experiments (Section 2.2.6.4). However cadmium was identified in many of the contexts sampled, which can be clearly seen in Table 3.14. No obvious relationship was identified between cadmium concentrations and smokers environments. Once again this does not categorically exclude cadmium as a possible ETS marker but perhaps shows that the technique used here was not sensitive enough for cadmium.

Table 3.14: Elements identified in literature of which one possible source is ETS.

Mean concentration (ng/m^3)	Chromium	Nickel	Arsenic	Selenium	Cadmium	Lead
Non smokers house (indoor)	1.8	41.3	0.0	0.0	15.7	2.2
Non smokers house (outdoor)	0.0	3.7	0.0	0.0	2.5	81.5
Smokers house (indoor)	342.8	65.6	0.3	0.0	0.7	15.6
Smokers house (outdoor)	1.9	2.2	0.1	0.0	20.2	0.0
Non Smokers office (indoor)	35.4	236.1	0.0	0.0	10.1	0.0
Non Smokers office (outdoor)	0.0	0.1	0.0	0.0	11.6	0.0
Smokers office (indoor)	2.4	19.8	0.6	1.1	6.9	1.3
Smokers office (outdoor)	4.1	8.4	0.2	0.7	7.2	0.4
Roadside	22.7	55.1	0.3	0.0	3.2	48.2
Countryside	22.2	3.8	0.0	0.0	0.3	0.0

These elements, (identified in Guerin et al (73)), are discussed as being released in tobacco smoke, thereby producing elevated concentrations in smokers contexts. Of these elements, Ni, As, Se and Pb are seen at elevated concentrations in smokers environments compared to non smokers environments. Ni and Pb would seem to be the most abundant. However both these elements have major outdoor sources, including vehicular emissions, oil burning and industrial processes.

Note.

Several of the mean results are artificially high due to one high result due to a point source or an erroneous result. These include Cr (smokers house, indoors), Ni (non smokers office, indoors), and Pb (non smokers house, outdoors).

As and Se seem to be the two consistent and more specific elemental markers for ETS however, their concentrations are low (0.3-0.6ng/m^3 and 1.1 ng/m^3 for smokers houses and smokers offices respectively). These are similar concentrations to those published in Guerin et al (73). As and Se also have a major outdoor pollutant source, as they are both released in coal emissions (51). (no house sampled contained a coal fire). Even so, the two elements could be of interest and specific work identifying the validity of As, Se and Cd as trace concentrations could categorically identify one of these elements as an ETS marker.

3.6 Statistical Analysis of the Field Study Results.

As all field study results (with the exception of the filter gravimetric analysis) were obtained from just one sample point, we are unable to state that the results are definitive, as sampling variation and experimental error were not accounted for through multi-sampling, as this was not logistically possible. It is therefore the wish of all associated with this work that the data published within this thesis be looked upon as preliminary data, onto which further work could be based.

The following section takes these data points and through the use of ratios determined in chapter 2 identifies possible percentage apportionment values for relevant analytes in each context. As these field results are from single point analysis the further statistical manipulation completed (such as the cigarette equivalents data for volatile and particulate associated analyses) was undertaken to compare these results with those published in the scientific literature.

3.6.1.1 Percentage contribution of selective organic compounds to an atmosphere due to Environmental Tobacco Smoke.

The calculation of the contribution of ETS to the concentration of the quantified volatile compounds in each sample was possible, using the ratio determined from the ETS atmospheric samples, (see Section 2.2.6.1). The volatile in question was measured and compared to an ETS specific marker compound found only in the vapour phase. The two volatile compounds identified as possible ETS marker compounds were 3-ethenylpyridine and pyrrole (16). Initially it was necessary to identify how many of the smokers sites contained quantifiable levels of 3-ethenylpyridine and pyrrole. The quantitative results for pyrrole are shown in Table A7 (Appendix A) and graphically in Figure 3.14, with the identification of both pyrrole and 3-ethenylpyridine in the sites is reported in Table 3.15.

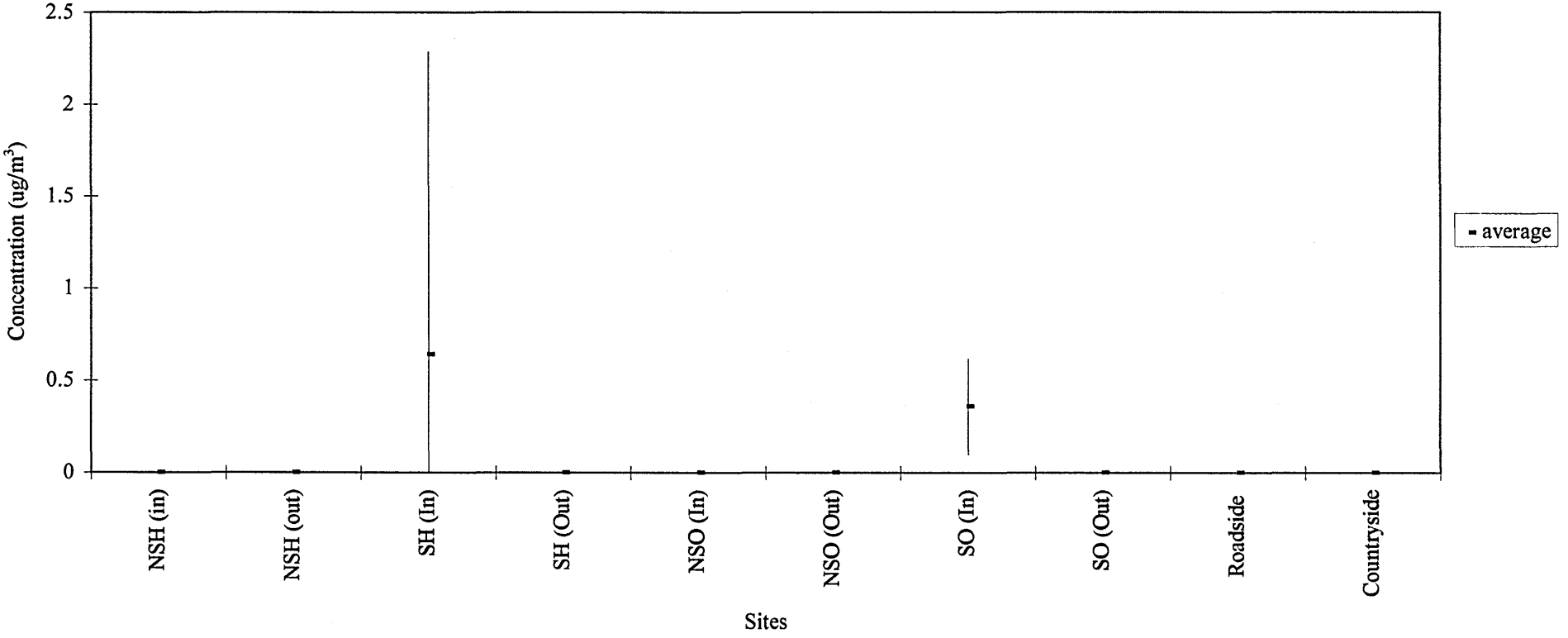

Figure 3.14: Chart to Identify the Highest, Lowest and Average Concentration of Pyrrole in All Atmospheric Contexts.

Table 3.15: Sites in which Quantifiable Levels of 3-Ethenylpyridine and Pyrrole were Present.

		Indoor	Outdoor
Location	Weather	**Pyrrole**	**Pyrrole**
Non smokers houses			
House 1	No rain	N.D.	N.D.
House 2	No rain	N.D.	N.D.
House 3	No rain	N.D.	N.D.
House 4	No rain	N.D.	N.D.
Smokers houses			
House 1	Rain	N.D.	N.D.
House 2	No rain	Yes and 3-EP	N.D.
House 3	No rain	N.D.	N.D.
House 4	Rain	Yes and 3-EP	N.D.
House 5	No rain	N.D.	N.D.
Non smokers offices			
Office 1	No rain	N.D.	N.D.
Office 2	No rain	N.D.	N.D.
Office 3	Rain	N.D.	N.D.
Office 4	Rain	N.D.	N.D.
Smokers offices			
Office 1	No rain	Yes	N.D.
Office 2	No rain	Yes	N.D.
Office 3	Rain	Yes	N.D.
Office 4	Rain	Yes	N.D.
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	N.D.
Roadside sample 2	No rain	N/A	N.D.
Roadside sample 3	Rain	N/A	N.D.
Roadside sample 4	No rain	N/A	N.D.
Roadside sample 5	No rain	N/A	N.D.
Roadside sample 6	Rain	N/A	N.D.
Roadside sample 7	Rain	N/A	N.D.
Roadside sample 8	No rain	N/A	N.D.
Countryside samples			
Countryside sample 1	No rain	N/A	N.D.
Countryside sample 2	Rain	N/A	N.D.

It can be seen from Table 3.15 that pyrrole was found in more smokers sites **(6)** compared to 3-ethenylpyridine **(2),** hence pyrrole was used as the volatile ETS marker compound. The individual quantitative results shown in Table A7 (appendix A), Figure 3.14 indicate that pyrrole is found only in the indoor smokers samples and that hence it is specific and that there is no measurable diffusion of volatile ETS compounds from indoor to outdoor environments.

Using pyrrole as a ETS marker compound, the contribution of the quantified volatile compounds that were attributable to ETS in indoor smoking environments are shown in Table 3.16.

Note. The standard deviation values provided with each individual site contribution value are through instrumental variations seen during the determination of the ratio value (see section 2.2.6.1). The average standard deviation is therefore the summated value of the relevant standard deviation values divided by the number of samples. This provides the variation in apportionment concentration produced from the instrument variation identified when producing volatile ratios associated with standard ETS atmospheres.

The percentage contribution of benzene due to ETS in the smoking house environments exhibits a range of 33.7-94.6% for smoking houses while office contribution were between 4.5-51.1%. Only two of the five house samples contained quantifiable pyrrole, so results for volatiles for these sites are less clear. The average for smokers house samples seems to be quite high, at 64.2%. This is due to the high value obtained from house two and arises since the actual benzene concentration measured was low, producing an erroneously high benzene ETS contribution. The possible reason for the lack of overall quantitative data for volatiles in smokers houses is that the room volumes in the house samples were often larger than the office rooms, increasing diffusion in the house samples. The reduced number of results for smokers houses reduces the confidence and validity of the house results and the majority of discussion will be associated with the office samples.

The average contribution of ETS to benzene levels in the office samples was 25.5%. If this value is calculated using the data given by Crump (12), (taking the difference

between the average concentrations of benzene in the smoking to non smoking house environments, to give an average contribution of benzene being produced from the additional smoking of cigarettes), a value of 25.4% is produced. Similar calculations can be carried out on data given by Heavener (6), producing a value of 30.3%, along with an earlier study by the same author producing a range of 0.2-39.0% in smokers homes (17). These data show that the contribution from ETS to the overall benzene levels are significant. However a previous study that used 3-ethenylpyridine as an ETS marker, identified a mean of 13% benzene contribution to an atmosphere from ETS and stated that this contribution was non-significant (18). However, ETS does seem to elevate benzene concentrations in indoor environments. This contribution has been determined as being between 13-30% in the literature whilst the value I obtained was 25.5% for smokers offices. The contribution to any smokers environment will of course depend upon the quantity of smoking that occurs in the environment over a length of time, in addition to ventilation and room size. However from this study and the published literature we can state that an "average" smoker's room seems to exhibit an increase of between 13-30% in benzene levels due to ETS.

There is an anomalous result in the study of ETS contribution to levels of toluene in the office samples. Sample 1 gives a value of 514% for the toluene concentration attributable to ETS. The reason for this odd result is unknown, presumably the low quantity of toluene identified in the sample results in a major overestimation as the pyrrole concentration in relation to toluene is quite high. If this sample is removed, the average contribution of toluene due to ETS is 27.75%. This is fairly significant, and has not been apparent in previous studies (6). However, the report by Heavner (2) gives a maximum of 27.9% (mean of 5.15%) for the amount of toluene due to ETS, suggesting that the values produced in this field study are slightly high, possibly due to the high ratio value for toluene obtained in the ETS atmospheric samples (see Section 2.2.6.1). This value may be higher than that determined by Heavner et al (2). However, we can to an extent explain this as the sampling system that was used was static. The sample is therefore taken from the smokers room, while personal sampling (as done by Heavner (2)) will also be sampling other atmospheres which may be "cleaner" than the one found in the smokers room. The higher contribution could therefore be explained by the longer sampling period of the field samples taken from the smokers atmosphere.

The contribution of ETS to o-xylene, p+m-xylene isomers and ethyl benzene levels in the smokers offices were 6.92%, 19.05%and 12.39% respectively. These compare to 5.11%, 14.94% and 4.95 % for o-xylene, p+m-xylene and ethyl benzene respectively, as published by Heavner et al (2) at smokers workplace environments. These published results are however from personal samples and not static samplers as in this thesis. This explains the higher concentrations, and the higher percentage apportionment's identified as being due to ETS in this thesis.

Table 3.16: Percentage Contribution of ETS to the Volatile Compounds Quantitatively Studied in the Field Samples.

Location	Weather	Benzene Indoor % Due to ETS	Toluene Indoor % due to ETS	O-xylene Indoor % due to ETS	P+M-xylene Indoor % due to ETS	Ethyl benzene Indoor % due to ETS
Non smokers houses						
Non smokers House 1	No rain	0.00	0.00	0.00	0.00	0.00
Non smokers House 2	No rain	0.00	0.00	0.00	0.00	0.00
Non smokers House 3	No rain	0.00	0.00	0.00	0.00	0.00
Non smokers House 4	No rain	0.00	0.00	0.00	0.00	0.00
Average.		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Smokers houses						
Smokers House 1	Rain	0.00	0.00	0.00	0.00	0.00
Smokers House 2	No rain	94.66±1.46	97.37±5.20	8.59±1.09	14.23±1.08	22.84±2.58
Smokers House 3	No rain	0.00	0.00	0.00	0.00	0.00
Smokers House 4	Rain	33.72±0.52	84.51±4.51	13.70±1.74	22.18±1.69	31.10±3.51
Smokers House 5	No rain	0.00	0.00	0.00	0.00	0.00
Average (2 samples).		**64.19±0.99**	**90.94±4.86**	**11.14±1.42**	**18.20±1.39**	**26.97±3.05**
Non smokers offices						
Non smokers Office 1	No rain	0.00	0.00	0.00	0.00	0.00
Non smokers Office 2	No rain	0.00	0.00	0.00	0.00	0.00
Non smokers Office 3	Rain	0.00	0.00	0.00	0.00	0.00
Non smokers Office 4	Rain	0.00	0.00	0.00	0.00	0.00
Average.		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**

Smokers offices						
Smokers Office 1	No rain	51.08±0.79	514.39 *	7.61±0.96	49.81±3.79	12.59±1.42
Smokers Office 2	No rain	16.59±0.26	9.90±0.53	1.30±0.16	1.93±0.15	3.42±0.39
Smokers Office 3	Rain	4.50±0.07	29.40±1.57	7.79±0.99	7.96±0.61	9.71±1.1
Smokers Office 4	Rain	29.73±0.46	43.95±2.35	10.97±1.39	16.50±1.26	23.85±2.69
Average.		**25.48±0.40**	**27.75±1.48**	**6.92±3.50**	**19.05±1.45**	**12.39±1.4**
Roadside samples (outdoor)						
Roadside sample 1	Rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 2	No rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 3	Rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 4	No rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 5	No rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 6	Rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 7	Rain	0.00	0.00	0.00	0.00	0.00
Roadside sample 8	No rain	0.00	0.00	0.00	0.00	0.00
Average.		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Countryside samples						
Countryside sample 1	No rain	0.00	0.00	0.00	0.00	0.00
Countryside sample 2	Rain	0.00	0.00	0.00	0.00	0.00
Average.		**0.00**	**0.00**	**0.00**	**0.00**	**0.00**

* Anomalous result not used. Average value obtained from the other three samples.

These percentage apportionment for the xylene isomers and ethyl benzene are not as significant as those for benzene and toluene (This is in agreement with previous work (2,6)). There is a quantity of these compounds released from cigarettes and this is apparent from the results obtained in this study. However, the contribution to o-xylene and ethyl benzene levels from ETS is small with the cumulative contribution to m+p-xylene levels being the most significant.

It can be concluded from the work on volatiles that pyrrole can be used as a possible marker compound for the determination of the ETS contribution to levels of VOC. The contribution to benzene and toluene levels has been shown to be significant in this study and to some extent this is confirmed in the literature. A lower significance of the contribution of ETS to levels of the other volatile compounds investigated was found. However, the low number of samples make the data far from conclusive and an increase in the size of the samples taken would have helped to confirm these preliminary data. Further work also needs to be completed, in order to identify the rate and pathways of pyrrole degradation in an atmosphere to ensure that the pyrrole is sufficiently stable volatile to be used as an ETS volatiles marker compound.

Using the percentage contribution identified as being from ETS and the average concentration of the volatiles under investigation, it was possible to identify the "extra" amount of each volatile compound inhaled in a year from exposure to such a smokers atmosphere for 37 hours a week for 48 weeks a year. Using the concentrations of volatile compounds found in mainstream smoke published recently (19), we could also identify the equivalent number of cigarettes that would need to be smoked per year to introduce that quantity of volatile material into an individual.

Table 3.17: Quantities of Additional Volatile Material Inhaled by a Non-smokers When Exposed to a Smokers Environment at Work. The Analogous Number of Equivalent Cigarettes Smoked is also Identified.

	Benzene	Toluene	O-xylene	P+M-xylene	Ethyl benzene
% contribution	**25.48±0.4**	**27.75±1.48**	**6.92±3.5**	**19.05±1.45**	**12.39±1.40**
Smokers Office (μg/m^3)	8.26	25.68	1.96	2.39	2.23
Conc. due to ETS (μg/m^3)	2.10±0.03	7.13±0.38	0.14±0.07	0.46±0.03	0.28±0.03
μg/year	2242.29±35.2	7593.81±404.9	144.47±73.5	485.22±37.3	294.45±33.0
μg/cig. **(ref 19)**	43.6	60.7	2.17	9.57	5.81
cigs/year (ETS)	**51.43±0.81**	**125.10±6.67**	**66.58±33.88**	**50.70±3.9**	**50.68±5.69**

The number of equivalent cigarettes inhaled by a non smoker exposed to a smoky work place over a year period, is very similar for benzene, p+m-xylene and ethyl benzene, with the equivalent of 50 cigarettes being inhaled. The values for o-xylene and toluene are slightly higher. However, in literature, the value obtained using toluene is thought to be high and these data appear to support this hypothesis.

If we assume that the equivalent of 50 cigarettes inhaled in a smokers environment is the approximately correct value we can see that volatile emissions from ETS are significant. A non smoker would inhale approximately the equivalent of one directly smoked cigarette per week. However the measurement is only approximate as the sampling method used in our study was different to that used to identify directly smoked cigarette emissions (i.e. a cryo trap). The brand of cigarette was also different with the quoted published results (19) using LGC monitor cigarettes while we used Rothmans cigarettes. These equivalent values are also specific to volatile compounds since these are likely to have a longer residence time in the atmosphere compared to ETS particulate material.

3.6.2 Particulates.

3.6.2.1 Diesel.

The results for the concentrations of particulate associated C24 (tetracosane) are shown in Table A10 (Appendix A). Using the diesel engine and the large air samples (as described in Section 2.2.6.3), the percentage contribution of diesel particulates to the total particulates measured in various contexts studied in the field samples was calculated. These data are shown in Table 3.18. It can be seen that these results confirm that a quantity of diesel particulate material penetrates indoor environments as has been previously described (7,14,30). For indoor samples the contribution of diesel particulate to total particulate is in the range 0-18.77% (mean of both contexts 6.22%) for suburban houses and 0-59.66% (mean 14.85%) for city centre office samples.

Note.
Non smokers office 4 sample gives a very high value compared to the others, this may be due to a preconcentration of diesel particulate material or more likely due to a source of C24 being present in the office, falsely producing a high contribution.

The values obtained for outdoor samples are generally higher (as would be expected) compared to those from indoor samples with the range of values for outdoor house samples and outdoor office samples being 1.19-52.41% (mean 15.95%) and 3.75-57.88% (mean 25.48%) respectively. The suburban house concentrations are generally lower than the average outdoor office values, which is expected as the office samples are situated in the city centre. However, these office diesel contributions could be artificially lower than the actual contribution due to the fact that the outside office samples were up to 20-30 metres above the roadside while all house samples were taken from no higher than three metres. The city centre office data do tend towards the roadside values (range 4.52-84.02% mean 45.26%) obtained from the city centre and adjacent to major roads radiating from Sheffields city centre.

Table 3.18: Percentage Contribution of Diesel Emissions to Total Particulate Material Found in Each Investigated Context.

	Indoor Filter	Outdoor Filter
Location	% Contribution	% Contribution
Non smokers houses		
House 1	0.56 ±0.09	1.19 ±0.19
House 2	2.07 ±0.33	12.31 ±1.95
House 3	18.77 ±2.97	18.44 ±2.91
House 4	4.45 ±0.70	52.41 ±8.28
Average.	**6.46 ±1.02**	**21.09 ±3.33**
Smokers houses		
House 1	11.94 ±1.89	4.10 ±0.65
House 2	0.00	15.60 ±2.46
House 3	0.00	25.08 ±3.96
House 4	1.10 ± 0.17	3.18 ±0.50
House 5	16.87 ± 2.67	6.02 ±0.95
Average.	**5.98 ±0.95**	**10.80 ±1.71**
Non smokers offices		
Office 1	25.16 ±3.98	19.00 ±3.0
Office 2	6.86 ±1.08	9.70 ±1.53
Office 3	7.44 ±1.18	3.75 ±0.59
Office 4	59.66 ±9.43	57.88 ±9.15
Average.	**24.78 ±3.92**	**22.58 ±3.57**
Smokers offices		
Office 1	1.31 ±0.21	18.00 ±2.84
Office 2	0.00	50.65 ±8.0
Office 3	8.42 ±1.33	24.07 ±3.80
Office 4	9.96 ±1.57	20.77 ±3.28
Average.	**4.92 ±0.78**	**28.37 ±4.48**
Roadside samples (outdoor)		
Roadside sample 1	N/A	41.40 ±6.54
Roadside sample 2	N/A	72.07 ±11.39
Roadside sample 3	N/A	19.69 ±3.11
Roadside sample 4	N/A	70.05 ±11.07
Roadside sample 5	N/A	4.52 ±.71
Roadside sample 6	N/A	9.46 ±1.5
Roadside sample 7	N/A	60.83 ±9.61
Roadside sample 8	N/A	84.02 ±13.28
Average.	**N/A**	**45.26 ±7.15**
Countryside samples		
Countryside sample 1	N/A	0.00
Countryside sample 2	N/A	11.88 ±1.88
Average.	**N/A**	**5.94 ±0.94**

The values obtained for the contribution of diesel particulates to total particulates for roadside samples has a mean of 45.26%. This compares well with results published in Quarg 1996 (31) where PM10/CO correlation's were used. Diesel contributions of between 40-50% were identified. A recent study of Leeds gave diesel emission contributions of 40-50% by mass of particulate material, using particulate sulphate as the marker compound (32). These city centre values are higher than those identified by Horvath (33) where 12-32% of particulate material was identified in the atmosphere as being attributable to diesel. Diesel vehicle numbers have increased since that time (1982) and the values obtained in this study seem a reasonable representation of the concentrations of particulate material. Sheffield, like many other large cities has a large numbers of buses and HGVs passing through it, which will produce the higher concentration of diesel associated particulate material.

Other possible sources of fine particulate material (≤10μm) in the UK which could be responsible for the other 55% of particulate matter include; other combustion sources including petrol (5%), and coal (used for power generation, 14%), heavy industry (15%), re-suspended road dusts (4%), construction (2%) in addition to secondary particulate material (unknown), (34). However, these are country approximations and specific sources would ensure that the quantities would be different if measured in Sheffield specifically. Due to the quantitation of the fine fraction of particulate material (<5μm) coarse material including suspended soil and salt particles are likely to be minor contributors in Sheffield. However, their presence should not be forgotten, and they will contribute in part to the particulate material in all the context samples.

Tetracosane is in fact a poor marker compound for the identification of diesel particulate material. The large air sample results (Section 2.2.6.3) show that there are other major sources of C24. These may include poorly maintained diesel vehicles (35), which allow increased quantities of lubricating oil to pass into the combustion chamber and other combustion sources including (non catalysed and catalysed) petrol engines (36) and even vegetation (36,37). Results obtained after the correction associated with 1-nitropyrene did produce results comparable with those published in literature from other UK sites.

1-Nitropyrene on the other hand has been shown in this work to be an excellent marker compound for particulate diesel emissions. Values from the large city centre particulate samples indicated that 65.3% of the total was due to diesel emissions at that time (see Section 2.2.6.3). The identification of 1-nitropyrene adsorbed to bark surfaces (38) has also demonstrated that the compound, once thought to be a possible by-product of reactions occurring on filter paper surfaces during diesel particulate sampling, is in fact released directly in diesel emissions. Emissions of 1-nitropyrene from other sources in Sheffield, that contribute to particulate material of 5μm and below, seem to be minor in comparison.

3.6.2.2 ETS.

The particulate nicotine concentrations were determined by GC/MSD using the dichloromethane extract (containing 0.01% triethylamine) (1). The quantitative results are shown in Table A11 (Appendix A). It can be clearly seen from these data, that a lower concentration of nicotine is associated with particulate material compared to the vapour phase. In fact 95% of the nicotine released in ETS is found in the vapour phase (39,40). However, once again the nicotine results are very inconsistent. The quantities determined do not follow the pattern of ETS concentration determined using the other particulate methods, observed in Figure 3.15. Besides the inherent difficulty in detecting the low concentrations of nicotine in some of the sites, a high level of ETS is not observed in house 4, and a perversely high concentration of particulate associated nicotine was identified in house 3. The problems associated with the use of nicotine as an ETS marker are discussed at great length in the literature and it is generally felt that nicotine is a poor maker for ETS analysis, due to its inconsistent phase distribution and its short half-life once released into the atmosphere.

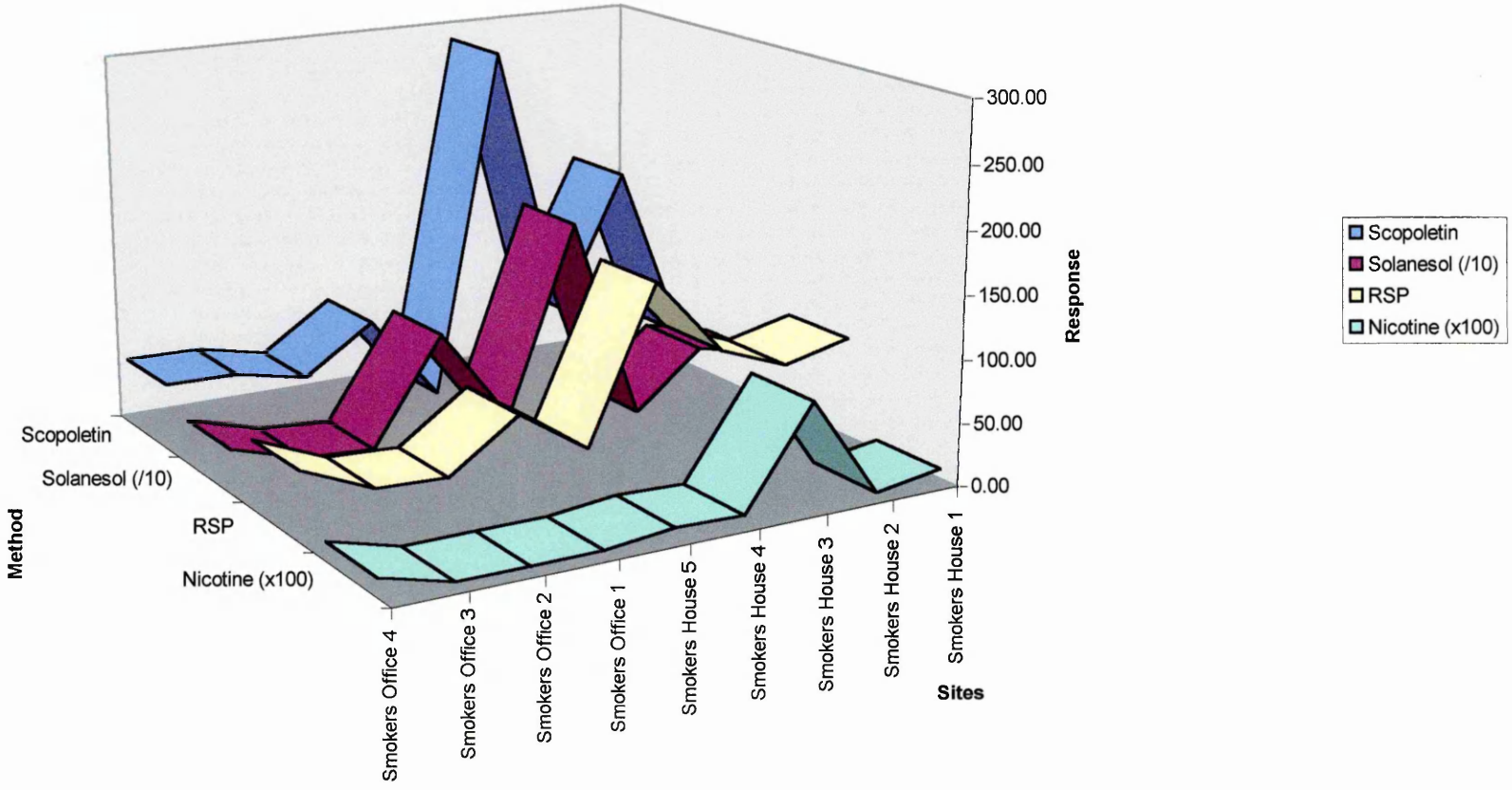

Figure 3.15: Comparrison of Particulate Associated Nicotine with Other Methods of Particulate ETS Analysis.

The contribution of ETS to particulate material in an atmosphere was initially measured using the quantity of respirable suspended particulates (RSP) determined in the sample (3,41,42). However the results obtained in this study for particulates of ≤5μm in diameter (Table 3.2) show that such particulate material is found ubiquitously. This is apparent in other publications from field studies (2,43). The use of RSP therefore overestimates the contribution of ETS to an atmosphere.

This overestimation was reduced to some extent by the use of a total UV method which quantified the UV absorbance of a methanol extract of the sampled particulate material (see Section 2.1.2). The total UV concentrations obtained in this study can be seen in Table A12 (Appendix A) and are represented graphically in Figure 3.16. These data clearly show that the sites in which smoking has taken place give higher average concentrations of total UV and also much wider ranges. The average concentration of total UV in the two indoor smoking contexts are 17.35μg/m^3 and 9.27μg/m^3 for houses and offices respectively. The next highest mean total UV value in all the other contexts is 2.56μg/m^3 which is the outdoor samples of smokers houses. This difference in total UV concentration in the smoking/non smoking contexts compares favourably with published data (2,44). In these papers higher concentrations are also seen in the smoking contexts. However, there is always a response for total UV in all sample contexts (this is also reported in the literature (2,45)) indicating that the total UV method is not specific to ETS and that overestimation is inevitable (45).

From the results obtained in this field study, and the ratio values obtained from ETS atmosphere analysis (Section 2.2.6.3), it was possible to identify the percentage contribution of ETS to the total particulates in the various contexts, using the total UV analytical method.

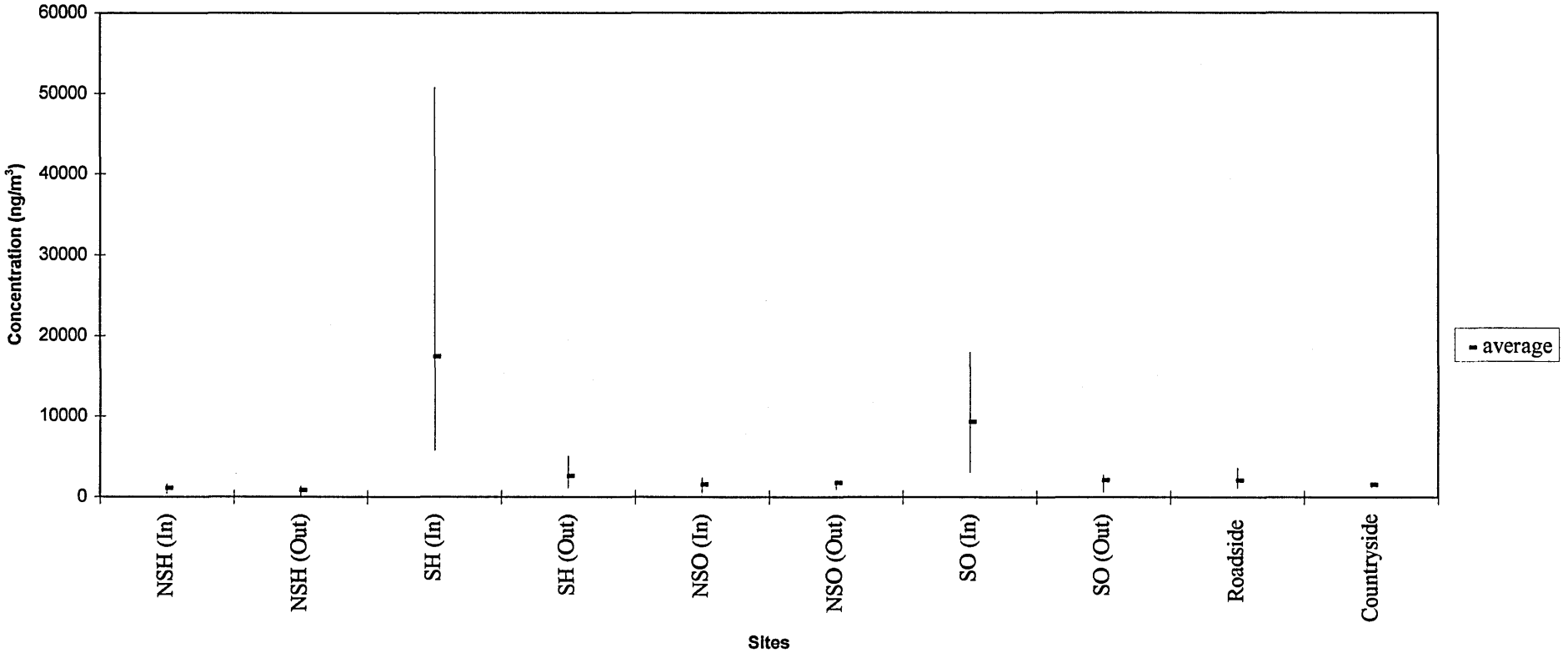

Figure 3.16: Chart to Identifying the Highest, Lowest and Average Concentration ofa Methanol Extract of Particulate Associated Organic Material Quantified by Total UV absorbance in All Atmospheric Contexts.

This was calculated by the following method:-

$$\% \text{ contribution} = (Y/X) \times 100$$

where Y = particulate material ($\mu g/m^3$) equivalent to total UV value obtained in the field sample.

i.e. Y = total UV value$_{(\text{field sample})}$ ($\mu g/m^3$) x ratio value

ratio value for total UV = 5.3 (as the ratio value is equivalent to the total UV response for every μg of ETS particulate material).

X = particulate material in field sample ($\mu g/m^3$).

The percentage contributions of ETS to total particulates to each sample site measured using the total UV analysis method can be seen in Table 3.19 and graphically in Figure 3.17.

It can be seen that once again, the average values are far higher in the two indoor smoking environments, with 67.3% and 71.3% total particulates being attributable to ETS in smoking houses and offices respectively. The next highest value is the outdoor samples of smokers offices at 51.6%. All other sample sites give a value for ETS contribution of above 10%. This clearly illustrates the overestimation obtained using this method. Values for a mean percentage contribution from ETS obtained by UV analysis given in the literature are 44.85% and 39.5% in smokers homes and smokers work environments respectively (2). These values are lower than those indicated by our work. This is as expected since the samples in the literature (2) were from personal monitors, whilst our work is based on static room sampling. The data reported by Phillips (45) also indicate that total UV analysis overestimates percentage ETS contribution, since he demonstrated that the use of marker specific compounds (solanesol and scopoletin) gave lower values.

Table 3.19: Percentage Contribution of Particulate Material Attributable to ETS in an Atmosphere Using Total UV as the Method of Analysis.

Location Non smokers houses	Weather	**Indoor**	**Outdoor**
House 1	No rain	19.04 ±1.62	19.84 ±1.68
House 2	No rain	4.54 ±0.39	7.37 ±0.63
House 3	No rain	8.88 ±0.75	1.60 ±0.14
House 4	No rain	12.68 ±1.08	17.01 ±1.44
Average		**11.29 ±0.96**	**11.45 ±0.97**
Smokers houses			
House 1	Rain	44.16 ±3.75	11.36 ±0.96
House 2	No rain	69.00 ±5.86	13.01 ±1.10
House 3	No rain	33.59 ±2.85	14.91 ±1.27
House 4	Rain	124.72 ±10.59	49.72 ±4.22
House 5	No rain	64.91 ±5.51	58.64 ±4.98
Average		**67.27 ±5.71**	**29.53 ±2.51**
Non smokers offices			
Office 1	No rain	53.30 ±4.53	26.96 ±2.29
Office 2	No rain	15.36 ±1.30	12.83 ±1.09
Office 3	Rain	28.54 ±2.42	15.97 ±1.36
Office 4	Rain	14.39 ±1.22	42.61 ±3.62
Average		**27.90 ±2.37**	**24.59 ±2.09**
Smokers offices			
Office 1	No rain	59.49 ±5.05	44.73 ±3.8
Office 2	No rain	42.23 ±3.59	7.37 ±0.63
Office 3	Rain	62.33 ±5.29	74.58 ±6.33
Office 4	Rain	121.18 ±10.29	79.67 ±6.76
Average		**71.31 ±6.06**	**51.59 ±4.38**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	77.70 ±6.60
Roadside sample 2	No rain	N/A	68.29 ±5.8
Roadside sample 3	Rain	N/A	31.35 ±2.66
Roadside sample 4	No rain	N/A	19.91 ±1.69
Roadside sample 5	No rain	N/A	27.64 ±2.35
Roadside sample 6	Rain	N/A	43.03 ±3.65
Roadside sample 7	Rain	N/A	27.54 ±2.34
Roadside sample 8	No rain	N/A	18.42 ±1.56
Average		**N/A**	**39.23 ±3.33**
Countryside samples			
Countryside sample 1	No rain	N/A	14.43 ±1.23
Countryside sample 2	Rain	N/A	14.53 ±1.23
Average		**N/A**	**14.48 ±1.23**

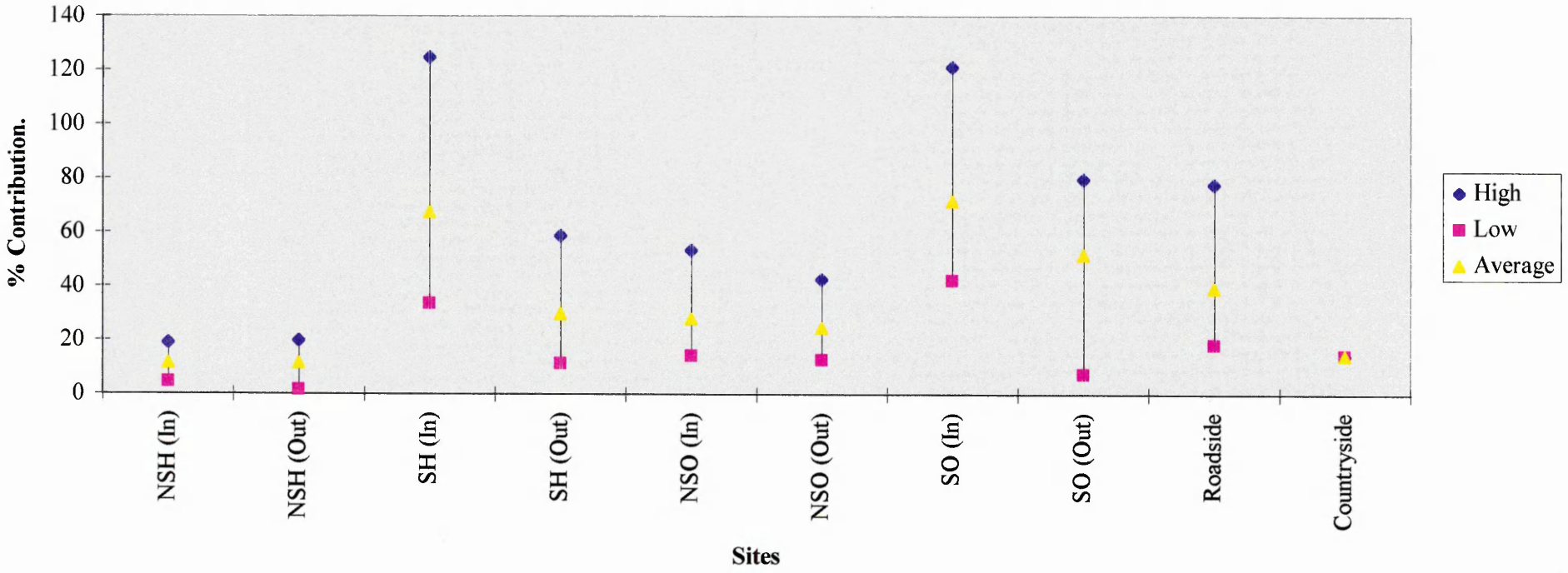

Figure 3.17: The Percentage Contribution of ETS to All Atmospheric Environments Calculated from Data Obtained by Using Total UV as the Method of Analysis.

Two of the smokers samples (smokers house 4 and smokers office 4) give a contribution to particulates from ETS of above 100% (124.7% and 121.2% respectively). These results further support the hypothesis that total UV analysis produces an over estimation of ETS particulate contribution in any sample.

Total UV analysis has been largely superseded by the use of a total fluorescence method (46) for ETS particulate material quantitation, as described in Section 2.2.5.2. The raw data for the total fluorescence values can be seen in Table A13 (Appendix A) and are represented graphically in Figure 3.18. It can be seen from these data, that the average fluorescence values are higher in the smokers indoor samples with smokers houses and smokers offices giving values of 2.06μg/m^3 and 1.61μg/m^3 respectively. These results are similar to those published in the literature (2), although the samples used were from personal monitors. However, once again it can be seen that there is a total fluorescence value obtained from all the sites. This once again indicates that the values for ETS particulate contributions calculated using the total fluorescence method, will be over-estimated.

These values are shown in Table 3.20 and represented graphically in Figure 3.19. The average percentage contribution seen in the two smokers contexts are lower than those identified by total UV (smokers houses 40.94% compared to 67.27% and smokers offices 62.11% compared to 71.31%). This shows that total fluorescence is a more specific method for the identification of ETS particulate contribution than total UV. The values of ETS obtained using the fluorescence method (using personal samplers), reported in the literature are 39.28% and 34.02% (for smokers houses and offices respectively (2)). These are lower than the median values from total UV measurements given in the same paper showing that total fluorescence is a more specific ETS method. However, it will still produce an overestimation compared to the use of specific marker compounds (45).

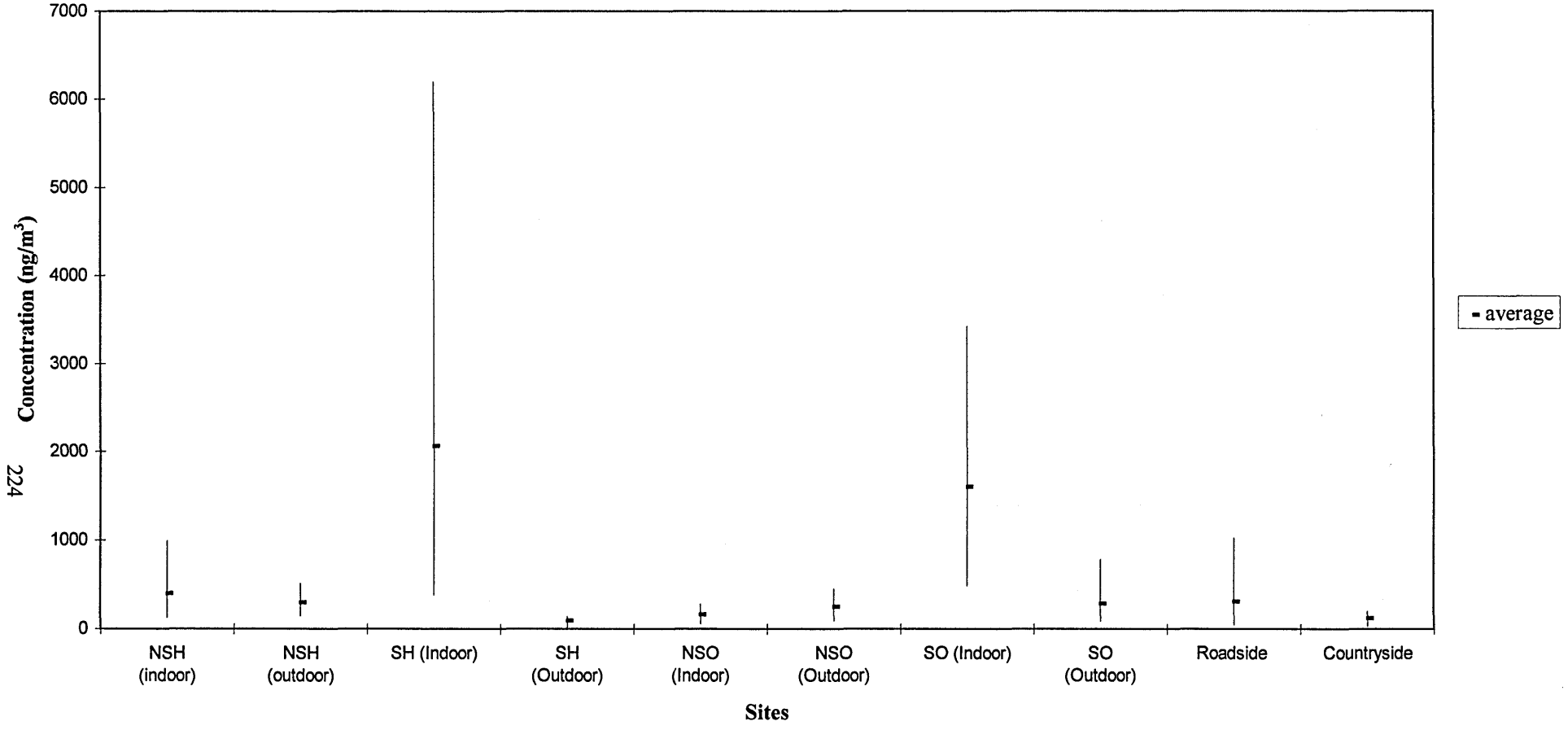

Figure 3.18: Chart to Identify Highest, Lowest and Average Concentration of Total fluorescence (ng/m^3 Scopoletin as Standard) in All atmospheric Contexts.

Table 3.20: Percentage Contribution of Particulate Material Attributable to ETS in an Atmosphere Calculated using Total Fluorescence as the Method of Analysis.

Location	Weather	Indoor	Outdoor
Non smokers houses			
House 1	No rain	7.87 ±0.90	12.64 ±1.44
House 2	No rain	23.39 ±2.66	32.52 ±3.7
House 3	No rain	34.11 ±3.89	66.45 ±7.57
House 4	No rain	10.00 ±1.14	10.84 ±1.23
Average		**18.84 ±2.15**	**30.61 ±3.49**
Smokers houses			
House 1	Rain	17.33 ±1.98	5.16 ±0.59
House 2	No rain	56.50 ±6.44	9.05 1.03±
House 3	No rain	25.36 ±2.89	2.97 ±0.34
House 4	Rain	82.47 ±9.4	0.26 ±0.03
House 5	No rain	23.04 ±2.63	9.11 ±1.04
Average		**40.94 ±4.67**	**5.31 ±0.61**
Non smokers offices			
Office 1	No rain	7.31 ±.83	11.54 ±1.32
Office 2	No rain	15.32 ±1.75	9.98 ±1.14
Office 3	Rain	22.77 ±2.59	40.00 ±4.56
Office 4	Rain	10.57 ±1.20	10.68 ±1.22
Average		**13.99 ±1.59**	**18.05 ±2.06**
Smokers offices			
Office 1	No rain	100.83 ±11.49	92.66 ±10.56
Office 2	No rain	36.04 ±4.11	7.28 ±0.83
Office 3	Rain	44.22 ±5.04	13.05 ±1.49
Office 4	Rain	67.34 ±7.67	21.26 ±2.42
Average		**62.11 ±7.08**	**33.56 ±3.83**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	17.85 ±2.03
Roadside sample 2	No rain	N/A	103.52 ±11.80
Roadside sample 3	Rain	N/A	64.12 ±7.31
Roadside sample 4	No rain	N/A	3.20 ±0.36
Roadside sample 5	No rain	N/A	11.50 ±1.31
Roadside sample 6	Rain	N/A	16.68 ±1.90
Roadside sample 7	Rain	N/A	12.91 ±1.47
Roadside sample 8	No rain	N/A	3.56 ±0.41
Average		**N/A**	**29.17 ±3.32**
Countryside samples			
Countryside sample 1	No rain	N/A	12.97 ±1.48
Countryside sample 2	Rain	N/A	1.29 ±0.15
Average		**N/A**	**7.13 ±0.82**

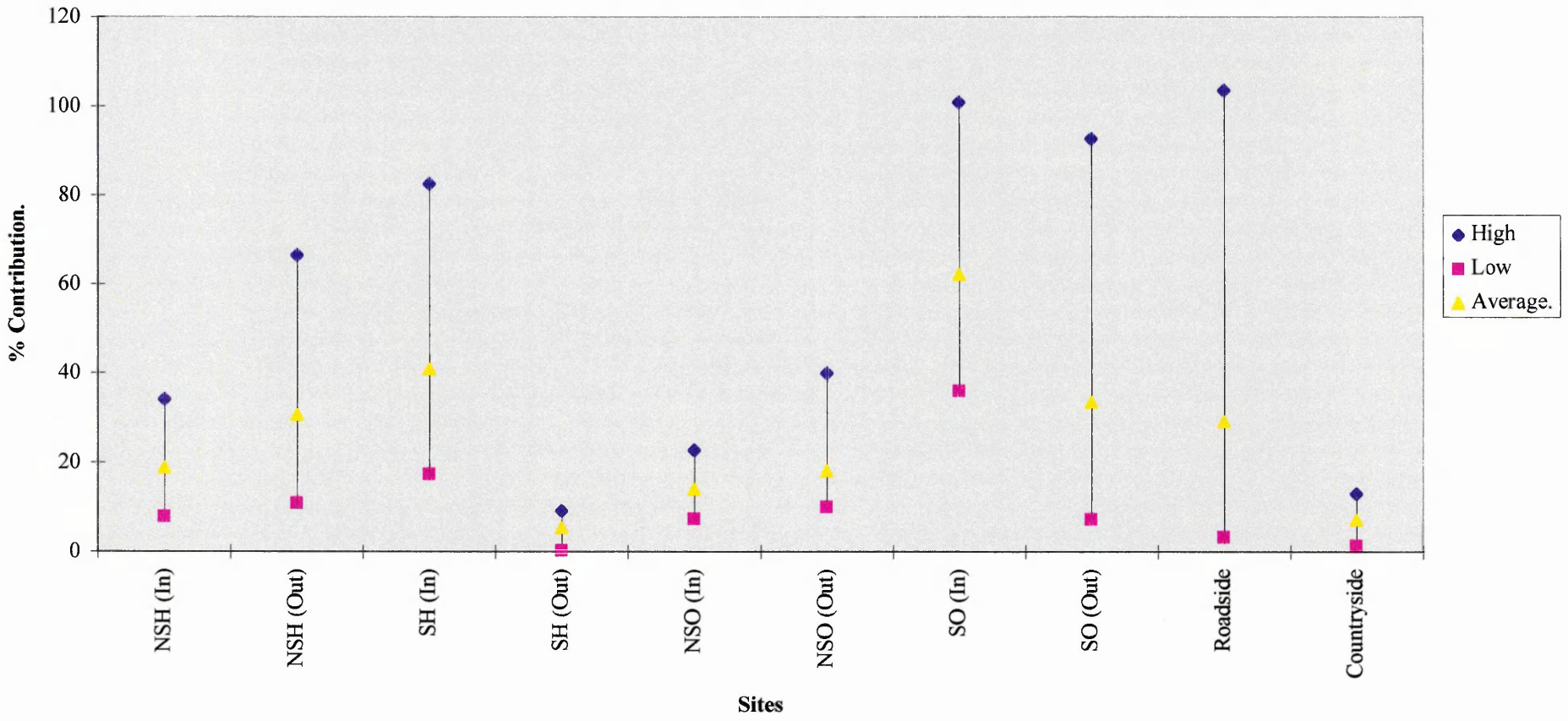

Figure 3.19: The Percentage Contribution of ETS to All Atmospheric Environments using Total Fluorescence as the Method of Analysis.

Since the total fluorescence method gives a response from all the other contexts, the range of contributions looks similar for many of the sampling sites (Figure 3.19). This indicates that there are other sources that can contribute to the total fluorescence value. An example of another source is diesel particulates and this may be very significant in roadside samples, which are seen to have a broad range of contributions (3.2%-103.52%). Particulate emission samples were taken from a test diesel engine (see Section 2.2.1.1) and analysed for total fluorescence as described in Section 2.2.5.2. From this analysis a value of 2336.50μg/g for diesel particulate material was obtained.

If we use this very approximate value to determine the contribution of roadside particulate material attributable to diesel emissions, we will be able to understand the effect that other sources are capable of having on the total fluorescence measurements from the various sites. The concentrations of total fluorescence were converted from ng/m^3 to μg/g and a percentage apportionment for diesel to roadside samples was calculated. These results can be seen in Table 3.21.

Table 3.21: Identification of other possible fluorescence sources in the atmosphere, such as diesel particulate material.

Site	% contribution
Roadside 1	93.97
Roadside 2	149.40
Roadside 3	76.49
Roadside 4	2.33
Roadside 5	19.41
Roadside 6	31.09
Roadside 7	10.70
Roadside 8	3.28
Average	48.33

It can be seen that diesel particulate apportionment by this method is highly variable with values being from 2.33%-149.4%, with a mean of 48.33% of the fluorescence in the roadside samples arising due to diesel emissions. These results indicate that the fluorescence method for diesel determination is poor, but they do show that numerous

sources (and specifically diesel particulate emissions) are likely to contribute to total fluorescence in the various sampling contexts.

It can therefore be seen that there is an over-estimation of ETS obtained by using total UV and total fluorescence methods. Even so, they have regularly been used for ETS apportionment. Recently, marker compounds specific to ETS have been identified, and used to obtain a more accurate apportionment value for ETS.

Solanesol.

Solanesol was determined in all the field samples, with the concentration data shown in Table A14 (Appendix A) and graphically in Figure 3.20. These data clearly identify that solanesol is found only in sites where smoking has occurred. This shows that solanesol is an ideal marker for ETS. Using the ratio for solanesol concentration to total particulate concentration determined in Section 2.2.6.3, a value for the percentage contribution of ETS to total particulates was calculated for all the sites. These data can be seen in Table 3.21 and are represented graphically in Figure 3.21. An average value of 21.7% and 23.3% for smokers houses and offices respectively, was obtained. These results are very similar to the solanesol particulate apportionment data published (2) of 31.3% and 27.2% for smokers houses and work places (personal sampling was undertaken in this study). These average contributions for ETS particulate material are far lower than those determined by the total UV and total fluorescence values as solanesol is more specific to ETS than the other methods.

The percentage contributions obtained from the smokers house samples vary quite considerably, ranging from 5.89-48.98%. These variations are due to the variation in room size, ventilation, number of cigarettes smoked, and the relationship between the site of smoking and the site of the sampler, as room samples were taken, not personnel samples. However, smokers house 4 is clearly identified as the site with the highest proportion of ETS particulate material. This would be expected from that particularly smokey atmosphere.

The office samples give more consistent values for the contribution of particulate material due to ETS. This is in part be due to the offices being of roughly the same size, having similar ventilation rates and since a similar number of cigarettes were smoked during the sampling period.

Given the data reported in this thesis and since solanesol is stable in the atmosphere when attached to ETS particulate material, (it has been shown to degrade little over a one hour period (20) and longer (22)), solanesol is an excellent marker method by which ETS particulate contribution can be determined.

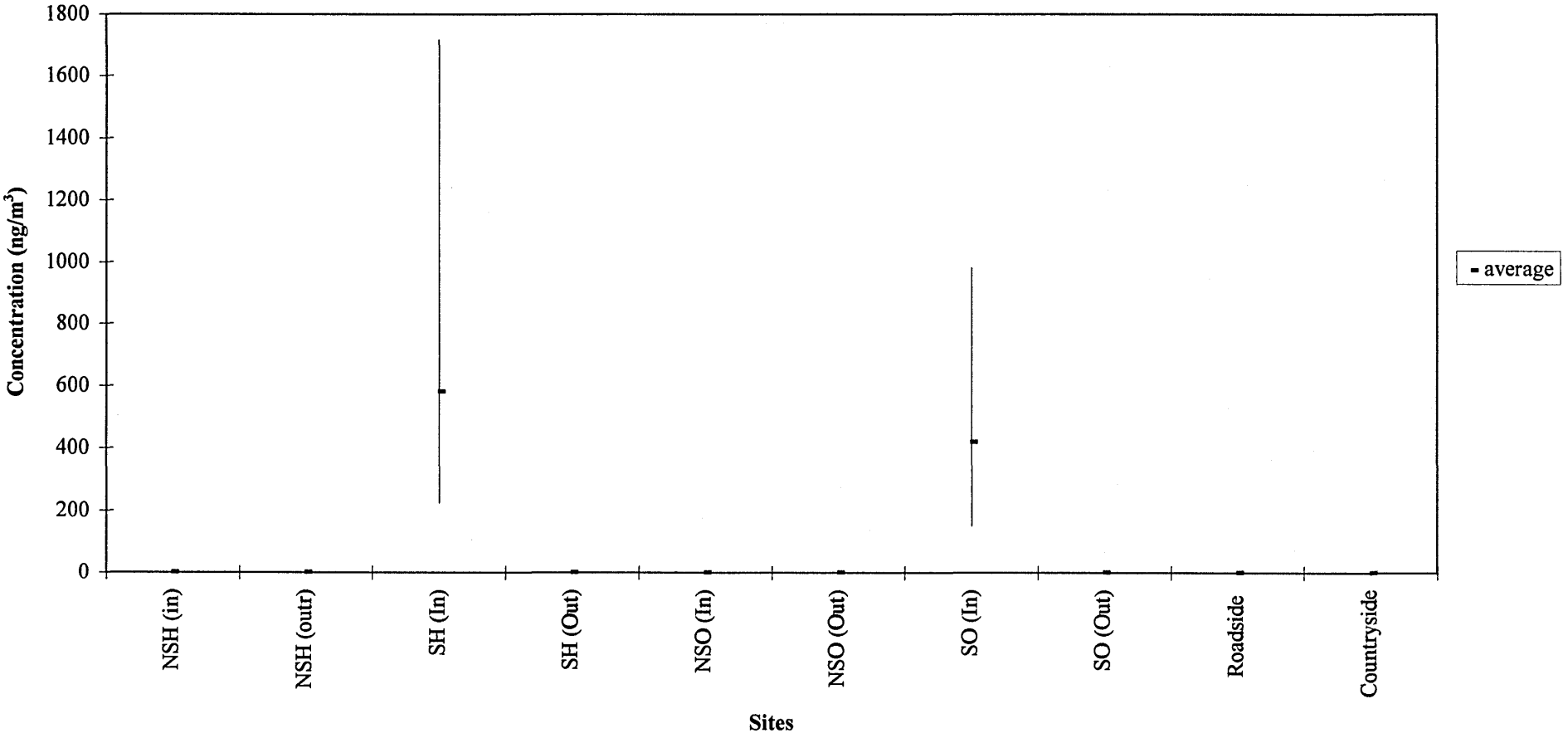

Figure 3.20: Chart to Identify the Highest, Lowest and Average Concentration of Solanesol (ng/m^3) in All Atmospheric Contexts.

Table 3.21: Percentage Contribution of Particulate Material Attributable to ETS in an Atmosphere Calculated using Solanesol as a Marker Compound Method of Analysis.

Location	Weather	Indoor	Outdoor
Non smokers houses			
House 1	No rain	0.00	0.00
House 2	No rain	0.00	0.00
House 3	No rain	0.00	0.00
House 4	No rain	0.00	0.00
Average		**0.00**	**0.00**
Smokers houses			
House 1	Rain	9.32 ±0.68	0.00
House 2	No rain	15.00 ±1.10	0.00
House 3	No rain	5.89 ±0.43	0.00
House 4	Rain	48.98 ±3.60	0.00
House 5	No rain	29.31 ±2.15	0.00
Average		**21.70 ±1.59**	**0.00**
Non smokers offices			
Office 1	No rain	0.00	0.00
Office 2	No rain	0.00	0.00
Office 3	Rain	0.00	0.00
Office 4	Rain	0.00	0.00
Average		**0.00**	**0.00**
Smokers offices			
Office 1	No rain	27.46 ±2.02	0.00
Office 2	No rain	10.57 ±0.78	0.00
Office 3	Rain	27.16 ±1.99	0.00
Office 4	Rain	27.99 ±2.06	0.00
Average		**23.29 ±1.71**	**0.00**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	0.00
Roadside sample 2	No rain	N/A	0.00
Roadside sample 3	Rain	N/A	0.00
Roadside sample 4	No rain	N/A	0.00
Roadside sample 5	No rain	N/A	0.00
Roadside sample 6	Rain	N/A	0.00
Roadside sample 7	Rain	N/A	0.00
Roadside sample 8	No rain	N/A	0.00
Average		**N/A**	**0.00**
Countryside samples			
Countryside sample 1	No rain	N/A	0.00
Countryside sample 2	Rain	N/A	0.00
Average		**N/A**	**0.00**

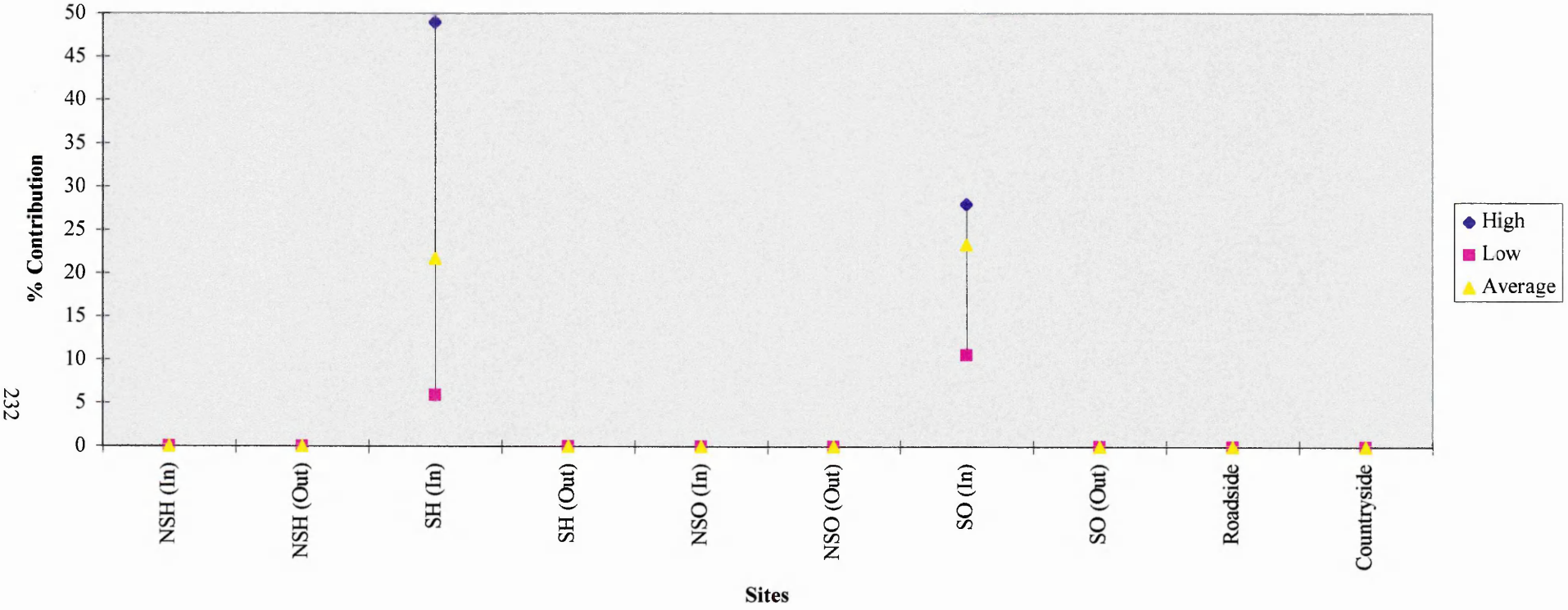

Figure 3.21: The Percentage Contribution of ETS to Total Particulate Material in All Atmospheric Environments Calculated by Using Solanesol as a Marker Compound.

Scopoletin.

The concentrations of scopoletin determined in all the field samples can be seen in Table A15 (appendix A) and represented graphically in Figure 3.22. The results show that scopoletin was found only in sample sites where smoking had taken place. Mean concentrations of 112.5ng/m^3 and 56.48ng/m^3 in smokers houses and offices respectively, were obtained. Scopoletin is therefore also a specific marker compound for ETS.

Using the ratio value for scopoletin determined in Section 2.2.6.3 the percentage contributions to total particulate due to ETS were calculated and are shown in Table 3.22 and represented graphically in Figure 3.23. The average are 8.32% and 9.59% for smokers house and offices respectively. Compared to the solanesol values, these are far lower for nearly all the sites. This indicates that scopoletin may under-estimate the contribution of particulate ETS to a sample. This is possibly due to its instability when exposed to UV radiation. Another reason for this underestimation could be due to an error in the ratio value obtained from the total smoke environment. The samples were taken over a short period of time after a number of cigarettes had been rapidly smoked by a smoking machine. The sample could therefore contain a higher proportion of scopoletin as it has had little time to "age" before being sampled onto the filter paper. This value was used on sample measurements that were collected over a twelve hour period, during which time ageing of the ETS will have occurred. This would produce a lower than expected value for scopoletin and ultimately produce an underestimation of the contribution of ETS to an environment.

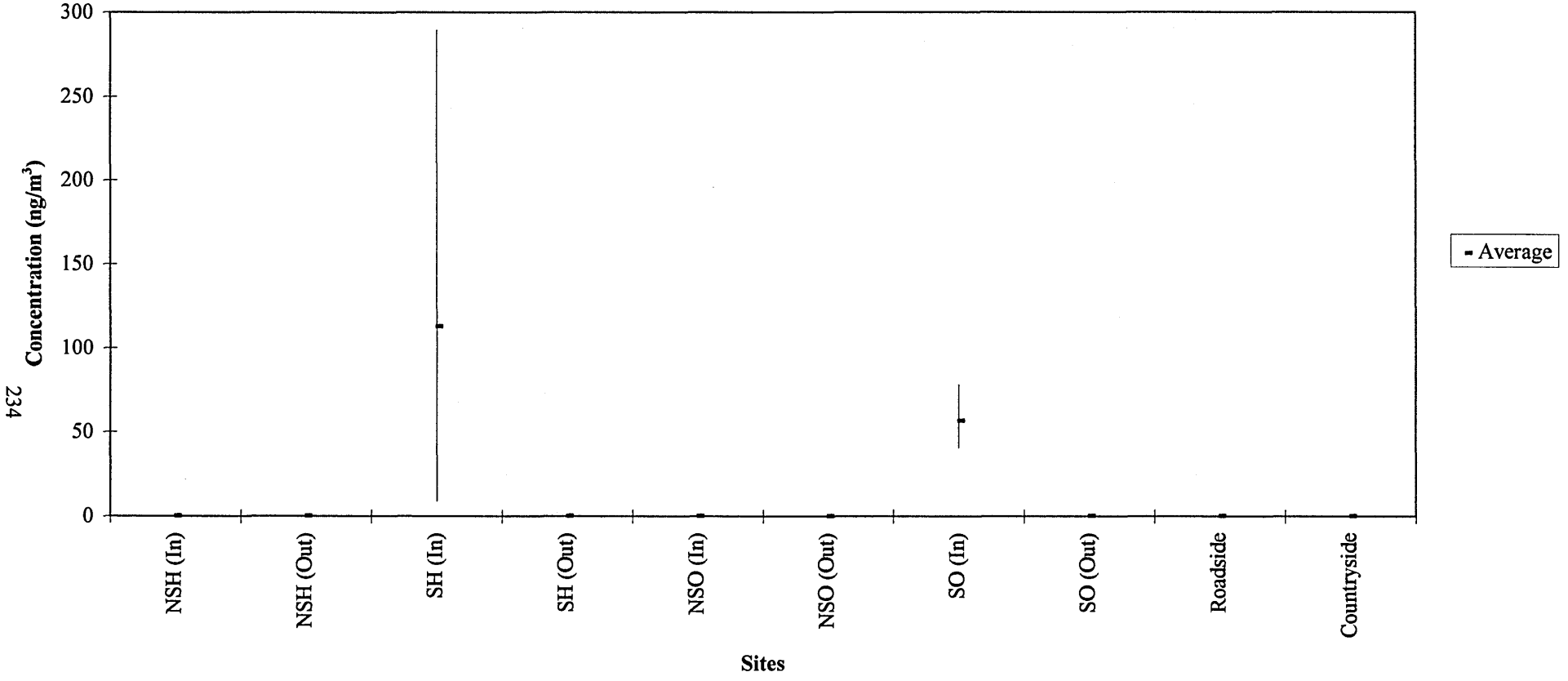

Figure 3.22: Chart identifying the Highest, Lowest and Average Concentration of Scopoletin in All Atmospheric Contexts.

Table 3.22: Percentage Contribution of Particulate Material Attributable to ETS in an Atmosphere using Scopoletin as a Marker Compound.

Location	Weather	**Indoor**	**Outdoor**
Non smokers houses			
House 1	No rain	0.00	0.00
House 2	No rain	0.00	0.00
House 3	No rain	0.00	0.00
House 4	No rain	0.00	0.00
Average		**0.00**	**0.00**
Smokers houses			
House 1	Rain	2.294 ±0.12	0.00
House 2	No rain	19.068 ±0.96	0.00
House 3	No rain	4.725 ±0.24	0.00
House 4	Rain	13.618 ±0.68	0.00
House 5	No rain	1.904 ±0.10	0.00
Average		**8.32 ±0.42**	**0.00**
Non smokers offices			
Office 1	No rain	0.00	0.00
Office 2	No rain	0.00	0.00
Office 3	Rain	0.00	0.00
Office 4	Rain	0.00	0.00
Average		**0.00**	**0.00**
Smokers offices			
Office 1	No rain	8.15 ±0.41	0.00
Office 2	No rain	10.65 ±0.53	0.00
Office 3	Rain	12.64 ±0.63	0.00
Office 4	Rain	6.92 ±0.35	0.00
Average		**9.59 ±0.48**	**0.00**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	0.00
Roadside sample 2	No rain	N/A	0.00
Roadside sample 3	Rain	N/A	0.00
Roadside sample 4	No rain	N/A	0.00
Roadside sample 5	No rain	N/A	0.00
Roadside sample 6	Rain	N/A	0.00
Roadside sample 7	Rain	N/A	0.00
Roadside sample 8	No rain	N/A	0.00
Average		**N/A**	**0.00**
Countryside samples			
Countryside sample 1	No rain	N/A	0.00
Countryside sample 2	Rain	N/A	0.00
Average		**N/A**	**0.00**

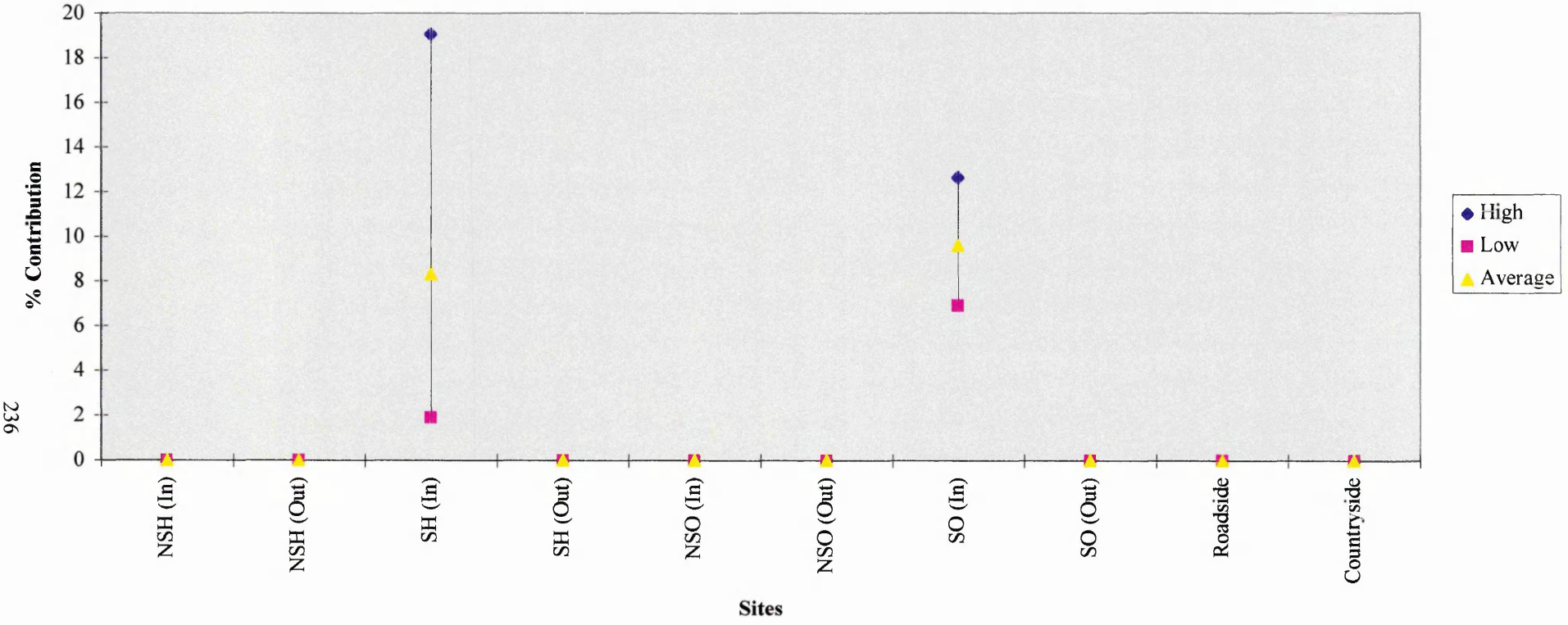

Figure 3.23: The Percentage Contribution of ETS to Total Particulate Material in All Atmospheric Environments Calculated by Using Scopoletin as a Marker Compound.

Scopoletin as a quantity of total fluorescence.

As total fluorescence and the scopoletin measurements were both quantified using scopoletin as an external calibrant, along with the same detection excitation/emission wavelengths, it was possible to identify the percentage of the total fluorescence attributable to scopoletin. This is useful as other possible fluorescent tracer molecules may be identified if different HPLC columns and eluents are used to achieve separation. The contribution of scopoletin to total fluorescence is given in Table 3.23.

Table 3.23: The Average Percentage Contribution of Scopoletin to Total Fluorescence Measurements.

% Scopoletin of total fluorescence	
Location Smokers houses	Indoor
House 1	3.74
House 2	9.54
House 3	5.27
House 4	4.67
House 5	2.34
Average	**5.11**
Smokers offices	
Office 1	2.28
Office 2	8.36
Office 3	8.08
Office 4	2.91
Average	**5.41**

The ETS contributions calculated using scopoletin ranged from 2.28% to 9.54% with an average of around 5% for the two smoking contexts. This indicates that scopoletin contributes only a small amount to the total fluorescence measurements and that there is a lot of other fluorescent material in ETS that may not as yet have been identified. These could include various PAH as well as a number of scopoletin derivatives.

Comparison of the four particulate ETS methods.

If we compare all the ETS related samples and the four methods for particulate ETS determination (Figure 3.24 and 3.25) several similarities become evident. All the particulate methods under investigation follow a very similar pattern, with house 4 consistently having the highest values and the variation in concentration indicated by each individual method being replicated by all the methods. Slight differences can be seen, i.e. solanesol goes up from office 3 to office 4 while the scopoletin concentration drops. However, overall the methods do seem to follow each other very well.

If we plot two of the different particulate ETS methods against each other, the correlation coefficient R^2 relates to how well the two methods compare with each other. The more closely the methods follow each other, the closer the R^2 value of the straight line approaches 1. Such plots can be seen in Figures 3.26-3.31 which clarify if the four methods are comparable with each other for samples taken from smoking contexts.

Figure 3.26 (total UV against total fluorescence) shows that the two methods increase uniformly with increased levels of ETS, the variation of some values will be due to other sources artificially increasing them. In fact, all four methods used (total UV, total fluorescence, solanesol and scopoletin) when plotted against each other do show good correlation with R^2 value ranging from 0.75-0.95 (The lower R2 values are produced when UV based detection methods are compared with florescence detection methods, producing higher variation). These value are a lot higher than those identified by Phillips et al (45). This may be because they had a larger sample in which larger variations occurred, and since they also included samples from non-smoking contexts. However, for smoking environments they found good correlation between total UV and solanesol as well as total fluorescence and solanesol. More recent work by Phillips (43) identified R^2 values of 0.82 for solanesol determination compared to total fluorescence, 0.86 for solanesol/total UV and 0.98 for total UV/total fluorescence. These values are very similar to those shown in Figure 3.29, 3.27 and 3.26, where values of 0.87, 0.95 and 0.84 were obtained for solanesol/total fluorescence, solanesol/total UV and total UV/total fluorescence respectively.

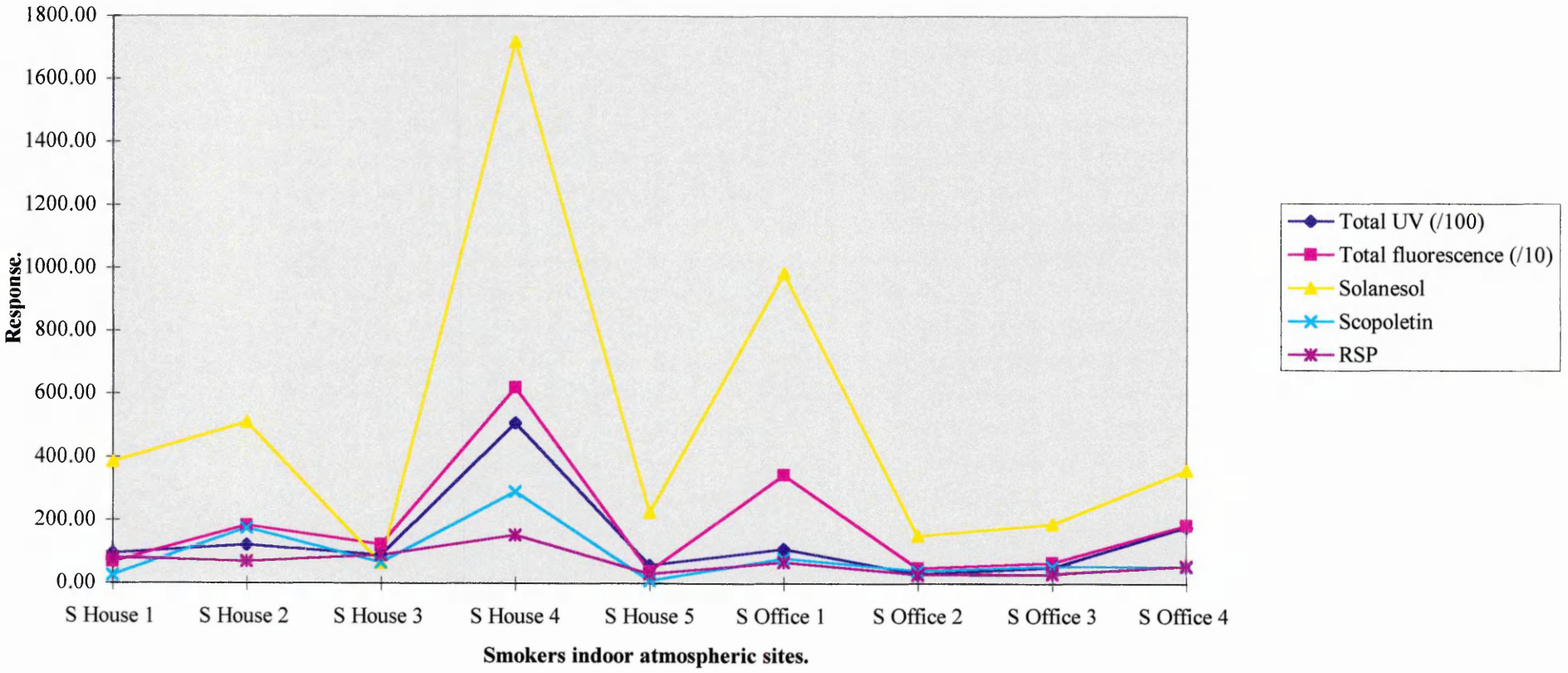

Figure 3.24: Comparrison of the Response for the particulate associated ETS Detection Methods

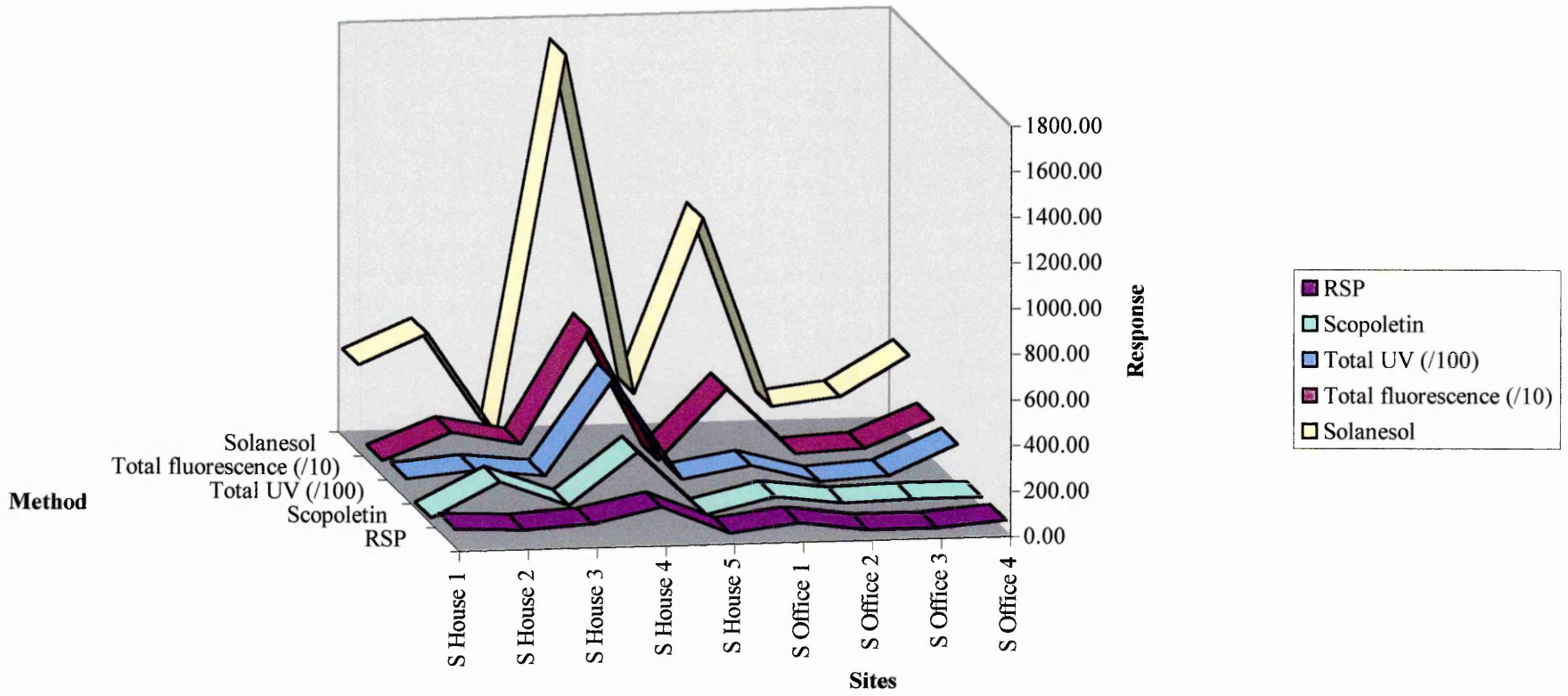

Figure 3.25: Comparrision of the Response for the ETS Particulate Related Detection Methods.

The results also follow the trend in concentrations and percentage contribution seen in the small number of papers released on this subject. These identify that RSP grossly overestimates the contribution of ETS to an indoor atmosphere, as particulate material can be released from a whole range of other sources. The introduction of total UV and total fluorescence reduced this overestimation to some extent (with fluorescence measurements producing a more accurate ETS contribution value). However, by the use of tracer molecules, i.e. solanesol, it has been clearly shown that both the total spectroscopic methods overestimated ETS contribution.

Table 3.24: shows the average overestimation of ETS in determinations carried out by total UV, and total fluorescence using the solanesol measurements as the accurate (true) data.

Table 3.24: Percentage Overestimation of ETS obtained from Total UV and Total Fluorescence measurements in all Contexts when Compared to Solanesol Measurements.

Site	Total UV	Total Fluorescence.
Non smokers house (In)	11.29 ±0.96	18.84 ±2.15
Non smokers house (Out)	11.45 ±0.97	30.61 ±3.49
Smokers house (In)	45.57 ±4.12	19.24 ±3.08
Smokers house (Out)	29.53 ±2.51	5.31 ±0.61
Non smokers office (In)	27.9 ±2.37	13.99 ±1.59
Non smokers office (Out)	24.59 ±2.09	18.05 ±2.06
Smokers office (In)	48.02 ±4.35	38.82 ±5.37
Smokers office (Out)	51.59 ±4.38	33.56 ±3.83
Roadside	39.23 ±3.33	29.17 ±3.32
Countryside	14.48 ±1.23	7.13 ±0.82

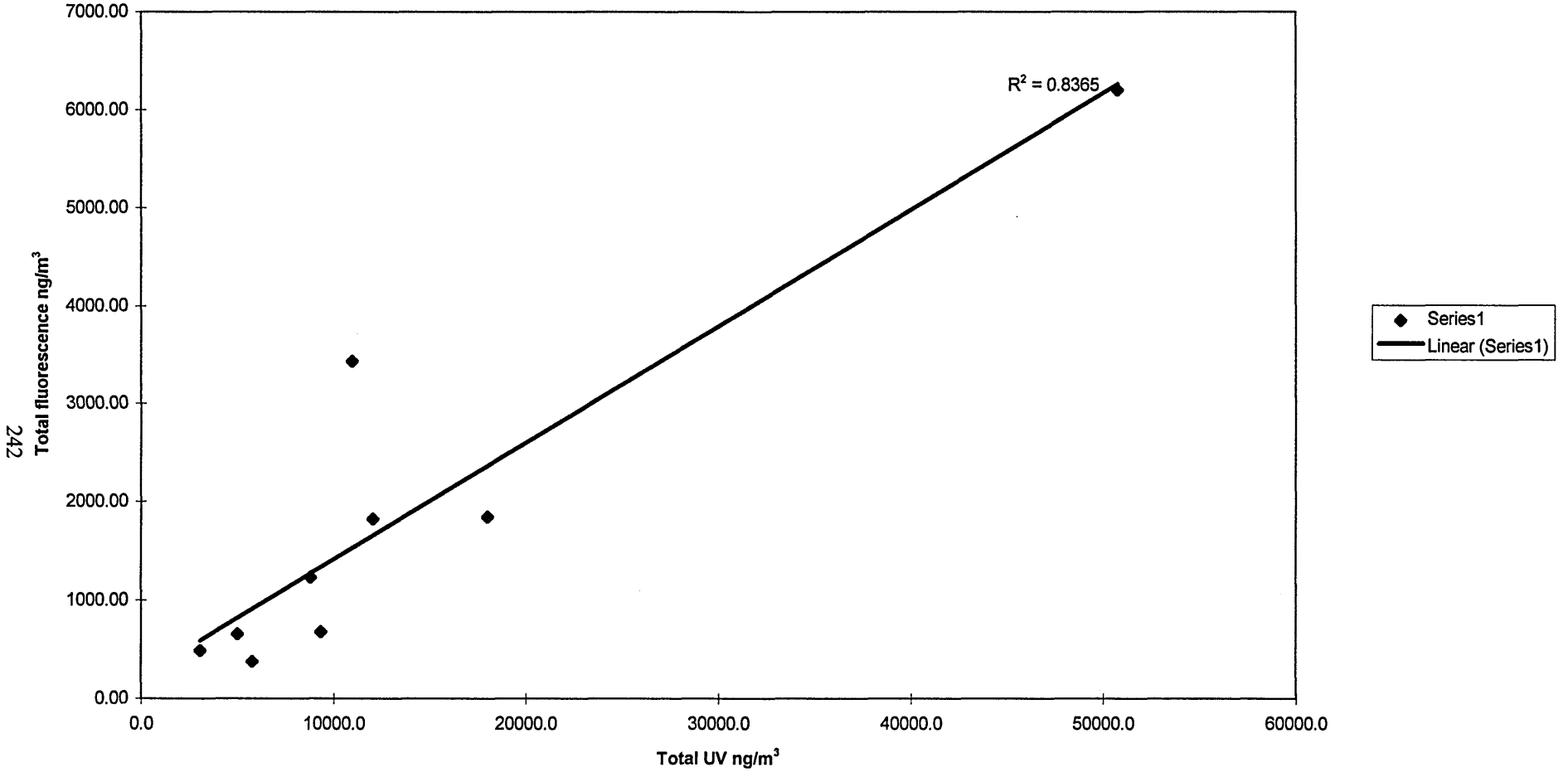

Figure 3.26: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Total UV and Total Fluorescence.

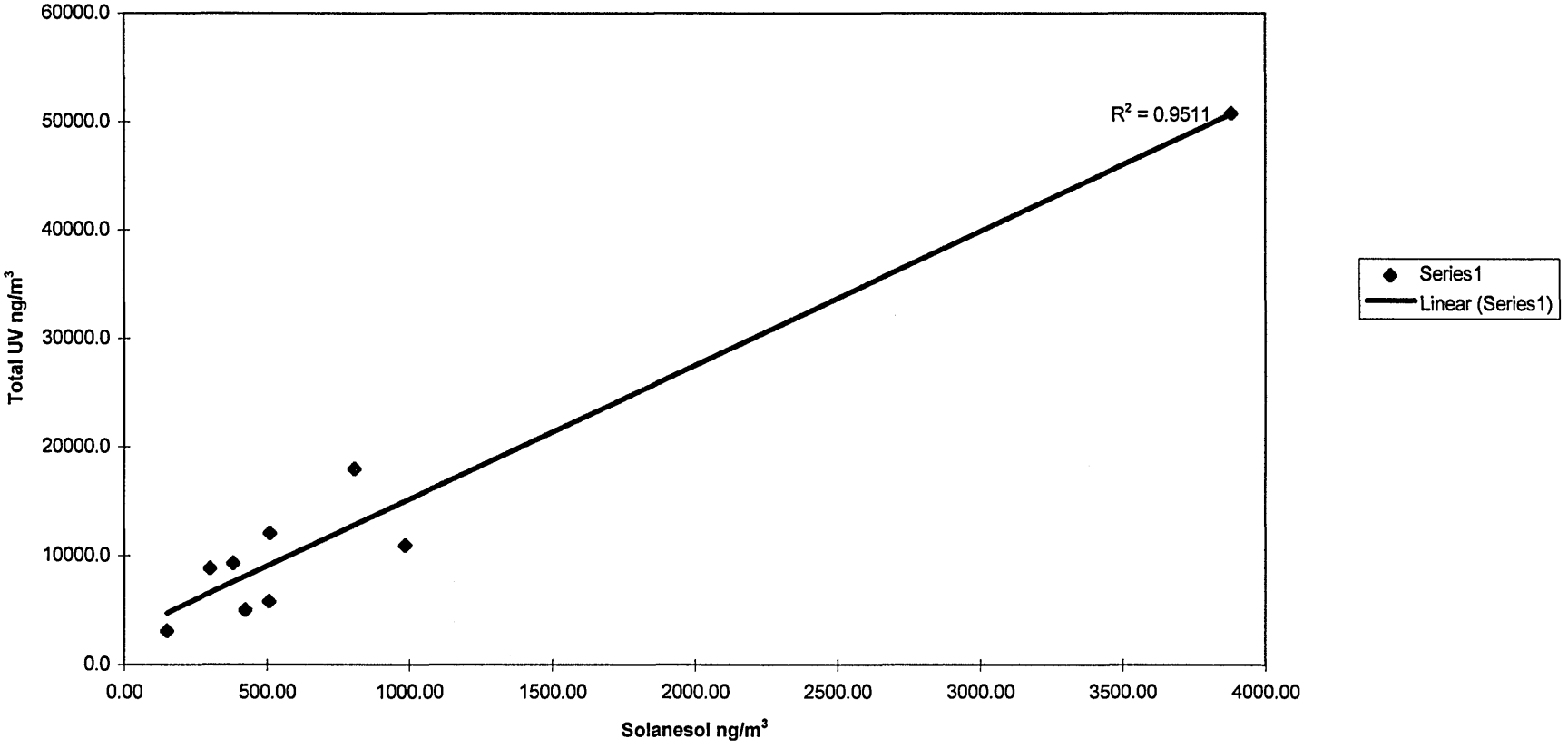

Figure 3.27: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Solanesol and Total UV.

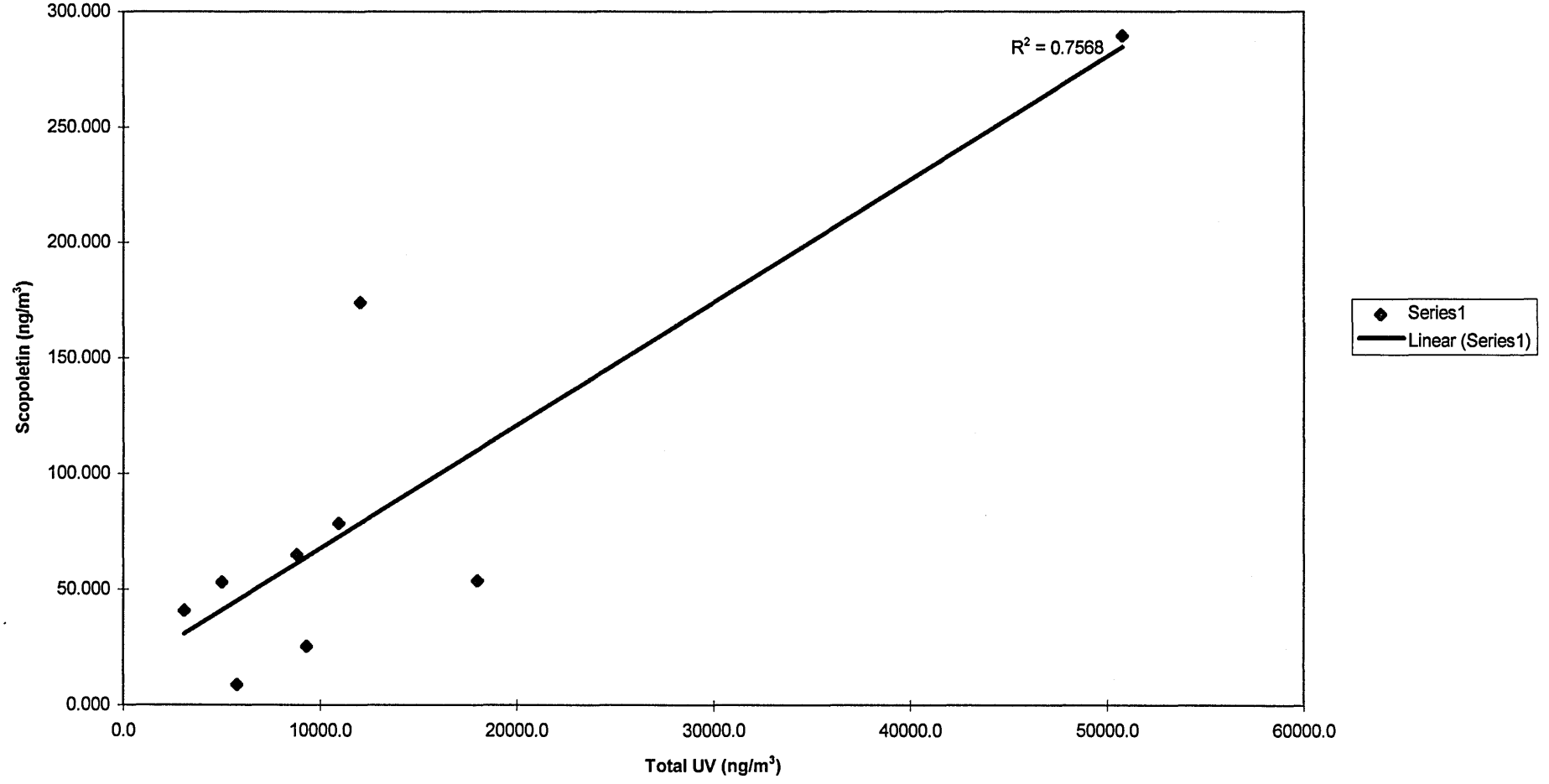

Figure 3.28: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Total UV and Scopoletin.

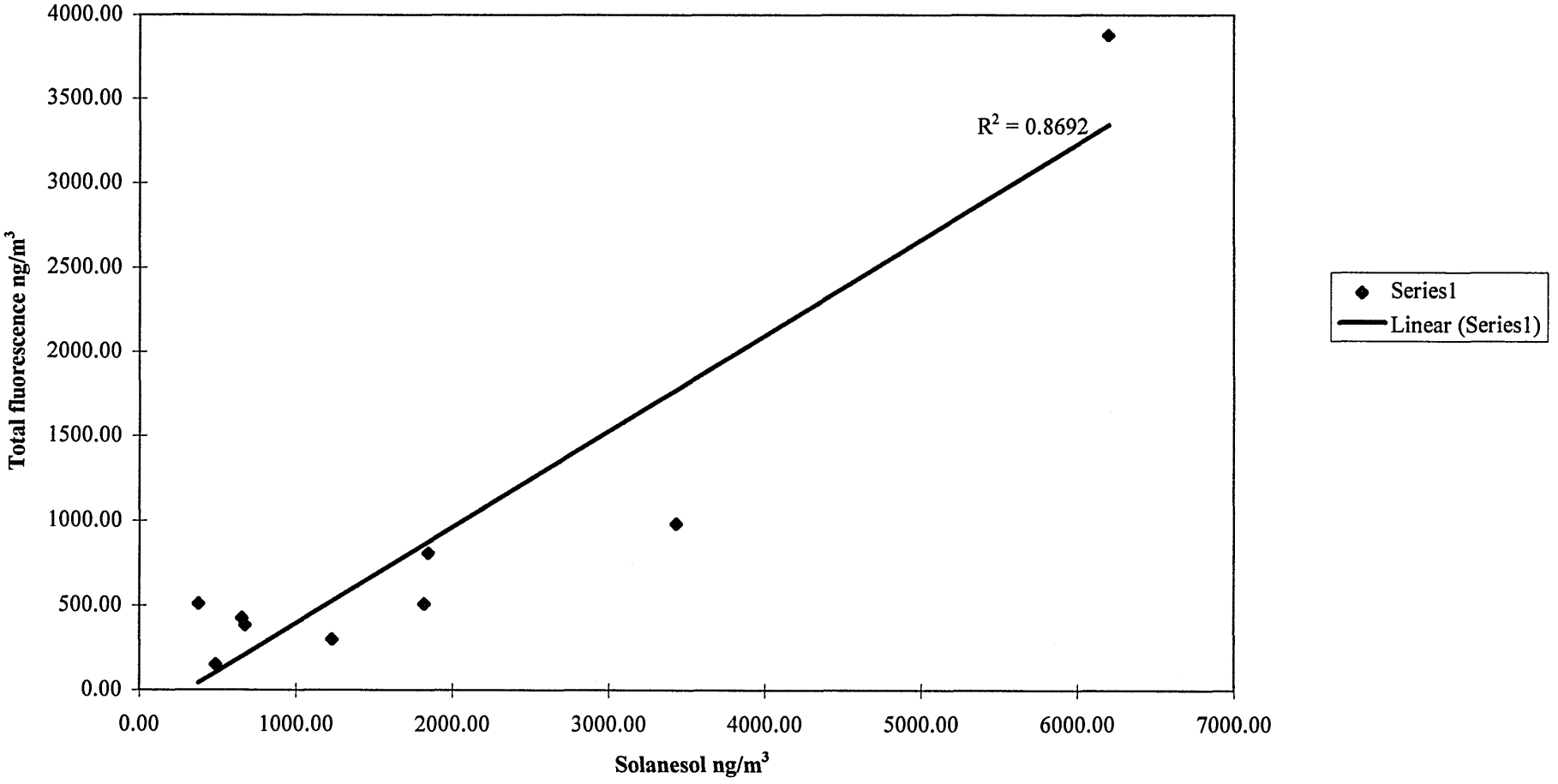

Figure 3.29: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Solanesol and Total Fluorescence.

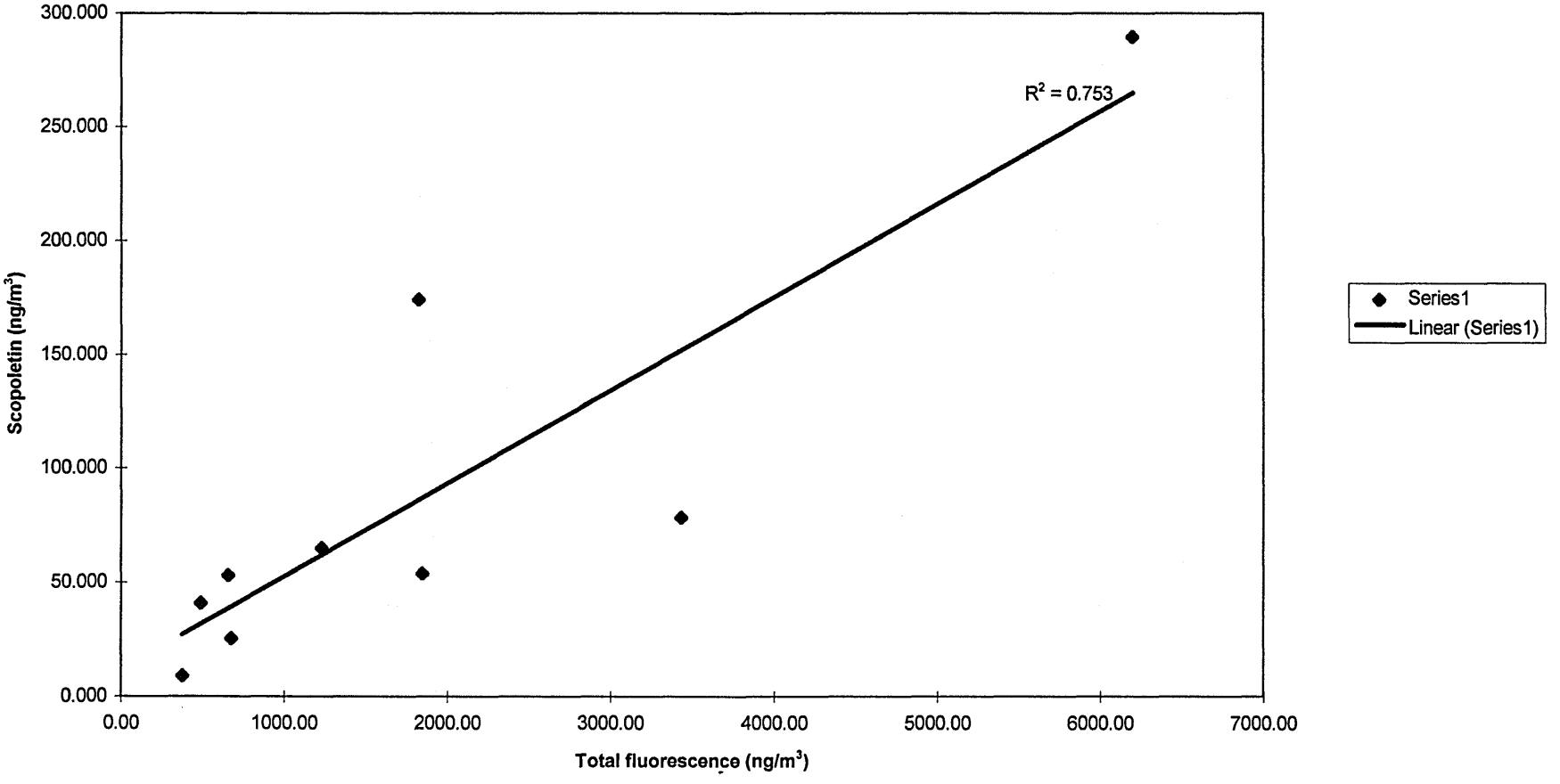

Figure 3.30: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Total Fluorescence and Scopoletin.

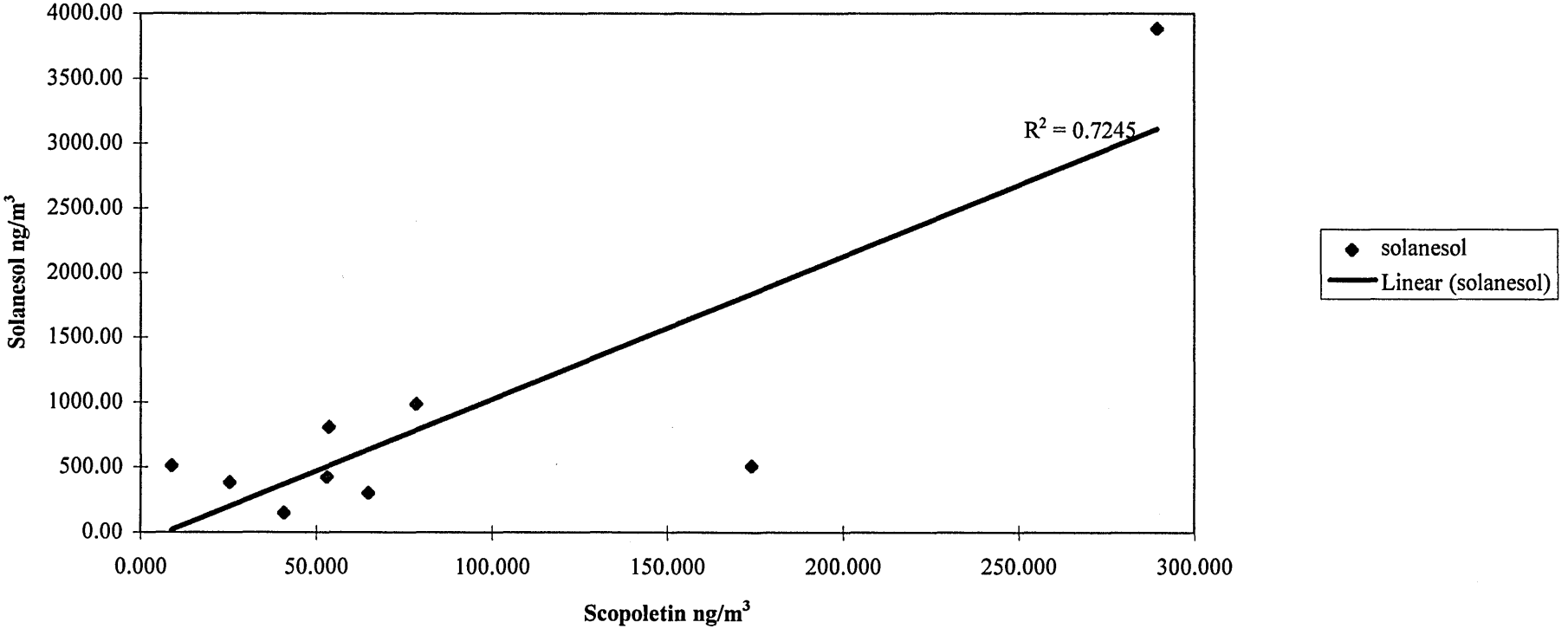

Figure 3.31: Correlation of the Concentrations of Particulate ETS (Smokers Houses and Offices) Determined by Solanesol and Scopoletin.

We can see that total UV clearly overestimates the contribution of ETS to a greater extent than total fluorescence in nearly all of the different contexts (except for the indoor and outdoor non smokers house sites). The reason for this is probably due to the presence of other sources of fluorescent material in these contexts, but the actual source was not identified.

Scopoletin was another possible ETS marker. However, the apparent poor stability of scopoletin leads to an underestimation of ETS contribution to an atmosphere. We therefore conclude that solanesol is the best particulate marker method by which the contribution of ETS can be measured.

Calculations of cigarette Equivalents from ETS Data "Passive Smoking".

An attempt to put into perspective the quantity of ETS taken in by a passive smoker has been used in previous publications (43). This is achieved by comparing the quantity of ETS aspirated by a non smoker over a period of time to the quantity of mainstream smoke, aspirated by a smoker. This produces an equivalent number of directly smoked cigarettes to that of ETS breathed by the non smoker.

The ETS concentrations calculated from the total UV, total fluorescence, solanesol and scopoletin determinations were taken for all smokers environments and a value for mg/year for each method/compound was obtained as follows.

Houses. An average breathing rate of $1m^3/hr$ (45) was taken along with a value of 14hrs/day at home indoor for 365 days per year.
Office. An average breathing rate of $1m^3/hr$ (45) was taken along with 8hr/day spent at work, 5 days a week for 48 weeks a year.

The concentrations of the four ETS methods in mainstream cigarette smoke were taken from the publication by Ogden et al (47).
The following table shows the equivalent number of cigarettes smoked calculated using the above parameters when subjected to the atmospheres sampled in this field study.

Table 3.25: Identification of Cigarette Equivalents for Individuals Subjected to Field Study Smokers Environments "Passive Smoking".

	ETS inhalation as Cigarette Equivalents. Number of Cigarettes/Year.			
Smokers houses	**Total UV**	**Total fluorescence**	**Solanesol**	**Scopoletin**
House 1	4.6	0.4	4.9	9.0
House 2	5.9	1.2	6.5	61.7
House 3	4.3	0.8	3.8	23.0
House 4	24.9	4.1	49.2	102.7
House 5	2.8	0.3	6.4	3.1
Average.	8.5	1.4	14.2	39.9
Smokers offices				
Office 1	2.0	0.8	4.7	10.5
Office 2	0.6	0.1	0.7	5.4
Office 3	0.9	0.2	2.0	7.1
Office 4	3.3	0.5	3.9	7.2
Average.	1.7	0.4	2.8	7.5

Home ETS emissions can be seen to contribute more than ETS encountered in the working environment, this has also been shown in a number of publications (43,45,47). House 4 can also been seen to be the sample with the largest amount of ETS. The household was indeed very smoky, the couple living there both smoked, and this produced a very high total ETS sample.

A variation of cigarette equivalents from the four methods of ETS determination is apparent in the results in Table 3.25. Assuming solanesol is the most accurate (and assuming the concentration of solanesol in mainstream cigarette smoke is equivalent to the concentration in ETS) we can see that the total UV and fluorescence methods underestimate the cigarette equivalents while scopoletin seems to overestimate. This could be due to higher levels of total UV and fluorescence material being present in mainstream emissions while lower concentrations of scopoletin are identified, compared to the concentrations found in mainstream smoke.

The static sampling procedure used in this field study will produce a high number of cigarette equivalents due to the inherent lack of dilution compared to personal samplers,

along with the sampling occurring during a weekend when the smoker was present for the longest period of time, producing a high ETS concentration. We can therefore identify the values obtained from the static study as the higher equivalents seen in such an environment.

The lung clearance of a non smoker is better than a smokers as the lung mechanisms have not been damaged through the inhalation of hot direct cigarette smoke. This was discussed by McAughey et al (48), who state that the average retention of particulate ETS material for total UV and solanesol determination were 38% and 40% respectively in male volunteers and 17% and 27% respectively for female volunteers. We can clearly see therefore that the cigarette equivalents identified in Table 3.25, will be the highest possible number as the individual would have to be in that environment all that length of time stated (and much of the time at home is likely to be spent asleep). These static samples will therefore produce results which will be very much on the high side of ETS exposure.

We can compare these values to those of cigarette equivalents that were obtained from other published studies, after identical mathematical manipulation, (Table 3.26).

Table 3.26: Cigarette Equivalents from Other Published Studies.

	ETS Inhalation of Cigarette Equivalents. Number of Cigarettes/Year.			
Cigarette equivalents	**Total UV**	**Total fluorescence**	**Solanesol**	**Scopoletin**
Phillips (43)				
Home	0.42	0.29	2.92	N/A
Work	0.15	0.16	2.38	N/A
Heavner (2)				
Home	10.74	12.86	5.83	3.90
Work	4.04	4.19	1.81	1.07
Jenkins et al (4)				
Home	3.66	3.14	0.39	0.05
Work	0.63	0.54	0.02	0.05

Note.

All the concentrations were applied to identical breathing rate parameters, used for Table 3.25.

All samples in Table 3.26 were obtained using personal sampling monitors.

From the two sets of data we can see that for all studies, the values obtained for the working environment are less than those associated with the home. The assumption that the smoky atmosphere is present throughout the household and throughout the night at a constant level ensures that the cigarette equivalent number is higher in our study compared to the personal monitoring studies. We sampled for 12 hours during the day, while many of the publications discussed sampled 24hrs (45), and in particular sampled during the night when ETS concentrations can drop significantly.

An interesting feature of the cigarette equivalents data shown in the two tables, is that our total UV and fluorescence values are lower than the solanesol equivalents value, this was also identified by Phillips (43), while the equivalent values identified by Heavner (2) and Jenkins (4) are higher. The scopoletin in our study produce a higher equivalent than solanesol while the other published results are lower. The reason for this is not known. However, the variation in American and European ETS cigarettes may account for it.

Another method for the identification of cigarette equivalents is to identify the quantity of particulate material produced by ETS in an atmosphere (using the solanesol concentration) hence to obtain the cigarette equivalents to particulate material produced in the main stream. This removes any variation that would occur from the concentration of the marker materials in mainstream and side stream cigarette smoke.

Table 3.27: Identification of Cigarette Equivalents using Particulate Material shown as being from ETS by Solanesol Measurements.

Smokers houses	CE per year
House 1	8.89
House 2	11.83
House 3	6.99
House 4	89.99
House 5	11.79
Average.	**25.90**
Smokers offices	
Office 1	8.58
Office 2	1.32
Office 3	3.70
Office 4	7.05
Average.	**5.16**

Note.

A mainstream concentration of $12mg/m^3$ (45) was used to produce the CE values.

These cigarette equivalent values are between the solanesol and scopoletin cigarette equivalents values shown in Table 3.25, identifying that there could be some sort of variation in the concentration of the two marker compounds in main stream and side stream smoke. If concentrations per gram could be obtained, of the marker compounds in side stream and main stream smoke, this difference could be identified, and a more accurate value for the equivalent number of cigarettes smoked in an environment could be obtained.

It can be seen from the above discussion on CE values that there is still some uncertainty in the method by which an accurate CE is obtained. This was discussed in some detail by Ogden (47) for earlier methods of ETS determination. It can be seen however that these methods show that an equivalent (if we remove the high value from the smokiest environment house 4) of between 3-7 cigarettes (home) and 1-5 cigarette (work) are inhaled using direct solanesol measurement data. Particulate measurements identify that 6-12 (home) and 1-9 (work) cigarettes equivalents will be inhaled during a year period by "passive smoking".

It is difficult to argue that the consumption of any pollution at whatever concentration is a good thing. However, the concentrations identified in these field studies inhaled by individuals seem to be quite low especially since these are the higher end of concentrations seen in an environment, by a non smoker breathing in a smokers environment.

The more startling discovery is the concentration identified in house 4 where a closed smokers environment produced a heavily contaminated atmosphere with a CE of 50 by solanesol determination and 90 by ETS particulate measurements. Young children and individuals with poor respiration systems would probably find such an atmosphere most unpleasant.

3.7 Conclusion.

The aim of this chapter was to use the marker compounds identified in Chapter 2 to identify percentage apportionment of diesel emissions and ETS to indoor and outdoor environments. These marker methods were compared against the more regularly used methods for such determination (where appropriate) in an attempt to identify if any of the previous, less specific methods, over-estimated the contribution of the previously stated sources.

Diesel.

No marker compound was identified for vapour phase diesel emissions. Hence the contribution of diesel emissions to vapour phase organics in an environment could not be quantitated.

Particulate matter apportionment for diesel emissions was calculated using C24 as the marker compound. It was known that this aliphatic alkane was not specific, but that this could be corrected, using large scale measurements against 1-nitropyrene (identified as an ideal marker compound for diesel emissions, but unfortunately at to low a concentration in the sample sizes taken in this study). The percentage apportionment

values were obtained with the highest mean value of 45.26% being obtained for city centre and major road samples. The contribution did drop from urban to suburban and rural area, with mean values of 25%, 15% and 5% respectively. Quantities of diesel associated material was also identified in indoor environments illustrating the diffusion of outdoor pollution into indoor environments.

Environmental Tobacco Smoke (ETS).

Using pyrrole as a marker compound for ETS, percentage contributions of a number of volatile compounds (benzene, toluene, xylene isomers etc.) were identified and used to identify the cigarette equivalents (CE) needed to be smoked directly that would be comparable to the ETS inhaled passively. A value of 50 cigarettes (approximately one a week) was identified for work place atmospheres. The number of cigarette equivalents is significant, but what needs to be clarified is that this constitutes being in the smokers atmosphere for 8 hours a day, 5 days a week for 48 weeks, which is seldom the case. This CE value is therefore a worst case scenario.

The use of nicotine as a marker compound was found to be highly problematic even with the use of triethylamine in the DCM used to improve nicotine recovery (1). The quantitative results produced by both our laboratory and Rothmans International Laboratory, Basildon Essex, were far from accurate and did not compare well with any of the other methods of ETS contribution. Thermal desorption quantitation of nicotine produced the best results (for the few sites that were quantifiable) with quantities mirroring other ETS contribution methods. This result was contradictory to the literature as the XAD sampling, extraction methods is proposed as the method of vapour phase nicotine determination (27-29).

Several methods had been used in the past to identify the ETS particulate contribution to an atmosphere. Many of these were not marker specific, and were thought to over-estimate the contribution of ETS quite dramatically. The recent introduction of marker methods (solanesol and scopoletin) identified a possible way by which the over-estimation could be identified and quantified. We were able to do this using solanesol as

the preferred marker method and identifying over-estimation of 11-51% by total UV and 5-38% by total fluorescence.

The use of cigarette equivalents identified that the number of cigarettes consumed in a year by a non smokers exposed to a smokers environment (14 hours a day, 365 days a year at home, office hours stated earlier) produced values of 14 and 3 cigarettes for smokers homes and offices respectively. Once again this is very much the worst case scenario as the 14 hours at home includes sleeping hours, meal times etc.

We can see that the CE values for vapour phase emissions are a lot higher than those identified for particulate material. This is probably due to the longer residence time of volatile material in an atmosphere compared to ETS particulate material which readily adsorbs to surfaces and is quickly removed from the atmospheric environment.

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4. Tree Bark as a Passive Sampler for Diesel Emissions.

4.1 Introduction

For the quantitative determination of diesel particulate material in an atmosphere (discussed in Chapters 3 and 4) the compound 1-nitropyrene was used as an indirect marker for diesel emissions. 1-nitropyrene in addition to other nitrated PAH has been identified in various anthropogenic emissions including diesel (1-12), gasoline (3,4) and wood (3,4). The nitration of PAH in the diesel exhaust system has been discussed extensively in the literature, electrophilic aromatic substitution has been identified as the main nitration mechanism. This yields isomers corresponding to the cationic (Wheland) intermediates that have the greatest resonance stability (see Section 4.2.3.2). The formation of these micropollutants has been thought to be an artefact of emission sampling, with one hypothesis being that the formation of nitrated PAH derivatives occurs on the filter paper (13). In this chapter these ideas are discussed and it is shown that 1-nitropyrene is found in the atmosphere and that its source is almost entirely diesel emissions. Other known atmospheric reactions appear to contribute little to the concentration of this compound in the environment.

To identify if nitrated PAH were in fact produced from the combustion of anthropogenic material and not being detected as an artefact of sampling, a method of sampling was needed in which nitration of PAH could not occur. The adsorption of particulate material from various sources onto solid surfaces has been apparent for many years in the urban environment with an estimated £79 million pound market for the cleaning of "soiled" buildings in Britain in 1992 (14). This adsorption of particulate pollution is not only specific to buildings, all surfaces are prone to soiling, the amount being dependant upon the position of the surface and the extent of the pollution. The use of vegetation as a sampler for atmospheric pollutants is widely reported in the literature, and suggests that it is a possible method of sampling for these nitrated PAH in a real atmosphere.

4.1.1 Use of Organic Vegetation as a Passive Sampler for Atmospheric Pollutants.

As 80% of the earth's land surface is covered with vegetation, and since vegetation has approximately 6-14 times more surface area than the land it is growing on, it is highly probable that it plays an important role in the annual cycle of organic molecules to and from the atmosphere (15).

Vegetation is abundant in many forms, several of which have been used as sampling systems to determine concentration of toxic substances. Examples include:-

1. Lichens used to determine PCB (16-18).
2. Tree bark used to determine PCB (19,20), Heavy metals (19,21), Acidic gases (18), PAH (19,22-23) and Radionuclides (24)
3. Pine needles used to determine PCB (17-18) and pesticides (18,25).
4. Mango foliage used to determine PCB (17).
5. Dried silage used to determine PCB (26) and PAH (26).
6. Plant leaves used to determine PCB (19,25) and PAH (19).
7. Humus layer to determine PCB, PAH, Heavy metals and pesticides (19).

The possible routes of sorption of pollutants by vegetation include direct adsorption of pollutants onto the external surfaces, or absorption of pollutants through the roots from the soil. Transportation of pollutants from the soil into vegetation (evapotranspiration - the uptake of water from soil into the roots for transportation to the extremities of the plant) has been shown to be of little importance. Lipophilic organic pollutants are hydrophobic and do not dissolve in water (27), so little is transported into the vegetation via this route. Buckley (25) showed that less than 1% of radio-labelled PCB in soil were adsorbed through the roots from contaminated soil. Transportation of PCB from heavily contaminated soil was identified as being via the pollutant evaporating from the soil surface and adsorption occurring directly onto the surface of the vegetation (27).

Advanced analytical techniques have been able to show that plant matter accumulates pollutants. However, it is not clear if these compounds are transported around the plant system. There are several suggestions for factors which effect the sorption of pollutants.

It is likely that the complete model will be a combination of several or all of these proposals.

Leaves and pine needles are both coated by a waxy, lipophilic layer (22,25) which prevents excessive evapotranspiration (15). Tree bark is a layer of dead cells, coated with suberim (a lipid mixture) which makes the bark impervious to water (28). Schuck (29) states that the waxy coating on the surface of pine needles (specifically a Scotch pine) is stable for up to two years, so presumably the lipid layer on leaves and bark are stable as long as they are attached to the tree.

Simonich et al (15) identified that during a year of growth, the quantitative total of semi-volatile PAH adsorbed by vegetation fluctuated. Not only was a larger amount adsorbed at times of cold ambient temperatures, but also during the growth of the plant, when the lipid content was higher than normal (around August). Larger quantities of PAH were also found in that part of the vegetation with the largest lipid content, i.e. the needles. A greater quantity of mutagenicity to the Ames test was identified (30) (modified Salmonella Typhimurium, sensitive to nitrated PAH), in extracted leaf matter compared to the soot washed off the leaf surface with water. This reinforces the idea that the organic pollutants are adsorbed into the leaf matter. However, the work of Gaggi (18) indicates that the lipid content of a plant does not provide a preferential route to the adsorption of pollutants. The majority of the PAH studied were found in the humus layer (surface layer), as there was little apparent movement of PAH into ground water or into the deeper layers of soil, due to their hydrophobic nature (31). At the very worst these results suggest that the lipid layer is a more favourable sorbent than water droplets. Such adsorption results have led to the derivation of a mathematical equation for the representation of the possible variables which effect adsorption to vegetation (20). They also indicated that the lipid content of the plant had a minor effect on the adsorption of pollutants. Conversely the individual vapour pressure of an organic molecule was shown to be of great importance. It can therefore be seen that no definitive model has been produced for the effect surface lipid concentration of vegetation has on the adsorption of pollutants, although due to the hydrophobic nature of the gaseous pollutants it seems likely that the lipid layer does play some small role in the adsorption process.

The vapour pressures of individual organic molecules are in fact deemed to be the major influence on their adsorption. It has shown that PCB with a high vapour pressure (i.e. volatiles) stay in the gas phase, while compounds of low vapour pressure (i.e. non-volatiles) are preferentially adsorbed onto a bark or herbage surface. It has been noted (15,18) that the ambient temperature and pressure have a great effect on the adsorption of organic pollutants. Larger amounts of volatile and semi-volatile compounds accumulate in vegetation in colder, or higher regions compared to warmer, low altitude areas. This has been called "the cold condensation effect," in which volatile molecules condense out onto surfaces such as bark or other vegetation, due to lower temperatures.

Temperature can have a major effect on the state in which different molecules will be found. Yamasaki et al (32) sampled PAH in both the vapour and particulate phases. He identified that with higher ambient temperatures the 3-5 ringed PAH were found predominantly in the vapour phase while during colder periods the same PAH were found adsorbed onto particulate surfaces. This phenomena could cause a lower than expected value of such pollutants to be found in vegetation samples. However, this is dependant upon the mechanism of adsorption that occurs between pollutants in the gaseous and particulate phases and the surface of the vegetation.

If all of these different effects are brought together a proposal can be put forward, pollutants both volatile and less volatile will accumulate more readily into/onto tree bark in a country such as Britain during the autumnal and winter periods. This is due to the low average temperature at that time, whilst the burning of fuels is high both for transportation and heating. Photodegradation of pollutants will also be low due to the lack of ultra violet radiation (31). Disciduous trees are also without leaves for a large amount of this period, therefore the only vegetative area pollutants are able to adsorb into/onto is bark. It has been proposed (20) that vegetation plays a larger role in the removal of high molecular weight molecules due to their higher lipophilicities and lower vapour pressure, and that such molecules will be preferentially adsorb onto a surface. However the transfer of pollutants contained in particulate material onto/into the tree bark is unknown. The lipid surface may be a preferred environment for some compounds but this is at the present time only conjecture.

Simonich et al. (22) suggest this very hypothesis and continues further by surmising that in spring and summer, pollutants are transferred to the leaves. So in autumn when the leaves are shed, the tree has removed the pollutants it has adsorbed throughout the year. This hypothesis is supported by the work of Thomas et al (19) who identified PAH in relatively large quantities in the humus of both deciduous and coniferous litter. However, another reason for the high levels could be the surface to mass ratio of the sample i.e. the large surface area compared to the mass of the sample. This could produce a high quantitative value for PAH per gram of vegetation. Other ways that the pollutants may be removed from the vegetation include the shedding of bark with time, or the increase in photodegradation that occurs as the sunlight strength increases during the summer months.

4.2 Formation of Substituted Polycyclic Aromatic Hydrocarbons.

4.2.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAH) have been extensively studied due to their production from the combustion of all varieties of organic fuels. PAH are a large family of molecules, many of which have been shown to be indirectly active to the "Ame's test" a procedure carried out to identify the mutagenicity of a compound .

4.2.2 Mutagenicity and Carcinogenicity

Mutagenicity and Carcinogenicity are two methods used to indicate the toxicity of compounds.

Mutagenicity.

The original method used to determine mutagenicity was developed by Ames B in 1975 (33). He proposed the use of Salmonella Typhimurium TA98 bacteria by exposing them to a chemical or the fraction of a complex mixture to produce a reverse mutation. Since this time, new strains of this type of bacteria have been introduced, which are sensitive to certain types of compounds (i.e. Salmonella Typhimurium strains YG1021 and YG1024 which are sensitive to some nitroarenes, in the absence of an external activation source, S9 (30)). S9 is a supernatant fluid prepared from Sprague-Dawley adult male rat liver, induced by Aroclor 1254 (33a). The components of the S9 activation system in addition to the rats liver supernatent include nicotinamide adenine dinucleotide phosphate -sodium salt (NADP), D-glucose-6-phosphate, magnesium chloride, potassium chloride and sodium phosphate buffer (pH 7.4) (33a).

It has been found that many mono and di nitrated PAH are "direct acting mutagens" compared to their analogous PAH which are "indirect mutagens". This terminology stems from the fact that PAH need an external activation source, "S9", to exhibit mutagenicity. Many nitrated PAH do not require "S9" activation and are capable of inducing mutagenicity directly.

The mutagenicity of nitrated PAH from different sources has been widely discussed in the literature, such sources include diesel exhaust fumes (34-36), ambient aerosols (37) and pollutants adsorbed to the leaves of woody plants (30).

Carcinogenicity

Carcinogenicity is the effect the administration of the compound in question has on a mammalian biological system. The majority of this type of work is carried out on mice, hamsters (38) or rats (39). Carcinogenicity is the effect the invading compound has on the DNA of the cells it is in direct contact with. Intravenous injection into systems can induce cancerous tumours at the point of injection (39).

How the compounds are taken into a system, such as ingestion, injection, inhalation (either as an aerosol or directly from the gaseous phase), can have a major effect on the overall damage to the system in question. Once present in the body, nitrated PAH are metabolised to amino, or glucuronide conjugates, and can further increase their overall polarity by the addition of hydroxy groups at different sites on the polycyclic molecule. The effects of these molecules once in the body on internal organs is not yet known, however, organic combustion sources have been tentatively linked with adverse health effects (see Chapter 1 Section 1.6).

A lot of attention has been directed towards derivatives of PAH and more specifically oxygenated and nitrated derivatives due to this toxicological data. Although the quantities of the nitrated compounds are up to a factor of 1 to 2 orders of magnitude below that of PAH (40), they have been shown to be there in sufficient quantities to make monitoring of these direct carcinogens and mutagens necessary.

In the following section, the routes to the formation of nitrated-PAH will be identified. These include the production of nitrated PAH in anthropogenic combustion, and also independent routes for the formation of these highly carcinogenic and mutagenic compounds in the atmosphere.

4.2.3 Nitrated Polycyclic Aromatic Hydrocarbons.

Nitrated-PAH are one of the many groups of compounds produced from the incomplete combustion of organic materials. However, this is not the only source of nitrated PAH that has been identified. It has also been shown that specific isomers can be formed by certain radical reactions that can occur in ambient air (41-44).

The major source of nitrated PAH is from the nitration of parent PAH molecules. Many factors can effect this nitration process, including the nature of the nitrating species, the chemical structure of the PAH, the chemical effects of substituent groups attached to the PAH molecule, and the environment in which the reaction occurs, (i.e. gas phase, in solution or on a surface i.e. particulate).

4.2.3.1 Nitrating Species.

In diesel exhaust emissions, NO is the dominant nitrogen containing species. This is quickly oxidised to NO_2 on mixing with ambient air (45). NO and NO_2 can react further with water vapour (46) to produce further reactive species including nitric acid and nitrate (45) along with nitrous acid (47) and with appropriate reagents peroxyacetyl nitrate (PAN) (48).

Hence numerous nitrogen containing species can be produced in exhaust emissions and ambient air. However, only nitrate, nitric acid, nitrogen dioxide, dinitrogen pentoxide, nitrous acid, alkyl nitrates, and alkyl nitrites are thought to nitrate PAH (41). As yet, there has been no evidence to show that NO acts as a nitrating species towards PAH (49). PAN is known to cause oxidation of PAH, not nitration (50), while the $NO_3\bullet$ has a low reactivity to unsubstituted PAH (41,51). Nitrous acid has been shown to catalyse the nitration of PAH in strongly acidic conditions (52) while N_2O_4 has been identified as a catalyst for nitration in weakly acidic conditions (52).

The reaction system containing gaseous NO_2 and HNO_3 (50) is known to cause nitration of PAH, especially with the larger molecules associated with surfaces and this is thought to be the dominant nitration reaction in diesel exhausts. This is an electrophilic aromatic

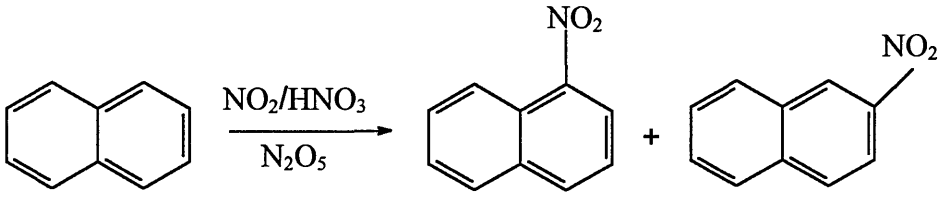
substitution reaction. Gaseous system of N_2O_5 along with small quantities of NO_2, HNO_3 and the NO_3 radical were identified as nitrating PAH that were attached to surfaces (42), but also preferentially with PAH found in the gaseous phase (43).

4.2.3.2 Formation of Nitrated PAH, by Electrophilic Aromatic Substitution in Combustion Sources

Nitration of Naphthalene.

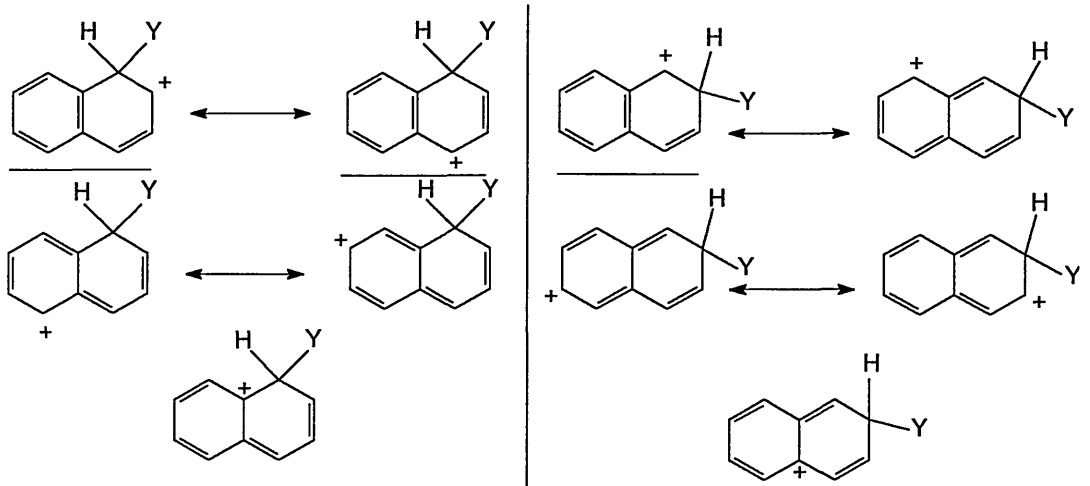
Naphthalene is readily nitrated by electrophilic aromatic substitution (53), preferentially at the 1 position. This is due to the resonance stability of this isomer being greater than that of the analogous 2 nitronaphthalene.

e.g.



1-Nitronapthalene : 2- Nitronapthalene
10 : 1

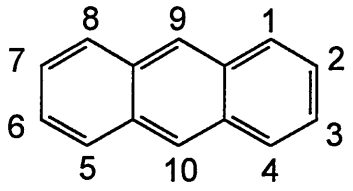
If we compare the resonance structures of 1 and 2 nitronaphthalene :-



1-Nitronapthalene 2-Nitronapthalene

NOTE. Y=NO_2

1-Nitronaphthalene contains two resonance structures with the added stability of a benzene ring while 2-nitronaphthalene contains only one. From this we can decern that 1-nitronaphthalene is the most abundant isomer, via this type of reaction. Anthracene reacts in a very similar way, with position 9 and 10 being the most reactive.

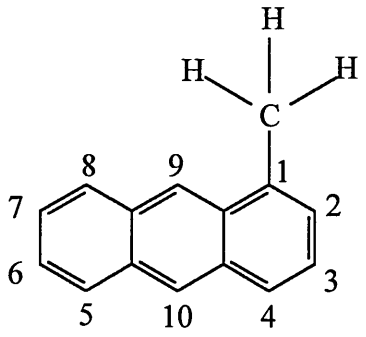


These two positions are the most reactive towards electrophilic substitution (in this case nitration), due to their increased resonance stabilities compared to the resonance stabilities of the other possible structural isomers (53).

Effect Of Chemical Substituents on the Reactivity of PAH.

The position and type of substituent group (steric effects and electron withdrawing/donating respectively) can have a drastic effect on the reactivity of PAH. For example, electron donating substituent groups (such as CH_3), increase the likelihood of nitration as long as steric effects are not an issue (54);

i.e. A methyl group at position 1 or 8 may sterically hinder nitration at position 9, however the nitration reaction can occur at position 10.



This introduces the possibility of methyl-nitro PAH being present in the atmosphere, (55) from their formation in exhaust emissions, as numerous alkyl PAH are present in diesel emissions.

Other substituent groups that can cause in increase in the nitration of PAH molecules includes the hydroxy group. It has been shown that 9-Hydroxyanthracene is 200 times more reactive than anthracene (54), therefore investigation into levels of this class of compounds on emissions could yield some interesting results.

Other chemical substituents studied include H, Cl, CN and NO_2 (54). It was observed that reactivity decreased from H to NO_2 group (for this set) as the NO_2 group is electron withdrawing. As an electron density is needed for electrophilic aromatic substitution to occur, it can be seen that dinitro-PAH would be an unfavoured compound while hydroxy-nitro and methy-nitro PAH would be the more favoured, and possibly the more abundant compounds found in diesel emissions. Dinitro-PAH have been observed in diesel emissions (1), therefore it seems possible that larger quantities of methyl and hydroxy nitro-PAH could be present.

4.2.3.3 Formation of Nitrated PAH derivatives in the Gas Phase.

Introduction.

The primary source of nitroarenes in air is from combustion emissions, with diesel being the largest identified source. The route taken to produce them is thought to be via electrophilic nitration of PAH (56) by N_2O_4 and NO_2/HNO_3, which occurs after combustion but before extensive dilution after emission (57,58). Other routes of formation for nitroarenes in the atmosphere include the nitration of PAH by N_2O_5 at night (42-44), and an OH radical initiated nitration reaction (59). However, the isomers produced from these reaction are not those favoured by electrophilic substitution, (e.g. the isomers identified from these reactions include 2-Nitronaphthalene, 2-Nitropyrene etc.)

For the hypothesis that electrophilic aromatic substitution is the dominant process to be true, the literature would show that organic extracts from exhaust emissions contain quantities of the most favourable electrophilic substitution products, e.g. 1 nitropyrene and 3- and 8-nitrofluoranthene. This is in fact the case (1,2). Fluoranthene and pyrene are released by diesel engines, in very similar quantities (34). However, pyrene is more susceptible to electrophilic substitution so larger quantities of 1-nitropyrene are detected in comparison to 3 and 8-nitrofluoranthene (3).

Arey et al (60) identified similar quantities of nitrated pyrenes and fluoranthenes in ambient air. 1- and 2-nitronaphthalene were detected at similar concentrations in ambient air samples (55), while only 1 nitronaphthalene was detected in diesel emission samples (1).

Other sources of nitrated-PAH, such as gasoline fuelled vehicles (3,4) and wood burning (3,4) have been shown to produce 1-nitropyrene, but not 2-nitropyrene or 2-nitrofluoranthene, identified in ambient air particulates (2,60,61).

It has therefore been proposed (60) that the reaction occurring in emissions from organic combustion is one of electrophilic substitution. Resonance stability will have a great effect upon the position of the nitro group, therefore the major mono-nitrated PAH species found in anthropogenic emissions include 1-nitronaphthalene, 4-nitrobiphenyl, 5-nitroacenaphthene, 2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene and 1-nitropyrene.

Other mono-nitrated PAH have been identified in ambient air sampling. e.g. 2-nitrofluoranthene and 2-nitropyrene (2,60,61), 2-nitronaphthalene (43,60), and 3-nitrobiphenyl (60) These are not the most resonantly favoured isomers produced by electrophilic substitution. These compounds are therefore being produced by a different reaction mechanism.

Two photochemical routes to the formation of nitrated-PAH in ambient air have been identified :-

1) Reaction of N_2O_5 with PAH.
2) Formation of nitroarenes from OH radical attack on PAH in the presence of NO_x.

Reaction of N_2O_5 with PAH

N_2O_5 is formed from the radical NO_3 and NO_2, at night (62), via the following reaction route :-

$NO_2 + O_3 \longrightarrow NO_3\bullet + NO_2$

$NO_3\bullet + NO_2 \longrightarrow N_2O_5$

Separate reactions of N_2O_5 (in the dark), with pyrene, perylene and fluoranthene (44), impregnated on glass filters, and naphthalene in the gaseous phase (43), have been studied. NO_2 was added to the system in excess, to push the equilibrium towards N_2O_5 formation, this increased the production of all the different nitrated PAH conjugates. However, the same reactions using only the NO_3 radical produced no nitrated PAH (42-44). It was found that pyrene was the more reactive PAH with N_2O_5 than perylene, which is the exact opposite when these two PAH react with gaseous NO_2/HNO_3 (50,54,63).

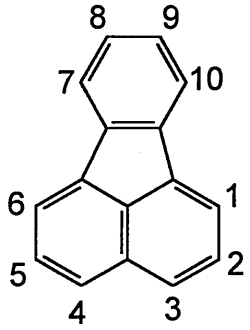
It can therefore be seen that there are a whole range of possible nitrating species, with each system reacting preferentially with different PAH. The NO_2/HNO_3 system seems to react with the higher mass PAH, therefore indicating the likelihood of this reaction occurring on the particulate surfaces.

The N_2O_5 system, seems to occur with the lower mass, semi-volatile PAH i.e. pyrene, fluoranthene and those with smaller molecular masses. This suggests that the reaction is probably occurring in the gaseous phase. An observation by Pitts (41) was that the nitrated fluoranthene isomers of 3-, 8-, 7- and 1- are all produced in almost equal amounts. This is not the expected result if electrophilic substitution was occurring, where the favoured isomer reaction order is 3- > 8- >> 7-≥ 1- (64,65). This indicates that the

reactions occurring here, even though they are happening without light, are occurring via a different process.

Formation of Nitrated PAH Species by N_2O_5

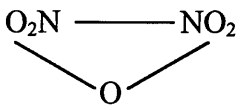
Extensive work has been completed on the chemical reactions of various PAH with N_2O_5 in different environments. Not only gaseous N_2O_5 but also systems in which N_2O_5 and the PAH are dissolved in solvent systems (protic or aprotic).



The Numbering system of Fluoranthene.

2-Nitrofluoranthene is the only mono-nitrated isomer of fluoranthene obtained from the reaction of gaseous N_2O_5 with gaseous fluoranthene. However, if the fluoranthene is impregnated onto a surface, the 3-, 7-and 8-nitrofluoranthene isomers are observed, with the 3-isomer being the most abundant due to its resonant stability.

Two different mechanisms drive the reactions in these two situations. The surface reaction appears to be a catalysed reaction in which the NO_2^+ ion is formed, inducing electrophilic substitution. The other seems to be a radical mechanism with N_2O_5 reacting as a covalent species:



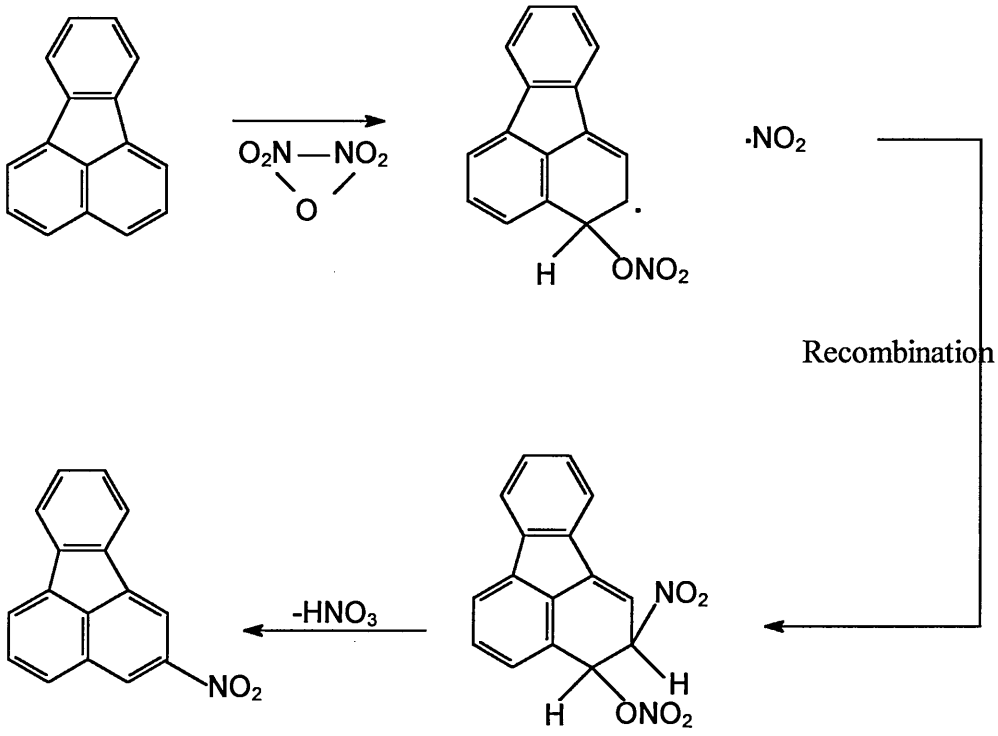
(44)

It is known that N_2O_5 and not the NO_3 radical induces nitration of PAH since the equilibrium can be forced to the right hand side of equation (43,44) with the addition of NO_2.

$$NO_2 + NO_3\bullet \rightleftharpoons N_2O_5$$

It was found that a larger quantity of nitration was observed in the system in which the NO_2 was added, signifying that N_2O_5 and not $NO_3\bullet$ induced nitration.

Large quantities of 2-Nitrofluoranthene are formed under these conditions (66).



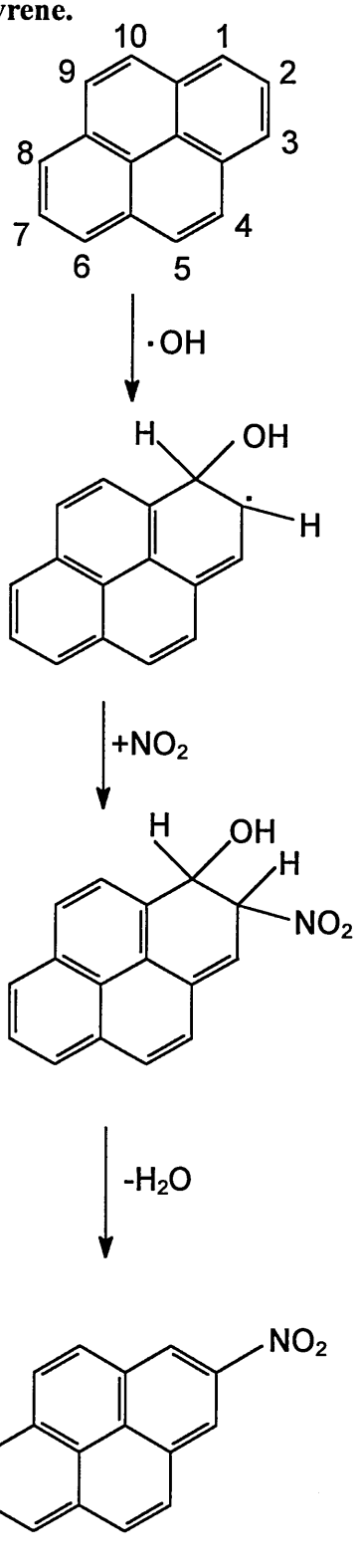
2-Nitrofluoranthene 3-Nitrito-2-Nitro-2-3-Dihydrofluoranthene

This radical reaction has been reported, and is a similar process for the production of 2-nitronaphthalene (43) i.e. an electrophilically unfavourable reaction. However, this reaction has been shown not to occur with pyrene to form 2-nitropyrene (42). The reaction of N_2O_5 with gaseous pyrene only produces 1-Nitropyrene, leading to the conclusion that there must be a further reaction occurring in air to produce the 2-nitropyrene isomer. This other atmospheric reaction has been identified as being initiated by OH•, with nitration due to NO_x (67,68).

One proposed route for the formation of the "unfavourable" isomers of nitroarenes is the following daytime radical reaction. The PAH is initially attacked in the gas phase by an OH• radical, followed by NO_2 addition, finally producing the nitrated-PAH after the loss of water.

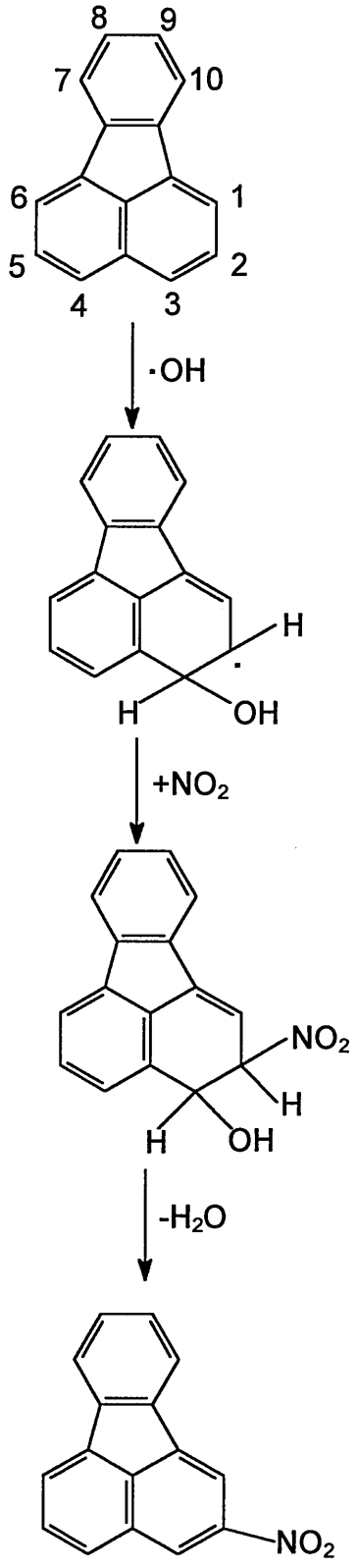
i.e. for Pyrene and Fluoranthene:-

Pyrene.



2-Nitropyrene

Fluoranthene.



2-Nitrofluoranthene

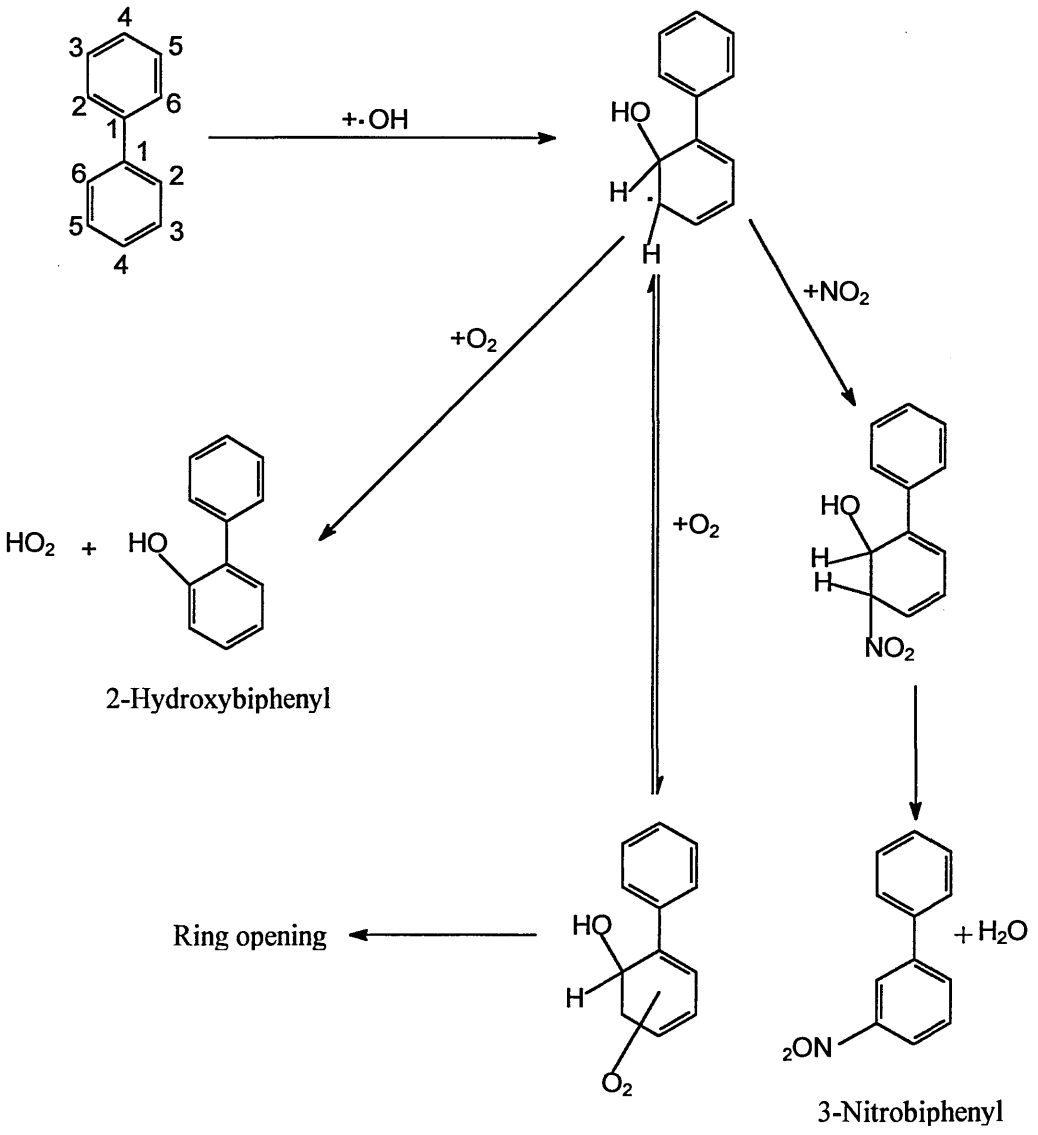
These reactions occur predominantly in the gas phase (69) as structurally smaller PAH are found almost entirely in the gaseous phase with pyrene and fluoranthene present at approximately 50% in this phase. These nitrated PAH isomers (of pyrene and fluoranthene) have been shown to be ubiquitous in the environment in association with particulate material (58,68). This is because although the two step nitration process occurs in the gaseous phase, the nitrated PAH products rapidly adsorb to particulate surfaces.

The reaction has been shown to be quite rapid in ambient air (69-70) and provide the route for NO_2 addition and the ultimate production of certain unfavourable nitrated PAH. However, this type of reaction system does not solely produce nitrated PAH. Products identified from naphthalanes after undergoing OH radical attack include 1- and 2-nitronaphthalene, 1- and 2- naphthols, and hydroxynitronaphthalene (59). Biphenyl products include 2-hydroxybiphenyl and 3-nitrobiphenyl, along with smaller quantities of 3- and 4-hydroxybiphenyl (59). Both sets of reactions take place in a system in which light was used to help induce the radical reactions. The OH radical reaction of PAH in the presence of NO_x follows the reaction route of monocyclic systems (i.e. Toluene etc.) under the same conditions.

e.g.

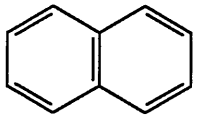
For Biphenyl, the OH radical initiates the reaction, hydrogen abstraction is not an important mechanism for this reaction to occur, therefore addition to biphenyl often occurs at the 2 position.

Biphenyl route.

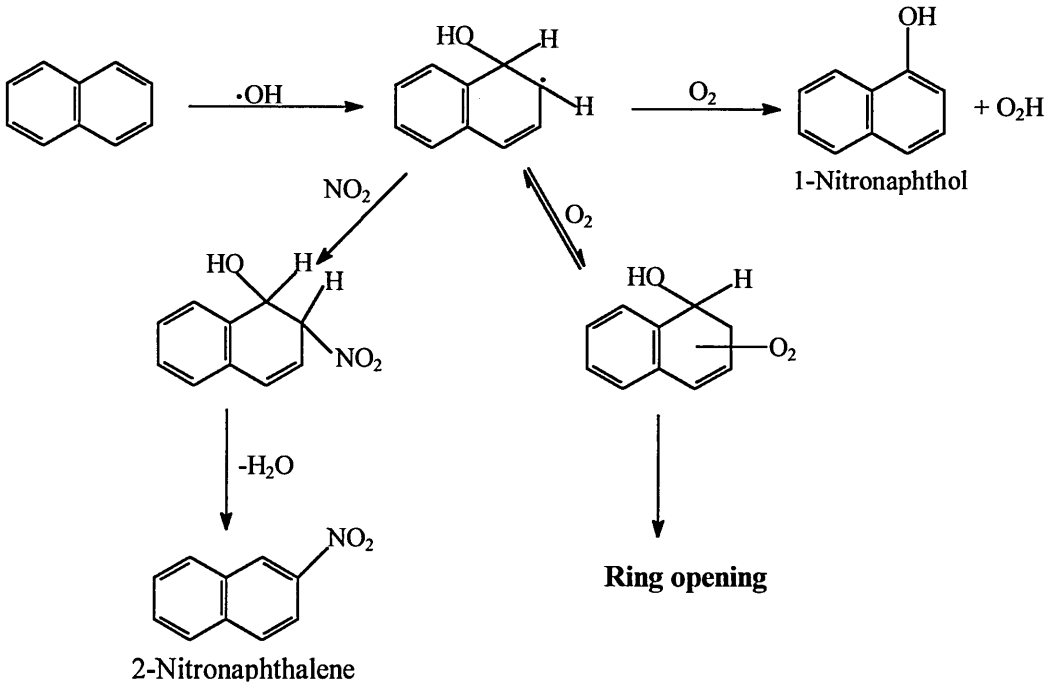


It can be seen therefore that the two major products formed from OH radical attack will be 3-nitrobiphenyl and 2-hydroxybiphenyl. Other compounds formed, to a lesser extent, include 3 and 4 hydroxybiphenyl along with even lower quantities of 3- and 4-nitrobiphenyl (59).

In the case of Naphthalene.



OH radicals react preferentially with positions 1 and 2. This leads to the formation of 1-(≈ 12%) and 2-(≈7.5%) naphthols. This in turn leads to the formation of a larger quantity of 2-nitronaphthalene compared to that of 1-nitronaphthalene.



This reaction does not occur in the exhaust emission system but rather is found in ambient air.

4.2.4 Conclusion.

Ambient air has been shown to contain high quantities of several nitrated-PAH including 1- and 2-nitronaphthalene, 3-nitrobiphenyl, 2-nitropyrene and 2-nitrofluoranthene. Except for 1 nitronaphthalene, these are not the expected nitro-PAH derivatives that have been identified from a range of combustion sources (diesel (1-12,71-74) gasoline (3,4,76,77),

wood smoke (3,4) and flue gases (104). These combustion sources produce nitrated PAH predominantly via electrophilic substitution (possibly occurring on the particulate surface, or in the gaseous phase) producing the more resonance stabilised isomers of PAH, including 1-nitronaphthalene, 4-nitrobiphenyl, 1-nitropyrene and 3-nitrofluoranthene. Atkinson (59) and Arey (60) have shown that these non resonance stabilised isomers found in ambient air samples are produced from PAH reacting with OH radicals in the presence of NO_x during the day, and also at night by N_2O_5 radical formation.

N_2O_5 in the gas phase was identified as a potent nitrating species both with gaseous PAH in addition to PAH adsorbed onto a surface (in this case a glass fibre filter). Of the PAH tested, pyrene was the most reactive, followed by fluoranthene> benzo(a)pyrene> benzo(a)anthracene> perylene. This is in complete contrast to the reaction order when N_2O_5 is used in an aprotic solvent (i.e. Carbon tetrachloride). In this system the reaction order is almost opposite, with perylene> benzo(a)pyrene> benzo(a)anthracene> pyrene> fluoranthene. This reaction order is closer to that established for electrophilic substitution systems, where the nitrating species is NO_2^+ (54) NO_2/N_2O_4 (78), or gaseous flow conditions of surface adsorbed PAH exposed to NO_2 with trace levels of HNO_3 (50,79). The reason for this behaviour is that the N_2O_5 reaction occurs predominantly in the gas phase (69). The reaction is favoured with PAH which are relatively volatile, thereby having a quantity of the PAH in the gas phase.

The major reaction route thought to be occurring in exhaust emissions is the NO_2/HNO_3 system. This is known to react mainly with molecules adsorbed onto particulate surfaces i.e. the larger less volatile PAH. This was confirmed by Pitts (42) who reacted adsorbed pyrene and perylene with N_2O_5 and separately with NO_2/HNO_3. 1-Nitropyrene was formed in the N_2O_5 system in large quantities (≈60-70%). The favoured route for the nitration of perylene is via the NO_2/HNO_3 route, thought to be occurring in diesel exhaust emissions. Nitration could therefore be occurring to a greater extent with the larger organic PAH adsorbed onto particulate surfaces via electrophilic substitution, as PAH, i.e. larger than pyrene, are found almost entirely adsorbed onto surfaces. These PAH will therefore follow this route for nitration when released and cooled to 50°C in the dilution tunnel.

Atmospheric reactions including the OH radical in the presence of NO_x and the N_2O_5 systems are both capable of producing nitrated PAH of the isomerically unfavourable type. Both 2-nitrofluoanthene and 2-nitropyrene have been found in relatively high quantities in ambient air (69). This is significant due to the fact that these isomers have been found in only minor industrial emissions (2).

Other related nitrated derivatives of PAH include methylnitro and hydroxynitro PAH (69). These were identified as possible major pollutants due to their increased reactivity towards electrophilic substitution. This type of reaction however occurs with PAH adsorbed onto particulate surfaces, which are mainly the larger ones. The volatile derivatives could of course be nitrated by this surface route, or by the gas phase reactions stated (55,80), posing the question will the non-volatile derivatives be more prolific in exhaust particulates with the volatile derivatives being found in ambient air. What effect will these substituents have on the rate of reaction for the two stated gas phase reactions? As yet, little actual quantitative data has been published on this area. However, Atkinson (80) did state that naphthalene and its alkyl derivatives were removed from the atmosphere by initial reactions with OH in the presence of NO_x or by the N_2O_5 route in artificial atmospheres, therefore they should be present in ambient air. However as yet little data is actually available in this area.

4.3 Identification of Nitrated PAH in/on Organic Vegetation.

4.3.1 Introduction

Nitrated PAH are released in far lower quantities than PAH making the analysis of these trace pollutants very difficult, when they are incorporated in complex samples. It is therefore necessary for the emission samples to be relatively large for a sufficient quantity of nitrated PAH to be obtained. If a naturally occurring sampling system could be found in the environment, which is both abundant and regularly available, it would be of great advantage compared to sampling devices which are both expensive to buy and use.

Tree bark and leaf foliage have been used as passive samplers for pollutants by several authors (44,50,52-54,62). Two such papers (52,62) state that PAH are adsorbed sufficiently for detection to be possible after extraction. However few papers have described the mechanism by which the pollutant attaches to the vegetative surface. Are the pollutants adsorbed/absorbed onto/into the bark or foliage. To try and answer this question, Scanning Electron Microscopy (section 4.3.2) was used to try and visually identify the pre-concentration method of the bark surface.

The low concentrations of nitrated PAH make them difficult to detect when incorporated in such complex sample matrices. Extracted vegetation will contain not only pollutants adsorbed onto the surface, but also the organic compounds found in the vegetation itself. It is therefore necessary for the extract to undergo some kind of fractionation procedure to produce a cleaner more concentrated fraction which contains all the nitrated PAH of interest before detection is possible.

Diesel exhaust extracts, along with other similar samples have been fractionated before. However the detection of nitrated PAH from a vegetation sample to my knowledge had not been previously undertaken.

4.3.2 Surface identification of pollutants and bark.

4.3.2.1 Introduction.

Scanning electron microscopy (SEM) uses a beam of electrons to produce pictoral and elemental data of samples placed into the instrument. Images of items μm-nm in length can be regularly obtained depending on the topography and structure of the sample. This technique requires the sample to be under vacuum to prevent the electron beam encountering gas molecules prior to reaching the sample. The instrument was used in an attempt to visually and elementally identify diesel particulate material on the surface of tree bark.

4.3.2.2 Experimental

A Phillips XL40 scanning electron microscope was used for the identification of material on various surfaces. The samples were initially dried to remove any volatile material (prior to exposure to the high vacuum in the SEM chamber). They were then attached to sampler holder devices by double sided sticky tape and a colloidal silver cement (DAG) to improve the conductivity of the sample, and finally coated in a fine layer of gold to induce conductivity over the surface and to improve picture quality. Backscattering imaging was attempted with some samples coated in carbon however, little elemental data was obtained from these carbon coated samples.

The samples were placed in the instrument and the chamber pumped out to a vacuum of 10^{-4}-10^{-6} millibar. An accelerating voltage of between 2 and 10 kv were used for the samples to prevent them from charging and become damage.

4.3.2.3 Results and Discussion.

Samples examined by SEM included diesel particulates, obtained directly from a diesel engine via a dilution tunnel (see Section 2.2.1.1), and several bark samples were also investigated in an attempt to identify if particulates adsorbed to the bark surface. If we

look at Figure 4.1 (diesel particulate material sampled on a glass filter paper), we can see that the non uniform glass fibre filter paper causes a great deal of depth variation producing quite a dark photograph. Individual fibres are apparent, along with a great deal of very small particulate material attached to the filter paper. This identifies that the majority of the particulate material released by a diesel engine is initially very small (nanometres) in diameter. In the centre and bottom centre of the figure, larger agglomerates of particulate material can be seen, both of which are below 5μm in diameter. This particulate material (<5μm) has regularly been described in literature (81) as being responsible for up to 90% of diesel particulate emissions.

Figure 4.2 is an image recorded at a lower magnification than Figure 4.1 of diesel particulates on a glass fibre filter paper. The surface of the filter paper is clearly visible. The formation of irregular agglomerates of smaller particulate material is also clearly visible. These are quite large in size probably due to the sampling method inducing greater agglomeration due to the restriction in diffusion. Figure 4.3 is a higher magnification of the larger masses of particulate material , and clearly identifies the large particle as an agglomeration of very small particulate material, nanometers in diameter. A very similar particulate was identified in atmospheric samples (82), the source was more than likely diesel engines.

Samples were taken from the silver birch (tree bark A) situated in the bus station and coated with carbon. Figure 4.4 was recorded at a relatively low magnification, and shows the surface of the bark, with the relatively flat surface being visible except for various cracks and fissures that are visible. Figure 4.5 shows spherical objects of approximately 5μm in diameter collecting under a crack in the bark, a clear picture could not be obtained at lower magnification due to non-conductivity of the wood sample, causing charging on the surface of the sample. This, in addition to the low accelerating voltage lead to poor resolution and meant that only low magnification pictures could be obtained. Figure 4.6 is even more startling with these spherical objects of around 5μm being clearly attached to the surface of the bark material. If these are the larger agglomerates formed from diesel emissions, there could be a great

Figure 4.1: A High Magnification Picture Identifying Diesel Exhaust Particulate Material on the Surface of a Glass Fibre Filter Paper after Sampling in a Dilution Tunnel.

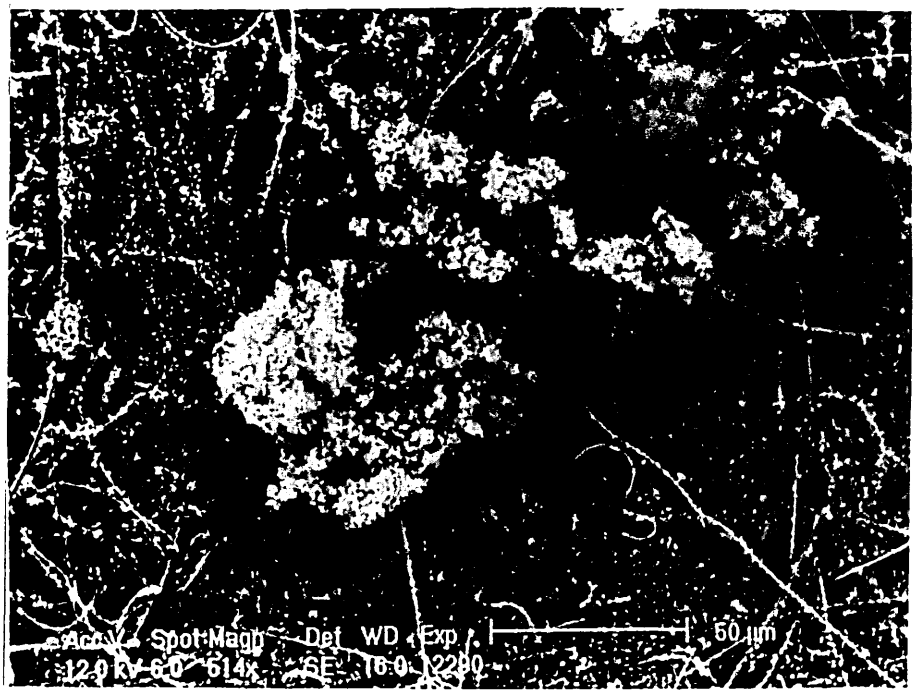


Figure 4.2: A Lower Magnification SEM Picture of Larger Agglomerates of Diesel Exhaust Particulate Material on the Surface of a Glass Fibre Filter Paper.

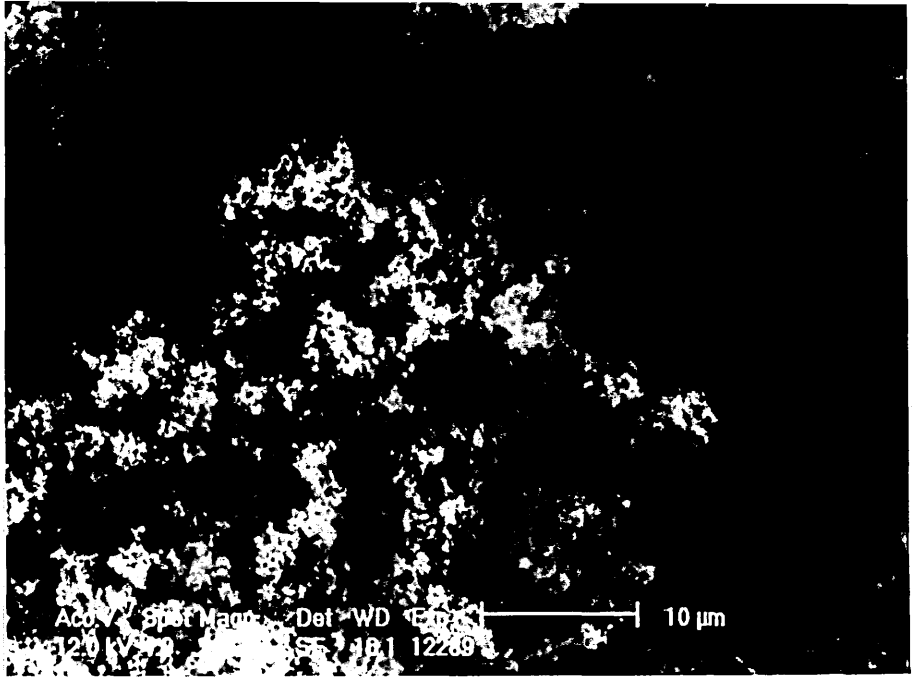


Figure 4.3: High Magnification of Larger Diesel Particulate Material due to Agglomeration of Smaller (Nanometer in Diameter) Particulate Material Sampled onto a Glass Fibre Filter Paper Situated in a Dilution Tunnel.

Figure 4.4: Low Magnification Experiment Looking at the Surface of Silver Birch Tree Bark.

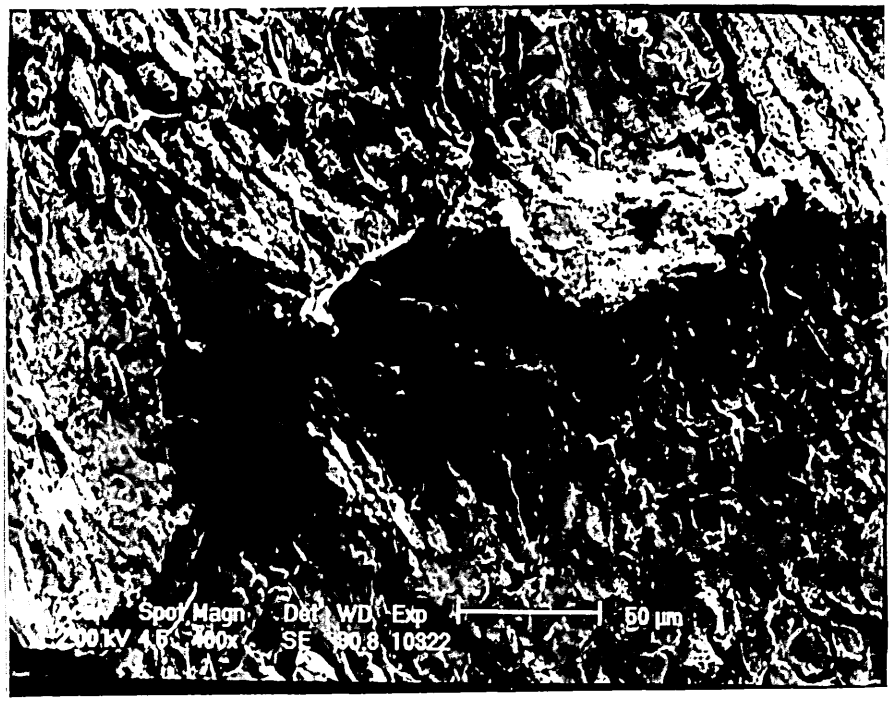


Figure 4.5: Identification of Spherical Objects (Approximately 5µm in Diameter) Collecting Under a Crack in the Bark.

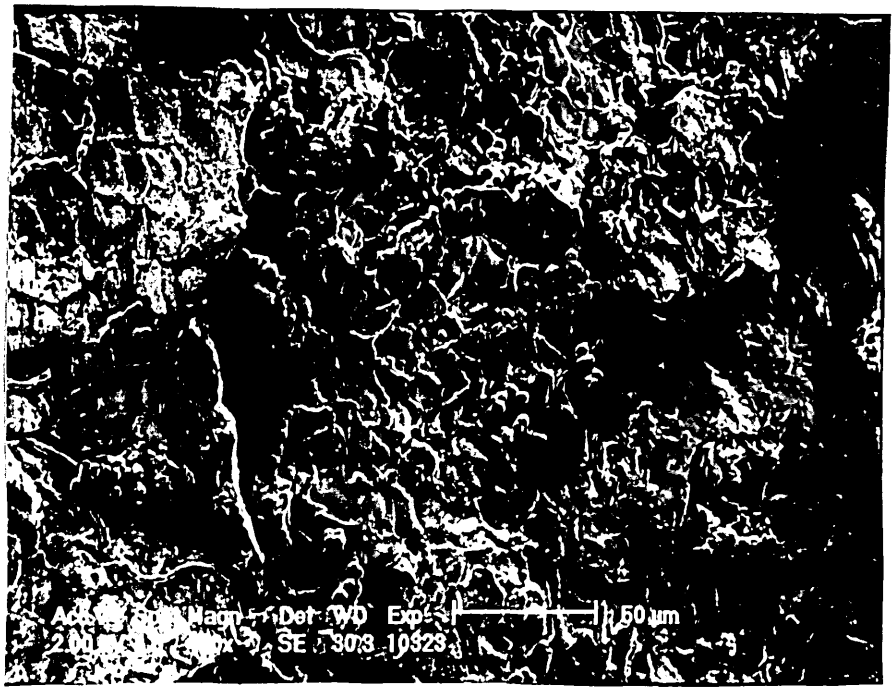


Figure 4.6: Spherical Objects Attached to the Surface of the Silver Birch Tree Bark.

deal of diesel particulate material of much smaller diameter which is attached to the bark surface which is not visible at this magnification. These spherical objects could also be pollen or other dust particles with the actual diesel material smaller and not clearly visible at this magnification. The use of backscattering electron microscopy was used to try and obtain some elemental data from the objects on the bark. The data obtained from this method of analysis was inconclusive as not enough sample was present.

4.3.3 Analysis for Nitrated PAH in/on Tree Bark, Leaf Material and Diesel Particulates.

4.3.3.1 Sampling.

Tree bark

Tree bark was sampled from two different locations around the city of Sheffield. Maple trees (which have a smooth bark) were identified in each locations and used for these experiments. The two locations were:

A - A tree situated in the central bus terminus of the city.

B - A tree situated in a park on the outskirts of Sheffield away from major roads and bus routes..

Samples of 1-3g of bark were removed from the surface of each tree, 1-2 metres above the ground. A surface area of approximately 15cm^2 of bark was removed, with the depth of bark removed not exceeding 2mm. Samples were stored in amber screw top vials at 0°C until they were extracted. Samples were taken on the following dates; 1/95, 7/95, 1/96.

Leaf Material.

The leaf vegetation was taken from Tree A on the 2/11/1995. The leaves were picked from the tree so no contamination from ground particulate matter was possible. The vegetation was stored in a brown envelope to avoid plastisizer contamination and were stored in a dark cupboard for five days until the remaining water in the leaf had evaporated. The dry leaf matter was then stored in a fridge at 0°C until extraction.

Diesel particulate samples were obtained from the system available in the engineering department at the university, previously described in Section 2.2.1.1.

4.3.3.2 Extraction.

Bark

A quantity of bark was finely chopped and placed into a cellulose extraction thimble in a soxhlet apparatus. The samples were then extracted with 80mls of dichloromethane for 96 hours. The soxhlet apparatus was wrapped in aluminium foil to minimise photochemical degradation of the desired analytes. This length of time was found to be necessary from earlier work (109) on the extraction of nitrated PAH spiked onto pre-extracted tree bark. In order to identify any contamination from the extraction process, clean thimbles were extracted and subjected to the same procedures as all other samples to produce reagent blanks.

Leaf

Approximately 10g of leaf material was broken up (due to its dry, brittle state), placed in a soxhlet apparatus and extracted for 96 hours with 200mls of dichloromethane.

Diesel particulates

Glass fibre filters, loaded with the particulate matter were placed in a soxhlet apparatus and extracted with 100 ml dichloromethane for 24 hours. All samples were reduced to residue to obtain an extracted mass of material before fractionation was undertaken.

4.3.4 Fractionation.

The extracts, obtained from the tree bark, leaf material and the diesel engine (particulate material), contained a very complex mixture of organic chemicals. Such an extract could

include; aliphatics, simple aromatics, PAH, nitrogen and sulphur containing derivatives of PAH (heterocycles) in addition to polycyclic ketones, quinones, anhydrides and organometallic molecules.

Some separation of this highly complex mixture, was necessary before analysis could be completed. Many different methods of initial fractionation/separation have been devised for diesel particulate extract fractionation, for the pre-concentration of nitrated PAH. These included:-

1) Liquid-liquid partition (84-85).
2) Semi-preparative chromatography (9,86).
3) Low and high resolution chromatography (5-7,87).
4) Chromatographic separation following a derivatisation step (8).

Solid Phase extraction systems.

More recently, attention has turned to the rapidly expanding separation method using small disposable cartridges containing separation media. These solid phase extraction cartridges are relatively quick and cheap whilst removing the possibility of cross contamination.

Scheepers (88) recently published a method for the determination of nitrated PAH found in exhaust contaminated ambient air. After extraction, samples were passed through a silica gel cartridge. 200µl of dichloromethane was used to load the extract, prior to the vacuum manifold being opened. Hexane was used to remove the non-polar compounds, with dichloromethane eluting the nitrated PAH compounds. The use of C18 (octadecylsilane) solid phase extraction cartridges in this area has also been described (89), here the selective fractionation of PAH and nitrated derivatives from three different environmental matrices was completed.

Fractionation Procedures.

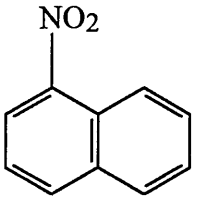
Several possible methods for the selective fractionation of nitrated PAH from diesel exhaust matrixes are described in the literature. These methods were attempted for the selective separation of nitrated PAH from vegetation matrixes (i.e. bark and leaf matter).

Methods attempted included those based on the use of:-

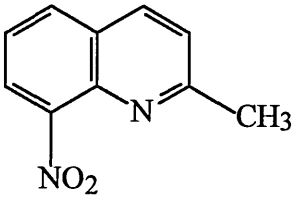
1. Alumina column on a HPLC system (Based on ref. 72).
2. Alumina semi-prep. column on a HPLC system (Based on ref. 72).
3. Aminosilane column on a HPLC system (Based on ref. 7).
4. Silica solid phase extraction (Based on ref. 88).
5. Alumina solid phase extraction.
6. Amino solid phase extraction.
7. Tandem Alumina and Amino solid phase extraction method.

A standard of seven nitrated PAH of known concentration, was put through each system to determine percentage recoveries, for evaluation purposes.

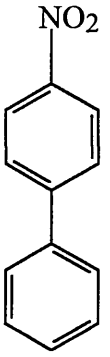
The structures of the seven nitrated PAH used, along with the internal standard (8-nitroquinaldine) are given in Figure 4.7.



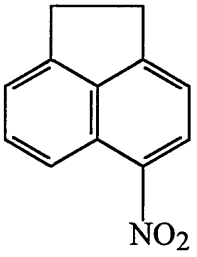
1-Nitronaphthalene.



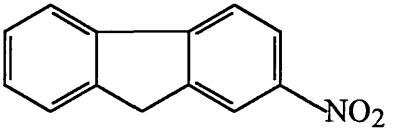
8-Nitroquinaldine.



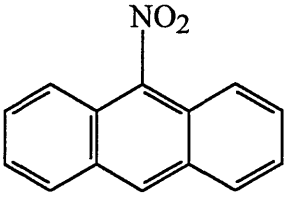
4-Nitrobiphenyl.



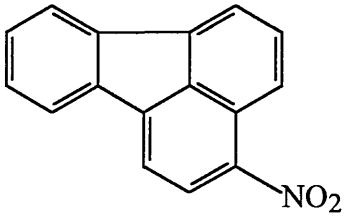
5-Nitroacenaphthene.



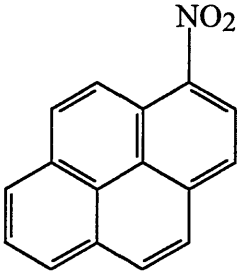
2-Nitrofluorene.



9-Nitroanthracene.



3-Nitrofluoanthene.



1-Nitropyrene.

Figure 4.7: Nitrated PAH and Internal Standard (8-Nitroquinaldine) used in This Study.

Unless stated otherwise, all standards were loaded onto each separation method in dichloromethane. Each fraction obtained after elution was reduced to residue under a stream of dry nitrogen and redissolved in the relevant quantity of solvent.

Due to cost and the inaccessibility of some instrumentation, it was decided that the first fractionation procedure used on tree bark residue would be the Basic Alumina HPLC column with step elution of compounds on an isocratic HPLC system.

HPLC procedures.

A HPLC column containing Brockman No.1 Basic Alumina was prepared. A Varian 5000 isocratic HPLC system was used with separation being followed by UV detection at 254nm. The step gradient elution system, and the classes of compounds separated are as follows:

Solvent	Class of Compounds Eluted
n-Hexane	Aliphatics
Dichloromethane	Polycyclic Aromatic Hydrocarbons
Acetonitrile	Derivatives of PAH
Acetonitrile:Methanol (3:1)	Polar PAH (multi-substituted)

The exact surface separation mechanism has not yet been identified, unlike silica where the free silanol groups are sites of adsorption for polar molecules. It was initially thought that alumina separation was achieved also due to terminal OH groups on the surface however, this was shown not to be the case. If both alumina and silica are heated above 200°C the loss of hydroxyl groups are observed. This reduces the activity of silica while increasing the activity of alumina (90). One theory is that the active alumina sites are exposed aluminium atoms or strained Al–O bonds (90). Along with the alumina active sites which are capable of adsorbing polar molecules, there are basic sites which are produced from the surface adhesion of chemical reagents. These basic sites are capable of strongly adsorbing acids (91).

This method was partially successful, with the separation of compound classes being observed. Nitrated PAH were observed in both GC-ECD results and GC-NICIMS-SIM however several problems were encountered:

Nitrated PAH are highly carcinogenic and mutogenic compounds that are found as micropollutants in the environment. With this HPLC system the maximum quantity that could be injected in one run was about 1mg of tree bark extract. (Even at this amount the column rapidly lost resolution). This meant only a very small amount of nitrated PAH material was available to be identified as the percentage recoveries were far from 100%.

To be able to increase the amount of extract being injected into the HPLC system, a semi preparative HPLC column of Brockman No.1 Basic Alumina was obtained and run as described for the previous alumina HPLC method.

Semi-preparative HPLC system.

Percentage recoveries of the seven nitrated PAH under investigation were particularly poor by this method with separation into one fraction not being achieved. Reproducibility was also poor with the percentage recoveries varying by a considerable amount. It has been proposed that the poor reproducibility could be due to irreversible adsorption of the slightly polar nitrated PAH molecules to the alumina basic sites due to their insolubility in the hexane mobile phase. The average length of time it took to perform one complete fractionation on this system was approximately 1½ hours. The quantity of residue that can be injected onto the column was also limited as large sample volume could produce contamination to the following sample. Though increasing the sample size that could be fractionated, this semi-prep alumina method was not used, due to poor reproducibility.

Amino HPLC system.

Previously used amino HPLC systems (7) employed a gradient HPLC system. A dual pump Gilson HPLC system, coupled to a UV-detector set at 254nm using a program of 100% hexane for 5 minutes with the addition of dichloromethane at 5% per minute until 100% dichloromethane is reached. It was held at this level for 5 minutes. The solvent

was then step changed to acetonitrile and run for a further 15 minutes. The flow rate was set at 1ml/minute.

The surface of the amino separating media consists of both silanol groups and an aliphatic chain capped with an amino group. Aliphatic material is not retained and passes through the column, eluting with hexane. Polar and moderately polar compounds are retained to different amounts by both the silanol and the amino sites. The nitrated PAH are thought to be adsorbed to the amino groups by dipole-dipole interactions that occur between the two nitrogen atoms. These interactions are not strong but they are sufficient to allow fractionation to occur as the polarity of eluting solvent is increased. Complete fractionation of the nitrated PAH was not achieved as trace levels were identified in the other eluent fractions.

These HPLC results were far more promising, although recoveries were still not ideal. Reproducibility also became a problem since the column began to rapidly lose resolution. Once again the problem of maximum sample size was a problem, with no more than 1mg being injected on column at any one time.

These problems pointed quite strongly to the use of solid phase extraction cartridges as they are quick and simple to use and a larger sample could be fractionated. Contamination of subsequent samples is also removed, as the individual cartridges are only used once.

Solid Phase Extraction Cartridges.

Loading techniques.

Cartridges initially used included silica and alumina separation media. Both were treated in the same way, with the eluting solvents being the same as the alumina HPLC step elution system. Several different methods of loading the sample onto the cartridge were attempted, as the extract preferred to be in dichloromethane. However, loading in dichloromethane reduced retention of nitrated PAH onto the separating media. Different loading methods included:-

Silica	Alumina
10% DCM, 90% Hexane.	10% DCM, 90% Hexane. Sample mixed with 1g of Alumina, dried, and added to the top of the cartridge

Little difference was observed in the percentage recoveries with these different loading techniques. The method which consistently produced the best results was to add the extract in a small amount of dichloromethane to the cartridge which had a quantity of hexane already covering the separating media. The dichloromethane is allowed to evaporate and the hexane pulled through the vacuum manifold with the initial quantity of hexane to remove the aliphatics. 10mls of the four eluting solvents are then passed through the cartridge fractionating the mixture.

Recoveries

Silica Cartridges.

Fractionation was not achieved as trace quantities of the nitrated PAH could be seen in all the fractions. The major quantity of nitrated PAH were found in the hexane fraction, indicating little retention by the silica separating media.

Separation from aliphatics and other organic molecules was therefore not achieved.

Alumina cartridges.

Better selectivity was achieved using the alumina cartridges as the majority of the eluting nitrated PAH were found in the dichloromethane fraction. However the percentage recoveries were still disappointingly low due to very poor reproducibility of fractionating nitrated PAH. Once again this could be due to strong adsorption forces between the nitrated PAH and the basic adsorption sites.

Amino solid phase extraction cartridges.

An identical method to that of the other solid phase extraction systems was used except the final eluting solvent was methanol. Once again, complete fractionation was not accomplished with many of the nitrated PAH being identified in other eluting fractions. The percentage recoveries were not as high as those obtained by the Amino HPLC system. However, the cartridges were far quicker to use with no problem of maximum sample size.

Amino and Alumina solid phase extraction in tandem.

To try and increase the percentage recovery and fractionation of the nitrated PAH a tandem system of an amino column on top of an alumina column was devised. cyclohexane was added as another eluting solvent to be used after hexane. This was done to ensure that all aliphatic material was removed from the sample. Another solvent eluent of 20% dichloromethane 80% cyclohexane was also added to improve the specificity of the fractionation system to nitrated PAH.

The rationale for this was that the bonded amino group should strongly interact with the nitrogen lone pair, hence selective fractionation of nitrated compounds should occur. Alumina suffered from poor reproducibility possibly from irreversible adsorption to the separating media when the sample was introduced to the system in insoluble hexane. How would this be effected by the nitrated PAH being loaded onto the column in a moderately polar solvent (dichloromethane)? The nitrated PAH should be selectively removed from the amino cartridge by a slightly moderately polar eluent. They should then pass through the alumina column with little retention while any polar compounds eluting or breaking through the amino cartridge should be retained by the basic sites on the alumina. The percentage recoveries can be seen in Table 4.1.

Four of the seven nitrated PAH have a recovery of greater than 95%. 9-Nitroanthracene and 3-nitrofluoranthene have recoveries of 50% and 70% respectively with 1-Nitronaphthalene having the lowest recovery at approximately 30%. This was found to be due to the volatility of 1-nitronaphthalene and the use of a stream of dry nitrogen to

reduce the residue to dryness. By reducing the extract to a small quantity of solvent the percentage recovery of 1-nitronaphthalene was increased.

TABLE 4.1: Percentage Recoveries of Nitrated PAH Achieved After Fractionation Through Amino/Alumina SPE System (n=6).

	Hexane		Cyclohexane		20% Dichloromethane		Dichloromethane		Acetonitrile	
Compound	% Recovery	S.D.	% Recovery	S.D.	% Recovery	S.D.	% Recovery	S.D.	% Recovery	S.D.
1-Nitronaphthalene	0	0	0	0	28.27	1.92	0	0	0	0
4-Nitrobiphenyl	0	0	0	0	105.25	6.78	0	0	0	0
5-Nitroacenaphthene	0	0	0	0	94.97	7.37	0	0	0	0
2-Nitrofluorene	0	0	0	0	106.15	1.02	0	0	0	0
9-Nitroanthracene	0	0	0	0	53.25	1.17	0	0	0	0
3-Nitrofluoranthene	0	0	0	0	72.15	2.24	0	0	0	0
1-Nitropyrene	0	0	0	0	108.31	10.2	0	0	0	0

4.3.4.1 Conclusion.

The original Alumina HPLC system worked quite well, even though only a small sample volume could be injected and reproducibility was rapidly lost. However the initial work produced good fractionation of the samples injected. The ECD chromatogram obtained of the fractionated bark was still very complex. Therefore a more rigorous clean up technique was needed for cleaner, chromatogram to be obtained.

The initial work carried out with solid phase extraction cartridges was very disappointing with the percentage recoveries being consistently low. With a more thorough understanding of the principles behind solid phase extraction the two stage system was devised, producing a relatively high percentage recovery and reproducibility. Even the introduction of further isomers and different nitrated PAH were found to be preferentially fractionated by this method.

At present separation of PAH up to pyrene, from the nitrated derivatives has been achieved with the PAH being eluted in an additional eluent of 5% dichloromethane in cyclohexane, and the nitrated derivatives and the larger PAH eluting out in a 20% mixture of dichloromethane and cyclohexane.

4.3.5 Separation and Detection of Nitrated PAH.

High Performance Liquid Chromatography (HPLC) Analysis.

Organic compounds and specifically nitrated PAH are released in low concentrations from the combustion of naturally occurring fuels. After fractionation various separation methods and a range of detectors have been used for the qualitative and quantitative determination of these micropollutants. High performance liquid chromatography (HPLC), (9,73) and multi dimensional HPLC (92) have been used in the final selective and sensitive identification of nitrated PAH in samples of diesel particulates. This method of separation (HPLC) with various detectors was recently reviewed (93).

A number of detection systems have been used for the identification of nitrated PAH, these include UV detection at 254nm (94). However, better sensitivity has been obtained from fluorescence detection after the nitrated PAH are reduced to their corresponding amines (95), this was recently carried out using an on-line zinc dust column (96), prior to selective fluorescence analysis for four nitrated PAH. Electrochemical (97) and chemiluminescence detection methods have also been used in the detection of these trace organic pollutants, due to the detectors increased selectivity and sensitivity (98-100).

Gas Chromatographic Analysis.

The majority of the work in this area seems to favour the use of capillary gas chromatography for the analysis of such low level contaminants. Reasons for this include the greater sensitivity of some common GC detectors compared to regularly used detectors in HPLC systems. Many of the extracts obtained are highly complex so the greater resolution of gas chromatography is a great advantage compared to HPLC.

It has been discussed that certain nitrated PAH are not stable (suffering from partial decomposition in various parts of the GC instrument, including the injector (101), column (102) and MS interface (102). HPLC with no heating necessary for separation to be completed seems the ideal method of separation and detection. However the lack of a

gradient HPLC system and a programmable fluorescence detector meant that GC with ECD and NICI-SIM were the best techniques available.

Numerous detectors have been used throughout the literature all having their advantages and disadvantages associated with the study of nitrated PAH. Detectors used include:-

1. Flame Ionisation Detector (FID) (8,71,72,86,103-105).
2. Electron Capture Detector (ECD) (8,105,106).
3. Nitrogen-Phosphorus Detector (NPD) (1,8,12,72,86,104,107).
4. Thermal Energy Analyser (TEA) (5,7,34,74,108).

Flame ionisation (FID) detects organic molecules (specifically CH_2 groups) through the combustion of the molecule after the addition of hydrogen and air to the capillary gas flow. The detector is therefore non specific, with nearly all organic molecules being detected. Interferences and co-elution are common with this detector.

The electron capture detector (ECD) is inherently sensitive to electronegative functional groups (halogens, nitro groups and quinones) due to the capture of electrons from ionised carrier gas by a Ni^{63} beta emitting source. The detector is more specific than an FID, as compounds without electronegative functional groups are not detected, thereby reducing interferences and co-elution. However, quinones and oxygenated compounds (prolific in diesel emissions) have been reported as causing interferences (8,86).

The nitrogen-phosporous detector (NPD) can be used specifically for the detection of nitrogen containing compounds. This specific detector should reduce interferences from organic molecules that do not contain nitrogen. However, interferences have been identified when using this detector with diesel emissions (16,47) and carbazole along with related compounds were found to interfere with samples from ambient air and industrial emissions (105). The limit of detection is not as low as that obtained by an ECD detector.

The thermal energy analyser is a very specific detector for the detection of nitrated compounds, due to its four stage pyrolysis/chemiluminescence mechanism.

1. Pyrrolytic cleavage of the C-NO_2 bond, can also cleave N-NO_2, C-NO and N-NO moities to produce nitro radicals.
2. Pyrolytic degradation of nitro to nitroso radicals. This step is highly specific to nitrated compounds, reducing interferences from other compounds in a mixture.
3. Reaction of these nitroso radicals with ozone to produce excited singlet state NO_2.
4. Decay of excited NO_2 to ground state NO_2 by the emission of a photon.

Detection of these photons can be achieved at very low concentrations, producing a limit of detection around 25-80pg for many nitrated PAH (109).

Mass Spectrometer Detectors

Many different methods of mass spectrometry have been used in an attempt to discover a quick and simple method for the analysis of nitrated PAH compounds. Methods which have been employed are as follows :-

1. Electron Ionisation (EI) (1,8,10-12,60,71,72,74,75,108,110,111).
2. Negative Ion Chemical Ionisation Mass Spectrometry. (NICIMS) (1,6,10,12,71,105,106).
3. Mass Spectrometry/Mass Spectrometry (MS/MS), using constant neutral loss, (11).

Electron impact (EI) ionisation is a well documented technique which compares mass spectra obtained from a sample against a library of predetermined spectra to help identify compounds. This spectral matching, in conjunction with retention time comparisons is a method of verifying results. However, EI is not a particularly sensitive method of detection.

One of the major problems with electron ionisation mass spectrometry is that almost too much fragmentation occurs, producing a spectra which is often devoid of the parent ion. NICI is a gentler ionisation procedure, with methane being introduced directly into the ion source, thereby acting as a moderator for the electrons. The result is a large population of "low energy" electrons. These are readily captured by electronegative

species, including nitrated-PAH, resulting in little fragmentation. This produces a selective and sensitive technique for the identification of electronegative compounds, by their parent ions, without the use of external standards

MS/MS using a triple quadrupole mass spectrometer and constant neutral loss scans can be used to obtain highly specific quantitative data for a particular class of compounds. GC separated compounds are introduced to the mass spectrometer source where e.g. chemical ionisation occurs (11). The ions pass through quadrupole 1 (in scan mode). These ions are then introduced into a collision cell where fragmentation is induced through collision with nitrogen. The 3rd quadrupole scans with, for example, an offset 17 daltons below quadrupole 1. Since the loss of 17 daltons (OH) is attributed to nitrated compounds under these conditions. It is an excellent method for the identification of unknown nitrated compounds in a complex mixture.

4.3.5.1 Instrumentation

GC/ECD.

The instrument used in all cases was a Hewlett Packard 5880 Gas Chromatograph using a 5% diphenyl wall coated open tubular capillary column (Rtx-5, Restek, Thames Chromatography U.K.) (20m x .32mm) with a film thickness of .25μm. The carrier gas used was nitrogen, at a flow rate of 1ml/min, with nitrogen as the makeup gas yielding a total flow of 30ml/min. 1μl of each sample was injected splitless using a fluffy Hewlett Packard 7673A autosampler. The injector temperature was set at 275°C with the detector at 300°C. The oven program temperature used was 40°C for four minutes, ramp 1; 25°C/min to 145°C hold for one minute, ramp 2; 5°C/min to 280°C with a final hold time of fifteen minutes.

GC/NICIMS-SIM.

This work was performed on two instruments due to the purchase of a more sensitive VG Trio III midway through the study. Initial work was completed on a Hewlett

Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 1 Mass Spectrometer (VG MassLab, Manchester U.K) with the MS working in the selective ion monitoring (SIM) mode.

The column used was a 30m x .32mm i.d. 5% diphenyl wall coated open tubular capillary column (Rtx-5 Thames Chromatography U.K.), with a film thickness of .25μm. Helium was used as the carrier gas at a flow rate of 1ml/min. The injector temperature was set at 275°C with the oven temperature program being 40°C, held for four minutes then increased at 25°C/minute to 175°C held for one minute the temperature was then increased at 5°C/minute to the final temperature of 280°C for 15 minutes. All samples (1μl) were injected manually in splitless mode.

Later work was undertaken using a Hewlett Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 3 mass spectrometer working in SIM mode. In both cases the reagent gas used for chemical ionisation was methane with an ion source temperature of 125°C. The NICI conditions were optimised by injecting a small quantity of methyl iodide via the septum inlet and tuning the instrument via the peak at m/z 127. A SIM experiment was set up monitoring each of the M-• shown in Table 4.2. The column used was a 60m x .32mm i.d. 5% diphenyl wall coated open tubular capillary column (Rtx-5) with a film thickness of .25μm. The injector temperature was set at 275°C and the oven temperature program was as described earlier. The carrier gas was helium at a flow rate of 1ml/min. 1μl of each sample was injected splitless.

4.3.6 Results.

The residue obtained from both the bark and leaf extracts were green/brown in colour and they were a complex mixture of organic compounds from the tree and pollutants, adsorbed to the vegetative surface. The particulate extract was black in colour due to the carbon particles extracted over by the soxhlet siphoning mechanism.

The following results (Tables 4.2 and 4.3) were obtained using gas chromatography with MS using NICI-SIM and ECD respectively.

Table 4.2: GC/NICI-SIM. Quantitative Results in ng of Compound in 1 gram of Bark or Leaf Material and μg in 1 gram of Diesel Particulates.

Compound	SIM Molecular Ion	Tree A Jan-95	Tree A Jul-95	Tree A Jan-96	Tree B Jan-95	Tree B Jul-95	Tree B Jan-96	Leaf material	Diesel Particulates
1-Nitronaphthalene	173	70.48	2.48	22.11	0.71	8.07	26.53	9.31	1.64
Internal Standard	188								
4-Nitrobiphenyl	199	37.99	16.42	37.26	8.19	6.23	16.59	5.41	6.14
5-Nitroacenaphthene	199	20.67	0.71	32.3	15.38	Trace	38.4	N.D.	2.48
2-Nitrofluorene	211	11.79	1.79	45.62	1.28	N.D.	30.59	2.1	N.D.
9-Nitroanthracene	223	76.19	Trace	23.77	D.S.	N.D.	7.69	8.94	4.13
3-Nitrofluoranthene	247		Trace	45.3	-	N.D.	26.69	3.29	Trace
1-Nitropyrene	247		N.D.	52.91	-	N.D.	25.4	1.56	21.73

Each quantitative result is from two samples analysed in duplicate.

N.D. None determined.

Trace. Peak present but below limit of detection.

D.S. Nitrated PAH had degraded in sample.

Obscured. The relevant peak was obscured beneath a large contamination peak.

Table 4.3: GC/ECD. Quantitative Results in ng of Compound in 1 gram of Bark and μg in 1 gram of Diesel Particulates.

Compound	Tree A Jan-95	Tree A Jul-95	Tree A Jan-96	Tree B Jan-95	Tree B Jul-95	Tree B Jan-96	Leaf material	Diesel Particulates
1-Nitronaphthalene Internal Standard	48.52	6.33	39.37	3.43	4.17	28.9	3.61	2.5
4-Nitrobiphenyl	38.99	Trace	26.33	3.3	Trace	35.4	N.D.	13.19
5-Nitroacenaphthene	20.67	N.D.	103.39	7.49	N.D.	71.09	N.D.	12.43
2-Nitrofluorene	11.79	Trace	91.49	3.4	N.D.	43.94	N.D.	N.D.
9-Nitroanthracene	N.D.	N.D.	57.49	Degraded	N.D.	11.09	1.88	9.79
3-Nitrofluoranthene		Obscured	Obscured		Obscured	Obscured	N.D.	Obscured
1-Nitropyrene		N.D.	89.98		N.D.	73.63	Trace	18.39

N.D. None determined.

Trace. Peak present but below limit of detection.

D.S. Nitrated PAH had degraded in sample.

Obscured. The relevant peak was obscured beneath a large contamination peak.

4.3.7 Discussion

Tree bark.

Initial analysis of the chromatograms obtained by GC/NICI-SIM (Figure 4.8 (standard) and Figure 4.9 (bark extract)) compared to the GC/ECD chromatograms (Figure 4.10 (standard) and Figure 4.11 (bark extract)), identify the GC/NICI-SIM detection method as being the superior. The chromatograms are a lot cleaner with baseline resolution being achieved. The difference in the chromatograms can be easily explained. The GC/ECD detector responds to all molecules that electron capture, and is highly sensitive to electronegative functional groups such as halogens, quinones, ketones, nitrated derivatives etc. This detector can be seen to be less selective (also due to the inherent specificity of NICI-SIM), as the GC/ECD chromatograms are far more complex containing a greater number of peaks. This makes quantitation of trace levels in this complex matrix very difficult, even after fractionation. This was one of the major reasons behind the method development work carried out on the fractionation method, so a fraction containing all mononitrated species could be selectively separated from the other numerous organic molecules.

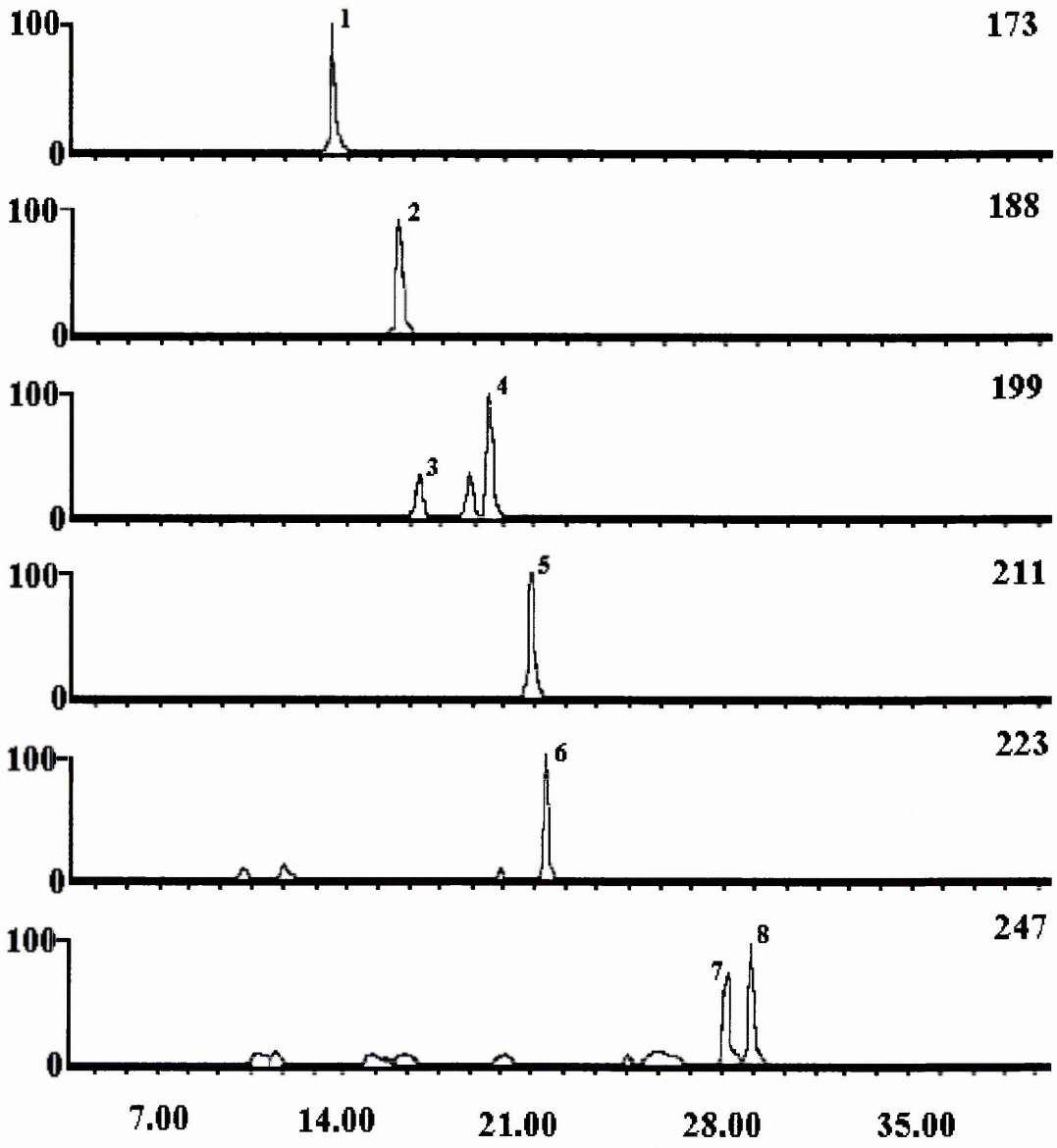


Figure 4.8: GC-NICI-SIM Chromatograms of a Standard Containing Seven Nitrated PAH and an Internal Standard: 1. 1-Nitronaphthalene, 2. Internal Standard, 3. 4-Nitrobiphenyl, 4. 5-Nitroacenaphthene, 5. 2-Nitrofluorene, 6. 9-Nitroanthracene, 7. 3-Nitrofluoranthene, 8. 1-nitropyrene.

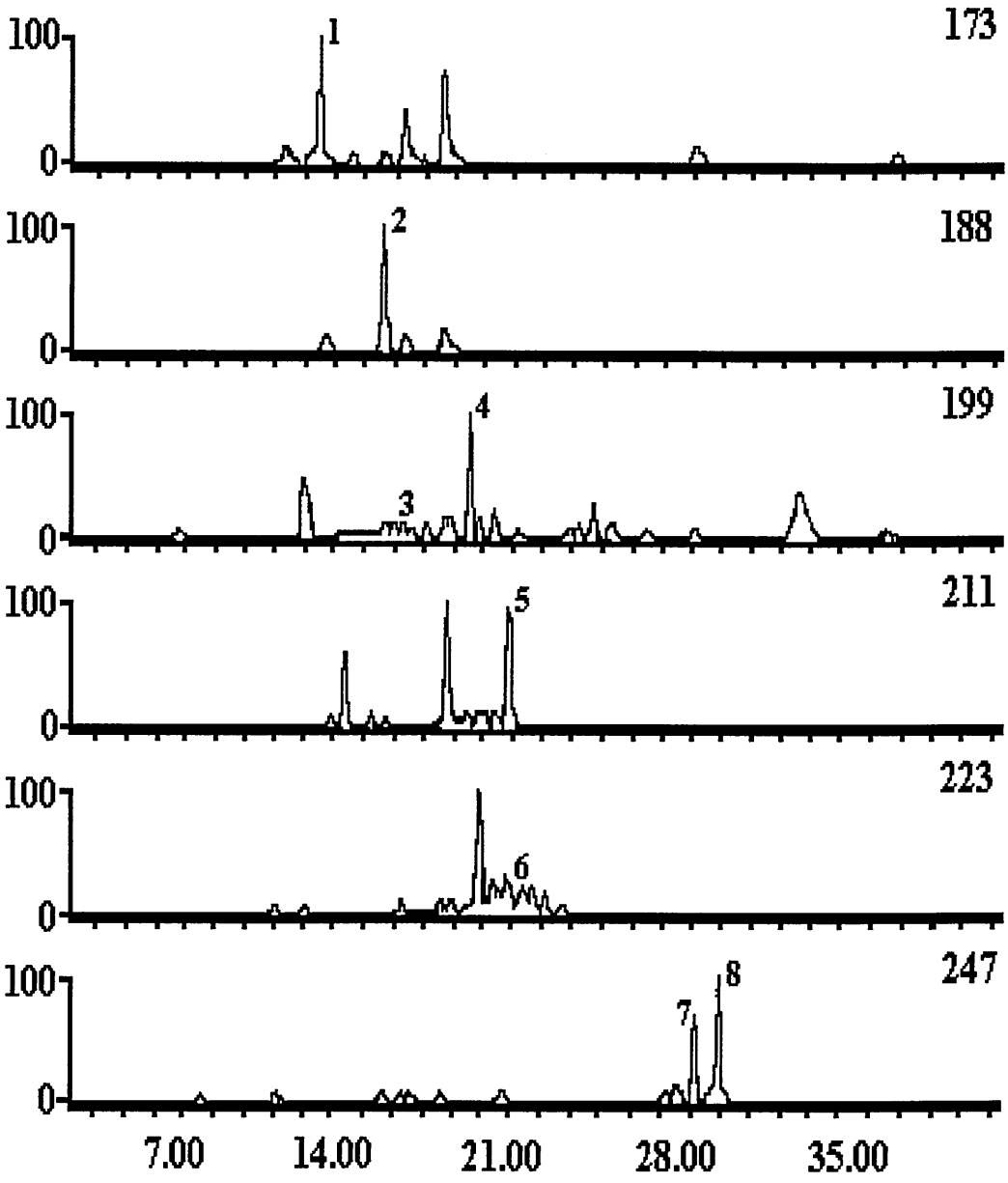


Figure 4.9: GC/NICI-SIM Chromatograms of Tree Bark A (2/96) After Fractionation, Identifying 1. 1-Nitronaphthalene, 2. Internal Standard, 3. 4-Nitrobiphenyl, 4. 5-Nitroacenaphthene, 5. 2-Nitrofluorene, 6. 9-Nitroanthracene, 7. 3-Nitrofluoranthene, 8. 1-Nitropyrene.

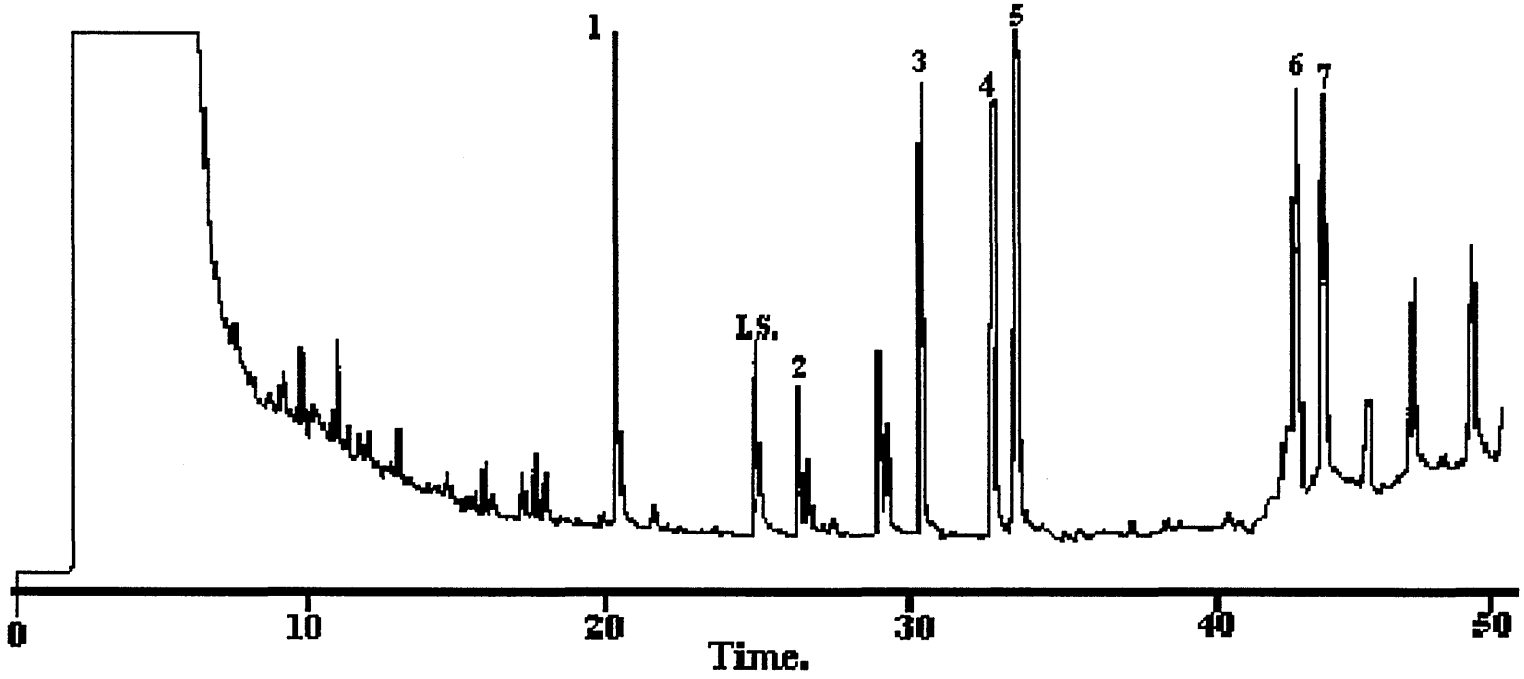


Figure 4.10: GC-ECD Chromatogram of Seven Nitrated PAH with Internal Standard: 1. 1-Nitronaphthalene, I.S. Internal Standard, 2. 4-Nitrobiphenyl, 3. 5-Nitroacenaphthene, 4. 2-Nitrofluorene, 5. 9-Nitroanthracene, 6. 3-Nitronaphthalene, 7. 1-Nitropyrene.

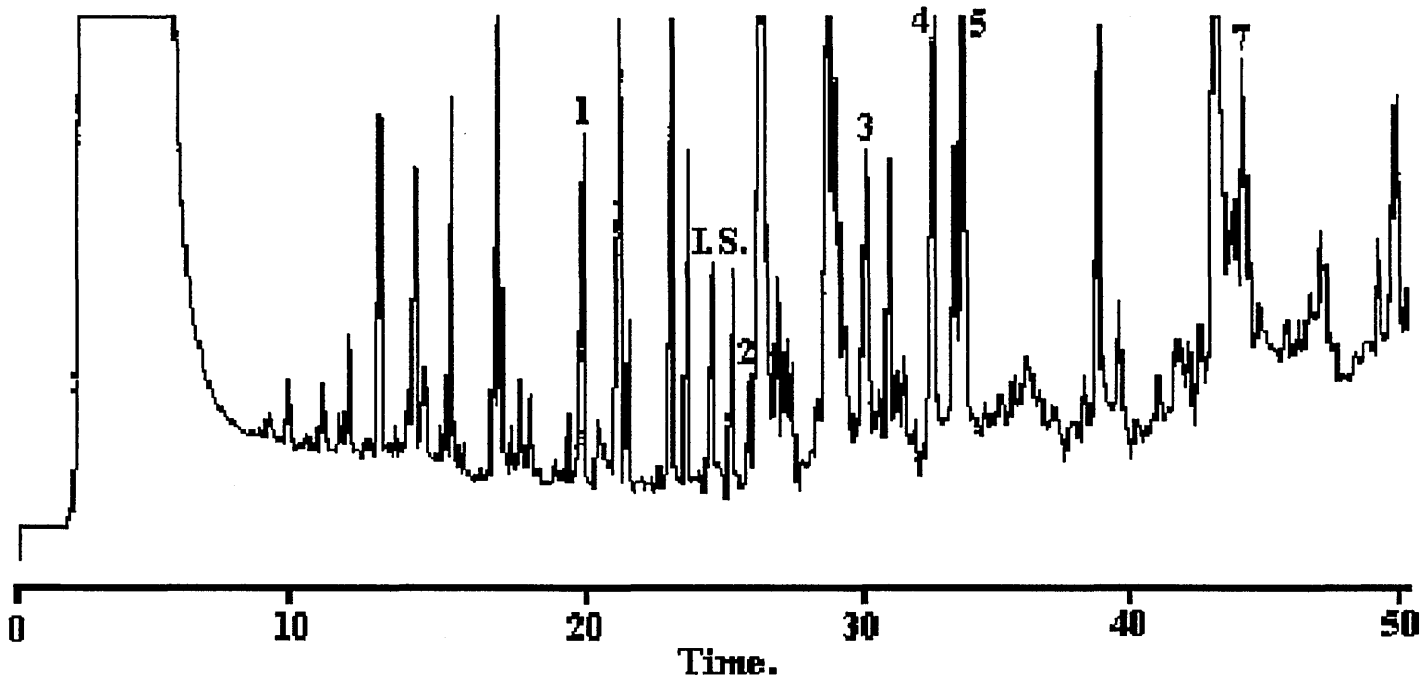


Figure 4.11: GC-ECD Chromatogram of Tree Bark (1/96) with Internal Standard: 1. 1-Nitronaphthalene, I.S. Internal Standard, 2. 4-Nitrobiphenyl, 3. 5-Nitroacenaphthene, 4. 2-Nitrofluorene, 5. 9-Nitroanthracene, 7. 1-Nitropyrene.

If we compare the results of tree barks A and B for the January samples by both GC/NICI-SIM (Table 4.2) and GC/ECD (Table 4.3) we can see that the total quantities identified correlate very well by the two methods. (Note. Except for 9-Nitroanthracene which could not be detected by GC/ECD as the molecule had rapidly degraded before quantitation could take place.

Another major observable difference is the quantities of the nitrated PAH found in the two trees from different environments. The quantitative results obtained from GC/NICI-SIM (Table 4.2, Figures 4.8 -Standards and 4.9 - bark A) identify tree bark A as containing a larger quantity of nearly all nitrated PAH than tree bark B throughout the year. The exceptions to this were 5-nitroacenaphthene (Jan/96) and 1-nitronaphthalene (July/95 and Jan/96) which were found to be higher in bark B than in bark A at these sampling times. The semi-quantitative values obtained by GC/ECD (Table 4.3, Figure 4.10 - standards, Figure 4.11 - bark A) show a similar trend to that in (Table 4.2) with tree bark A consistently containing a larger amount of individual nitrated PAH compared to tree bark B. Here, the only exception is 4-nitrobiphenyl which is seen to have a greater amount in bark B than in the bark A (Jan/96).

This is what you would expect as tree bark A is situated in Sheffield's city centre bus station surrounded by the major source of these isomers of nitrated PAH i.e. diesel engine exhaust emissions. Tree bark B on the other hand is situated in a park on the outskirts of Sheffield away from major diesel sources.

Over the three sampling dates both the GC/NICI-SIM data (Table 4.2) and the GC/ECD data (Table 4.3), show higher levels of nitrated PAH in bark samples taken during January compared to July. The only compounds quantified in both trees during the summer sampling period were 1-nitronaphthalene and 4-nitrobiphenyl, with a further two nitrated PAH, 5-nitroacenaphthene and 2-nitrofluorene, being detected in the bus station bark (July/95). With the exception of 1-Nitronaphthalene in bark B (Jan 95), all nitrated PAH were detected at higher concentrations in the January samples compared to the July 1995 sample. This seasonal variation of organic pollutants in the environment has been identified by others (112), with increased concentrations identified in the spring and autumn seasons. The reasons for this may be a combination of the following:

1. All nitrated PAH investigated in this study are found to some extent in the vapour phase at ambient temperatures. Average temperature and pressure will therefore have a great effect on the condensation of pollutants onto surfaces. For example, compounds will condense out during times of cold ambient temperatures (i.e. November-February in Britain) this is called the "Cold Condensation effect".

2. Physical effects could induce the preferential adsorption/absorption onto/into the bark matrix. The amount of shade the bark samples get from direct sunlight as these compounds are known to photodegrade. These organic molecules are likely to photodegrade due to the higher levels of UV radiation and the presence of radicals capable of causing degradation i.e. •OH during the summer months.

3. The cold winter months always induce an increase in the emissions of organic combustion material due to the extra use of vehicular transport by commuters and travellers. More organic fuel is also burnt due to the increased use of electricity for heating and lighting.

4. In winter, disciduous trees are without any foliage so any gaseous or particulate associated pollutants condensing out onto vegetation can only condense upon the bark.

5. Preferential adsorption of certain nitrated PAH could be a reason for the increased quantities of some compounds observed. The ambient temperature and the individual vapour pressures will determine whether the compound is predominantly in the gaseous phase or adsorbed onto a particulate surface throughout the year. Variations in annual phase distribution of nitrated PAH have been identified (113). A variation in the degradation rate of certain compounds [e.g. 9-nitroanthracene which is known to rapidly degrade to anthraquinone (114) and 1-nitropyrene, thought to degrade initially to hydroxypyrene (115)] may also play a part.

6. Bark also grows in the spring and summer months thereby removing the surface adsorbed material.

However the small number of samples taken in this present study only allow us to present these ideas "for discussion" rather than make any definitive conclusions.

Work was also undertaken to reduce the tree bark extraction time by using extracted cotton wool and dichloromethane to swab an area of tree bark and remove the particulate material adsorbed to the surface of the tree. This produced a blackened suspension in the dichloromethane after the swabbing was complete, and left a "clean" area of tree bark which could be seen to be several shades lighter (less soiling) than an untreated area (116). These extracts provided us with the knowledge that nitrated PAH could be quantified this way, adding to the hypothesis that particulate material and possibly some of the gaseous pollutants adsorb to the surface of vegetation and that tree bark can be used as a passive sampler.

Leaf results.

The quantitative results (obtained by GC/NICI-SIM, Table 4.2), for the leaf extract compare quite favourably with the tree bark values from January 1995, as both the 1-nitronaphthalene and the 9-nitroanthracene are found in the largest amounts, followed by 4-nitrobiphenyl. The only difference is that 5-nitroacenaphthene was not detected in the leaf extract.

The only quantitative values obtained by GC/ECD (Table 4.3) were for 1-nitronaphthalene and 9-nitroanthracene, which have the largest quantitative values by GC/NICI-SIM. This poor response indicates the low concentrations of nitrated PAH on/in the leaf material was often beyond the GC/ECD limit of detection.

The results obtained from the NICI-SIM detection method contained several peaks on one mass line. These additional peaks could possibly be isomers of the same nitrated PAH (2-nitronaphthalene, which is known to be formed in ambient air from the reaction of naphthalene and nightime levels of N_2O_5 (43)) along with the chance of it being a compound with the same mass. If this was to be proved to be true it would show that leaf vegetation is capable of adsorbing organic pollutants from the gaseous phase as 2-

nitronaphthalene has been tentatively identified in diesel particulates (74). However, the majority is likely to be produced from gaseous reactions occurring in ambient air.

Diesel particulates.

The particulate results identify that all the nitrated PAH (except surprisingly 2-nitrofluorene as this has been previously identified in diesel exhaust particulates (1)) were present in the GC/NICI-SIM chromatograms. The GC/ECD also identified five of the seven nitrated PAH. 3-Nitrofluoranthene could not be identified by GC/ECD due to an impurity in the solvent obliterating this area of the chromatogram. The quantities of nitrated PAH identified by the two methods are similar. However, the GC/ECD results do seem to be consistently higher than the GC/NICI-SIM results (excluding 1-nitropyrene). 1-Nitropyrene is often identified as the major nitrated PAH present in diesel exhaust fumes (1) and these data agree with this.

4.3.8 Conclusion.

Through this study, we have shown that tree bark and leaf material can be used as passive samplers to identify atmospheric pollutants, in this case nitrated PAH. Of the seven nitrated PAH investigated, five were positively identified in diesel particulate matter with four of these being found in the leaf extract and four being found in January 1995 Tree bark. This indicates that diesel emissions and possibly other anthropogenic emissions are produced in large quantities that are not being rapidly removed from the environment. It does identify one route of removal of these compounds from the air, as the concentration found on bark is lower in the summer than during the winter. This was seen by Librando. and co-workers (5) who analysed air samples over a one year period. The identification of the major routes of removal and the products formed need to be investigated further to ensure these toxic chemicals are not being deposited into the food chain. The possible identification of how the pollutants are adsorbed into vegetation i.e. from the gaseous phase or directly from particulates is also of interest as the sampling method could be expanded to the analysis of nitrated PAH isomers produced in ambient air (69,117). With such knowledge, possible sources and routes to removal could be investigated further with the result being a mass-balance model of nitrated PAH and their

ultimate removal from the environment. The necessity for quick, robust methods for the determination of these molecules is therefore imperative along with the identification of any other major sources. If the other sources of nitrated PAH are of little consequence, nitrated PAH (specifically 1-nitropyrene) could be used as a diesel marker to identify heavily polluted areas.

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Conclusion.

Outdoor environments.

The results obtained for particulate associated material associated with diesel emissions have provided a great deal of interesting data. The results on outdoor emission of particulate material identified diesel engines as a major contributor to urban atmosphere pollution (an average of 45%), such a result is similar to results published in literature for UK sites (ie. 40-50% (1)). In fact, the value of 64% for particulates ≤5μm (identified in the large volume sample using 1-nitropyrene as the marker) being from diesel engines in Sheffields city centre, supports recent percentages attributed to diesel of 86% (for PM10 (2)) and 77% (3) both centred on the city of London. Such quantities are higher than those identified in Vienna during 1984, probably due to the higher proportion of diesel buses and HGV's found in and around the Sheffield area (Vienna had an extensive tram system and Sheffields tram system was very much in its infancy when the sampling regime was taking place). The geological position of Sheffield (nestled in a valley surrounded by seven hills also produces a great deal of atmospheric stagnation during certain meteorological conditions. The Vienna study also sampled total suspended particulate material while we sampled material 5μm and below, which is more specific to diesel combustion. Such sampling would increase the percentage apportionment associated to the diesel emissions discussed in the Vienna study.

This initial apportionment data of diesel emissions has provided some interesting results. However, if the sampling methods were to be used again, a number of methodological improvements could be incorporated. The use of C24 as a marker for diesel emissions was far from ideal even though plausible results were obtained. A larger volume of air could be sampled (using a high flow pump which can sample up to $1m^3$ on polyurethane foam plugs) to obtain a sample from which quantitative values of 1-nitropyrene are possible. A sufficient sample size in an urban environment would be between $30\text{-}40m^3$ producing a particulate mass sample of approximately 900μg. Duplicate sampling of perhaps 20 sites would ensure accurate sampling analysis and identify any instrumental and experimental error.

Diesel emissions and specifically particulate associated organics have been shown to include highly carcinogenic/mutagenic compounds These include certain nitrated PAH, dinitrated pyrenes and 3-nitrobenzanthrone, recently identified as the most highly mutagenic compound (by the Salmonella Typhimurium TA98 test) and suspected as being a human carcinogen (4). It can be seen that associated compounds known to be released in such emissions (NO, NO_2 and aliphatic material) will also be released in relatively large quantities. These emissions can react in the atmosphere to produce secondary pollutants including nitric acid, ozone and to a lesser extent, sulphuric acid. This cocktail of compounds released into such an atmosphere can react further with various reactive species. These can include oxidative species identified in urban atmospheres during the day (Section 1.4.1), in addition to nitration known to occur during the night (Section 1.4.2). A number of both primary and secondary organic compounds released/produced in the atmosphere, are suspected of having major effects on the health of certain individuals, especially those with weakened/developing pulmonary or cardiovascular systems (specifically the elderly and children). Such results show the necessity for further research into the effect of anthropogenic emissions within

an atmosphere, to identify the routes of degradation and the effects such products can have on such an environment.

The association of particulate material with vegetation has provided one route for the removal of particulate material released from anthropogenic emissions, known to pollute urban atmospheres. We were also able to show the diffusion of such particulate material into an indoor atmosphere (specifically diesel particulates). However, as these are only short distance transportation routes for such material, what is the fate of such material when it is transported over greater distances? This demonstrates the need for a diesel engine catalytic converter, or an emission trap to remove a large proportion of the particulate urban pollution, ultimately resulting in a cleaner atmosphere. This could subsequently reduce the formation of secondary pollutants, reducing smog formation and prevent health problems associated with air pollution.

Indoor environments.

The more traditional methods of ETS analysis (carried out on all samples) were shown to over-estimate the contribution of ETS to an atmosphere through the use of specific marker compounds. This was often due to the increase in response of non ETS material in the non specific ETS techniques. We identified solanesol as the most appropriate marker compound for particulate ETS, as scopoletin seemed to under-estimate the contribution of ETS, possibly due to rapid photochemical degradation of scopoletin with UV radiation.

The following cigarette equivalent calculations were carried out to provide a result which could be clearly understood, and compared to equivalent values published in associated literature. However, the data used to calculate these values were based upon a single data point sample from a small number of sites. These preliminary results are therefore dependant upon the usual restrictions associated with such data; these include uncertainties from instrumentation (both sampling based and analytical) in addition to experimental analysis, through non duplicate sampling at each site. Such a sampling regime was undertaken due to the time left for the field study. This restricted the analysis to either a broad analysis structure seen in this thesis, or a reduction in the analytical methods with samples taken in duplicate. The preliminary nature of the field study, and the dictate from the industrial sponsor contributing to this study, meant that the broad analysis structure was favoured. It was decided that this would provide the most useful data, and identify more clearly areas of tracer analysis and associated contribution results that could be investigated more thoroughly at a later date.

The results from the indoor field samples were also used to quantify the amount of ETS particulate material consumed by a non smoker in a smokers room. This was found to be of little significance due to the low concentration of material in a smokers atmosphere (because of the rapid adhesion of ETS particles to surfaces), and also due to the healthy lung clearance of a non smoker. In fact the cigarette equivalence for particulates of a non smoker exposed to a smoky atmosphere (over a period of a year) is 14 and 3 cigarettes for home and work environments respectively. These are the highest conceivable values due to the way the equivalence was calculated. More alarming are the cigarette equivalence identified when looking at certain volatile compounds released in ETS. We determined that an equivalent of approximately 50 cigarettes would be aspirated per year by a non smoker in the same smoky environment. The effects these compounds have on

the respiratory system is unknown. However, benzene is a suspected carcinogen and such a source is additional and to some extent unnecessary. Further research into the effects of volatile material released by cigarettes may produce some interesting results into this highly controversial area of pollution.

The ETS methodology could possibly be improved with the size of sample being increased for the volatile samples. This would have provided a larger sample and therefore the number of sample sites in which quantitative values of volatile material would have increased. The problem with increasing such samples is the possible breakthrough of volatile compounds at higher flows due to poor adsorption to the adsorbent. Such work would need to clarify such possibilities before proceeding. A comparison between pyrrole and 3-ethenylpyridine would provide clarification of the robustness of pyrrole as a marker. The size of samples used seemed sufficient for all particulate analysis. Replicate sampling would once again have provided accurate sampling analysis and identify any instrumental and experimental error. A larger sampling regime (perhaps 20 smokers/non-smokers, houses/offices) would produce results that would solidify the preliminary results obtained in this thesis.

References. Conclusion.

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Table A1: Benzene Concentrations in All Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3)of Bezene in ATD tubes			Outdoor (ug/m^3)of Bezene in ATD tubes		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
Non smokers House 1	No rain	3.93	5.84	9.77	3.36	1.19	4.55
Non smokers House 2	No rain	1.88	2.18	4.06	1.68	2.01	3.69
Non smokers House 3	No rain	0.74	0.58	1.32	0.78	0.35	1.12
Non smokers House 4	No rain	4.39	0.00	4.39	0.00	3.42	3.42
Average.				**4.88**			**3.20**
Smokers houses							
Smokers House 1	Rain	0.94	1.10	2.04	0.26	0.00	0.26
Smokers House 2	No rain	3.10	0.00	3.10	1.14	0.04	1.17
Smokers House 3	No rain	1.12	2.23	3.35	0.00	7.65	7.65
Smokers House 4	Rain	9.30	13.03	22.34	3.76	5.38	9.14
Smokers House 5	No rain	1.32	0.49	1.80	0.83	1.50	2.33
Average.				**6.53**			**4.11**
Non smokers offices							
Non smokers Office 1	No rain	3.85	2.73	6.57	0.90	0.86	1.76
Non smokers Office 2	No rain	1.47	6.10	7.57	2.50	7.19	9.68
Non smokers Office 3	Rain	1.67	0.40	2.07	2.48	0.09	2.56
Non smokers Office 4	Rain	2.05	2.85	4.90	2.77	2.22	4.99
Average.				**5.28**			**4.75**

Smokers offices							
Smokers Office 1	No rain	2.97	1.04	4.01	2.05	5.67	7.72
Smokers Office 2	No rain	0.88	1.15	2.03	1.02	1.16	2.18
Smokers Office 3	Rain	17.97	4.67	22.64	0.91	0.35	1.26
Smokers Office 4	Rain	1.29	3.05	4.33	1.07	1.84	2.90
Average.				8.26			**3.51**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A	-	4.05	0.00	4.05
Roadside sample 2	No rain	N/A	N/A	-	6.98	3.34	10.32
Roadside sample 3	Rain	N/A	N/A	-	4.74	0.54	5.28
Roadside sample 4	No rain	N/A	N/A	-	0.73	5.33	6.06
Roadside sample 5	No rain	N/A	N/A	-	0.93	0.38	1.31
Roadside sample 6	Rain	N/A	N/A	-	0.96	3.88	4.84
Roadside sample 7	Rain	N/A	N/A	-	3.96	0.15	4.12
Roadside sample 8	No rain	N/A	N/A	-	3.08	0.00	3.08
Average.							**4.88**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A	-	1.27	1.25	2.52
Countryside sample 2	Rain	N/A	N/A	-	2.36	0.44	2.80
Average.							**2.66**

Table A2: Toluene Concentrations in all Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3)of Toluene in ATD tubes			**Outdoor** (ug/m^3)of Toluene in ATD tubes		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
Non smokers House 1	No rain	3.93	5.84	9.77	3.36	1.19	4.55
Non smokers House 2	No rain	1.88	2.18	4.06	1.68	2.01	3.69
Non smokers House 3	No rain	0.74	0.58	1.32	.78	1.79	2.56
Non smokers House 4	No rain	107.52	116.58	224.10	51.96	11.90	63.86
Average.				**59.81**			**18.67**
Smokers houses							
Smokers House 1	Rain	4.29	3.79	8.07	11.83	0.43	12.26
Smokers House 2	No rain	22.33	8.04	30.37	9.99	14.30	24.29
Smokers House 3	No rain	89.58	45.56	135.23	10.14	67.96	78.10
Smokers House 4	Rain	42.72	47.06	89.78	14.30	0.56	14.85
Smokers House 5	No rain	44.01	6.70	50.71	0.76	1.76	2.52
Average.				**62.83**			**26.40**
Non smokers offices							
Non smokers Office 1	No rain	6.44	10.71	17.16	3.58	1.50	5.08
Non smokers Office 2	No rain	47.47	179.23	226.70	244.73	87.60	332.33
Non smokers Office 3	Rain	136.98	27.65	164.63	245.05	1.76	246.82
Non smokers Office 4	Rain	91.45	83.73	175.18	99.42	12.53	111.95
Average.				**145.92**			**174.04**

Smokers offices							
Office 1	No rain	2.97	1.04	4.01	2.05	5.67	7.72
Office 2	No rain	16.08	18.20	34.28	22.55	22.86	45.41
Office 3	Rain	33.45	1.47	34.92	35.20	4.16	39.36
Office 4	Rain	15.17	14.35	29.53	9.61	13.77	23.38
Average.				**25.68**			**28.97**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		4.25	3.04	7.29
Roadside sample 2	No rain	N/A	N/A		6.98	3.34	10.32
Roadside sample 3	Rain	N/A	N/A		4.74	1.90	6.64
Roadside sample 4	No rain	N/A	N/A		141.62	100.23	241.86
Roadside sample 5	No rain	N/A	N/A		4.99	8.19	13.18
Roadside sample 6	Rain	N/A	N/A		4.17	16.12	20.30
Roadside sample 7	Rain	N/A	N/A		97.86	9.58	107.44
Roadside sample 8	No rain	N/A	N/A		60.79	2.17	62.96
Average.							**62.17**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		7.54	21.47	29.01
Countryside sample 2	Rain	N/A	N/A		29.37	7.73	37.10
Average.							**33.06**

Table A3: Ortho-xylene Concentrations in all Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3) of o-xylenes on ATD			Outdoor (ug/m^3) of o-xylenes on ATD		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
House 1	No rain	4.60	0.08	4.67	1.51	0.00	1.51
House 2	No rain	1.10	0.03	1.13	1.36	0.00	1.36
House 3	No rain	1.46	0.00	1.46	0.54	0.77	1.30
House 4	No rain	1.96	0.00	1.96	0.42	0.00	0.42
Average.				**2.305**			**1.149**
Smokers houses							
House 1	Rain	1.13	0.00	1.13	0.04	0.08	0.12
House 2	No rain	3.45	0.00	3.45	0.67	0.34	1.01
House 3	No rain	0.29	4.75	5.04	1.21	0.00	1.21
House 4	Rain	5.55	0.00	5.55	3.91	0.00	3.91
House 5	No rain	1.38	0.00	1.38	0.33	0.00	0.33
Average.				**3.310**			**1.316**
Non smokers offices							
Office 1	No rain	1.74	0.07	1.81	1.08	0.06	1.14
Office 2	No rain	2.26	0.11	2.36	2.85	0.00	2.85
Office 3	Rain	2.65	0.00	2.65	3.20	3.08	6.28
Office 4	Rain	1.52	0.00	1.52	2.40	0.00	2.40
Average.				**2.084**			**3.168**

Smokers offices							
Office 1	No rain	2.72	0.00	2.72	2.09	0.17	2.26
Office 2	No rain	2.62	0.00	2.62	1.52	2.42	3.94
Office 3	Rain	1.32	0.00	1.32	1.98	0.00	1.98
Office 4	Rain	1.19	0.00	1.19	0.63	0.00	0.63
Average.				**1.960**			**2.203**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		2.05	0.00	2.05
Roadside sample 2	No rain	N/A	N/A		6.92	0.00	6.92
Roadside sample 3	Rain	N/A	N/A		4.56	1.05	5.60
Roadside sample 4	No rain	N/A	N/A		4.26	0.00	4.26
Roadside sample 5	No rain	N/A	N/A		0.46	0.00	0.46
Roadside sample 6	Rain	N/A	N/A		0.84	0.00	0.84
Roadside sample 7	Rain	N/A	N/A		1.484	0.00	1.48
Roadside sample 8	No rain	N/A	N/A		2.313	0.00	2.31
Average.							**2.990**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		0.535	0.000	0.54
Countryside sample 2	Rain	N/A	N/A		0.888	0.000	0.89
Average.							**0.712**

Table A4: Para+Meta-Xylene Concentrations in All Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3) of p+m-xylenes on ATD			Outdoor (ug/m^3) of p+m-xylenes on ATD		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
House 1	No rain	1.41	0.02	1.43	0.45	0.00	0.45
House 2	No rain	0.13	0.01	0.14	0.18	0.00	0.18
House 3	No rain	0.14	0.00	0.14	0.07	0.70	0.77
House 4	No rain	3.27	0.18	3.45	0.60	0.00	0.60
Average.				**1.29**			**0.50**
Smokers houses							
House 1	Rain	1.64	0.02	1.66	0.04	0.00	0.04
House 2	No rain	4.68	0.00	4.68	0.85	0.14	1.00
House 3	No rain	0.31	0.23	0.53	1.74	0.00	1.74
House 4	Rain	7.67	0.04	7.71	5.20	0.00	5.20
House 5	No rain	1.71	0.00	1.71	0.42	0.00	0.42
Average.				**3.26**			**1.68**
Non smokers offices							
Office 1	No rain	1.35	0.08	1.43	1.64	0.00	1.64
Office 2	No rain	2.96	0.15	3.11	3.83	0.06	3.89
Office 3	Rain	3.76	0.07	3.84	4.91	0.00	4.91
Office 4	Rain	2.04	0.08	2.12	3.19	0.00	3.19
Average.				**2.62**			**3.41**

Smokers offices							
Office 1	No rain	0.91	0.02	0.93	0.63	0.04	0.67
Office 2	No rain	3.96	0.00	3.96	2.14	0.03	2.17
Office 3	Rain	2.91	0.00	2.91	4.06	0.00	4.06
Office 4	Rain	1.77	0.00	1.77	0.96	0.00	0.96
Average.				**2.39**			**1.96**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		3.18	0.00	3.18
Roadside sample 2	No rain	N/A	N/A		1.97	0.00	1.97
Roadside sample 3	Rain	N/A	N/A		1.41	0.00	1.41
Roadside sample 4	No rain	N/A	N/A		5.79	0.00	5.79
Roadside sample 5	No rain	N/A	N/A		0.70	0.04	0.74
Roadside sample 6	Rain	N/A	N/A		1.09	0.00	1.09
Roadside sample 7	Rain	N/A	N/A		2.379	0.00	2.38
Roadside sample 8	No rain	N/A	N/A		3.433	0.00	3.43
Average.							**2.50**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		0.786	0.054	0.84
Countryside sample 2	Rain	N/A	N/A		1.248	0.00	1.25
Average.							**1.04**

Table A5: Ethyl Benzene Concentrations in All Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3) of Eth. benzene on ATD			Outdoor (ug/m^3) of Eth. benzene on ATD		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
House 1	No rain	4.16	0.00	4.16	1.39	0.00	1.39
House 2	No rain	3.17	0.00	3.17	1.17	0.00	1.17
House 3	No rain	4.84	0.00	4.84	0.46	3.48	3.93
House 4	No rain	7.79	0.00	7.79	0.33	0.00	0.33
Average.				**4.99**			**1.70**
Smokers houses							
House 1	Rain	1.41	0.00	1.41	0.05	0.00	0.05
House 2	No rain	2.73	0.00	2.73	0.61	0.00	0.61
House 3	No rain	0.54	0.00	0.54	1.02	0.00	1.02
House 4	Rain	5.05	0.09	5.15	3.58	0.00	3.58
House 5	No rain	0.41	0.00	0.41	0.77	0.00	0.77
Average.				**2.05**			**1.21**
Non smokers offices							
Office 1	No rain	2.16	0.08	2.24	1.34	0.00	1.34
Office 2	No rain	4.35	0.00	4.35	2.59	0.00	2.59
Office 3	Rain	2.87	0.18	3.05	2.96	0.00	2.96
Office 4	Rain	1.72	0.00	1.72	1.95	0.00	1.95
Average.				**2.84**			**2.21**

Smokers offices							
Office 1	No rain	2.77	0.68	3.46	2.16	0.21	2.37
Office 2	No rain	2.09	0.00	2.09	1.18	0.00	1.18
Office 3	Rain	2.23	0.00	2.23	3.16	0.00	3.16
Office 4	Rain	1.15	0.00	1.15	0.58	0.00	0.58
Average.				**2.23**			**1.82**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		2.56	0.00	2.56
Roadside sample 2	No rain	N/A	N/A		5.58	0.00	5.58
Roadside sample 3	Rain	N/A	N/A		4.02	0.00	4.02
Roadside sample 4	No rain	N/A	N/A		3.34	0.00	3.34
Roadside sample 5	No rain	N/A	N/A		0.37	0.10	0.47
Roadside sample 6	Rain	N/A	N/A		2.52	0.00	2.52
Roadside sample 7	Rain	N/A	N/A		3.056	0.00	3.06
Roadside sample 8	No rain	N/A	N/A		2.703	0.00	2.70
Average.							**3.03**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		0.572	0.000	0.57
Countryside sample 2	Rain	N/A	N/A		3.828	0.000	3.83
Average.							**2.20**

Table A6: Para-Dichlorobenzene Concentrations in All Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3) of para-Dichlorobenzene on ATD			Outdoor (ug/m^3) of para-Dichlorobenzene on ATD		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
House 1	No rain	1.06	0.00	1.06	0.42	0.00	0.42
House 2	No rain	1.27	0.00	1.27	0.00	0.00	0.00
House 3	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 4	No rain	0.00	1.69	1.69	0.00	0.00	0.00
Average.				**1.01**			**0.10**
Smokers houses							
House 1	Rain	0.17	0.00	0.17	0.00	0.00	0.00
House 2	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 3	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 4	Rain	8.17	1.07	9.25	0.00	0.00	0.00
House 5	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Average.				**1.88**			**0.00**
Non smokers offices							
Office 1	No rain	9.40	0.00	9.40	1.19	0.00	1.19
Office 2	No rain	3.48	0.00	3.48	3.91	0.00	3.91
Office 3	Rain	0.91	0.00	0.91	0.00	0.00	0.00
Office 4	Rain	2.20	0.00	2.20	2.08	0.00	2.08
Average.				**4.00**			**1.79**

Smokers offices							
Office 1	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Office 2	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Office 3	Rain	1.36	0.00	1.36	0.00	0.00	0.00
Office 4	Rain	16.34	0.00	16.34	2.15	0.00	2.15
Average.				**4.43**			**0.54**
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 2	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 3	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 4	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 5	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 6	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 7	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 8	No rain	N/A	N/A		0.00	0.00	0.00
Average.							**0.00**
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		0.00	0.00	0.00
Countryside sample 2	Rain	N/A	N/A		0.00	0.00	0.00
Average.							**0.00**

Table A7: Pyrrole Concentrations in All Sample Sites Quantified on both Tenax and Carboxen.

		Indoor (ug/m^3) of pyrrole on ATD			Outdoor (ug/m^3) of pyrrole on ATD		
Location	Weather	Tenax	Carboxen	Total	Tenax	Carboxen	Total
Non smokers houses							
House 1	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 2	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 3	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 4	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Average.				0.00			0.00
Smokers houses							
House 1	Rain	0.00	0.00	0.00	0.00	0.00	0.00
House 2	No rain	0.89	0.00	0.89	0.00	0.00	0.00
House 3	No rain	0.00	0.00	0.00	0.00	0.00	0.00
House 4	Rain	2.29	0.00	2.29	0.00	0.00	0.00
House 5	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Average.				0.64			0.00
Non smokers offices							
Office 1	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Office 2	No rain	0.00	0.00	0.00	0.00	0.00	0.00
Office 3	Rain	0.00	0.00	0.00	0.00	0.00	0.00
Office 4	Rain	0.00	0.00	0.00	0.00	0.00	0.00
Average.				0.00			0.00

Smokers offices							
Office 1	No rain	0.62	0.00	0.62	0.00	0.00	0.00
Office 2	No rain	0.10	0.00	0.10	0.00	0.00	0.00
Office 3	Rain	0.31	0.00	0.31	0.00	0.00	0.00
Office 4	Rain	0.39	0.00	0.39	0.00	0.00	0.00
Average.				0.36			0.00
Roadside samples (outdoor)							
Roadside sample 1	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 2	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 3	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 4	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 5	No rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 6	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 7	Rain	N/A	N/A		0.00	0.00	0.00
Roadside sample 8	No rain	N/A	N/A		0.00	0.00	0.00
Average.							0.00
Countryside samples							
Countryside sample 1	No rain	N/A	N/A		0.00	0.00	0.00
Countryside sample 2	Rain	N/A	N/A		0.00	0.00	0.00
Average.							0.00

Table A8: Nicotine Cncentrations in the Vapour Phase of All Sample Sites.

Location	Weather	Sheffield Resin tube		Basildon Resin tube	
Non smokers houses		Indoor	Outdoor	Indoor	Outdoor
House 1	No rain	ND	ND	ND	ND
House 2	No rain	ND	ND	ND	ND
House 3	No rain	ND	ND	ND	ND
House 4	No rain	ND	ND	ND	ND
Average.		**ND**	**ND**	**ND**	**ND**
Smokers houses					
House 1	Rain	0.00	ND	4.50	ND
House 2	No rain	1.57	ND	4.30	ND
House 3	No rain	14.88	ND	0.80	ND
House 4	Rain	0.16	ND	3.60	ND
House 5	No rain	0.08	ND	7.40	ND
Average.		**3.34**	**ND**	**4.12**	**ND**
Non smokers offices					
Office 1	No rain	ND	ND	ND	ND
Office 2	No rain	ND	ND	ND	ND
Office 3	Rain	ND	ND	ND	ND
Office 4	Rain	ND	ND	ND	ND
Average.		**ND**	**ND**	**ND**	**ND**
Smokers offices					
Office 1	No rain	0.00	ND	2.50	ND
Office 2	No rain	0.34	ND	2.10	ND
Office 3	Rain	0.00	ND	No sample	ND
Office 4	Rain	0.41	ND	2.10	ND
Average.		**0.19**	**ND**	**2.23**	**ND**
Roadside samples (outdoor)					
Roadside sample 1	Rain	-	ND	-	ND
Roadside sample 2	No rain	-	ND	-	ND
Roadside sample 3	Rain	-	ND	-	ND
Roadside sample 4	No rain	-	ND	-	ND
Roadside sample 5	No rain	-	ND	-	ND
Roadside sample 6	Rain	-	ND	-	ND
Roadside sample 7	Rain	-	ND	-	ND
Roadside sample 8	No rain	-	ND	-	ND
Average.		-	**ND**	-	**ND**
Countryside samples					
Countryside sample 1	No rain	-	ND	-	ND
Countryside sample 2	Rain	-	ND	-	ND
Average.		-	**ND**	-	**ND**

Table A9: Nicotine Concentrations in the Vapour Phase of All Sample Sites, Analysed by Thermal Desorption-GC/MS.

Location	Weather	Indoor Nicotine	Outdoor Nicotine
Non smokers houses		Tenax resin tube	Tenax resin tube
House 1	No rain	0.00	0.00
House 2	No rain	0.00	0.00
House 3	No rain	0.00	0.00
House 4	No rain	0.00	0.00
Average.		**0.00**	**0.00**
Smokers houses			
House 1	Rain	2.96	0.00
House 2	No rain	6.09	0.00
House 3	No rain	0.00	0.00
House 4	Rain	20.95	0.00
House 5	No rain	0.00	0.00
Average.		**6.00**	**0.00**
Non smokers offices			
Office 1	No rain	0.00	0.00
Office 2	No rain	0.00	0.00
Office 3	Rain	0.00	0.00
Office 4	Rain	0.00	0.00
Average.		**0.00**	**0.00**
Smokers offices			
Office 1	No rain	0.00	0.00
Office 2	No rain	0.00	0.00
Office 3	Rain	0.00	0.00
Office 4	Rain	4.69	0.00
Average.		**1.17**	**0.00**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	0.00
Roadside sample 2	No rain	N/A	0.00
Roadside sample 3	Rain	N/A	0.00
Roadside sample 4	No rain	N/A	0.00
Roadside sample 5	No rain	N/A	0.00
Roadside sample 6	Rain	N/A	0.00
Roadside sample 7	Rain	N/A	0.00
Roadside sample 8	No rain	N/A	0.00
Average.			**0.00**
Countryside samples			
Countryside sample 1	No rain	N/A	0.00
Countryside sample 2	Rain	N/A	0.00
Average.			**0.00**

Table A10: Tetracosane (C24) Concentrations Associated with Particulate Material.

		Indoor		Outdoor	
		Filter	XAD-4 resin	Filter	XAD-4 resin
Location	Weather	Total C24		Total C24	
Non smokers houses		(ug/g)of C24		(ug/g)of C24	
House 1	No rain	4.39	0.00	9.31	0.00
House 2	No rain	16.23	0.00	96.53	0.00
House 3	No rain	147.15	0.00	144.60	0.00
House 4	No rain	34.87	0.00	410.94	0.00
Average.		**50.66**	**0.00**	**165.34**	**0.00**
Smokers houses					
House 1	Rain	93.61	0.00	32.17	0.00
House 2	No rain	0.00	0.00	122.29	0.00
House 3	No rain	0.00	0.00	196.63	0.00
House 4	Rain	8.65	0.00	24.93	0.00
House 5	No rain	132.32	0.00	47.23	0.00
Average.		**46.92**	**0.00**	**84.65**	**0.00**
Non smokers offices					
Office 1	No rain	197.30	0.00	148.97	0.00
Office 2	No rain	53.82	0.00	76.02	0.00
Office 3	Rain	58.33	0.00	29.43	0.00
Office 4	Rain	467.82	0.00	453.86	0.00
Average.		**194.32**	**0.00**	**177.07**	**0.00**
Smokers offices					
Office 1	No rain	10.26	0.00	141.15	0.00
Office 2	No rain	0.00	0.00	397.17	0.00
Office 3	Rain	66.03	0.00	188.75	0.00
Office 4	Rain	78.09	0.00	162.89	0.00
Average.		**38.59**	**0.00**	**222.49**	**0.00**
Roadside samples (outdoor)					
Roadside sample 1	Rain	N/A	N/A	324.62	0.00
Roadside sample 2	No rain	N/A	N/A	565.16	0.00
Roadside sample 3	Rain	N/A	N/A	154.44	0.00
Roadside sample 4	No rain	N/A	N/A	549.31	0.00
Roadside sample 5	No rain	N/A	N/A	35.48	0.00
Roadside sample 6	Rain	N/A	N/A	74.20	0.00
Roadside sample 7	Rain	N/A	N/A	476.99	0.00
Roadside sample 8	No rain	N/A	N/A	658.86	0.00
Average.				**354.88**	**0.00**
Countryside samples					
Countryside sample 1	No rain	N/A	N/A		0.00
Countryside sample 2	Rain	N/A	N/A	93.18	0.00
Average.				**46.59**	**0.00**

Table A11: Nicotine Concentrations Associated with Particulate Material.

Location Non smokers houses	Weather	Indoor Nicotine ($\mu g/m^3$) Particulate phase	Outdoor Nicotine ($\mu g/m^3$) Particulate phase
House 1	No rain	ND	ND
House 2	No rain	ND	ND
House 3	No rain	ND	ND
House 4	No rain	ND	ND
Average.		**ND**	**ND**
Smokers houses			
House 1	Rain	0.08	ND
House 2	No rain	0.00	ND
House 3	No rain	0.82	ND
House 4	Rain	0.04	ND
House 5	No rain	0.06	ND
Average.		**0.20**	**ND**
Non smokers offices			
Office 1	No rain	ND	ND
Office 2	No rain	ND	ND
Office 3	Rain	ND	ND
Office 4	Rain	ND	ND
Average.		**ND**	**ND**
Smokers offices			
Office 1	No rain	0.00	ND
Office 2	No rain	0.00	ND
Office 3	Rain	0.00	ND
Office 4	Rain	0.15	ND
Average.		**0.04**	**ND**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	ND
Roadside sample 2	No rain	N/A	ND
Roadside sample 3	Rain	N/A	ND
Roadside sample 4	No rain	N/A	ND
Roadside sample 5	No rain	N/A	ND
Roadside sample 6	Rain	N/A	ND
Roadside sample 7	Rain	N/A	ND
Roadside sample 8	No rain	N/A	ND
Average.		**ND**	**ND**
Countryside samples			
Countryside sample 1	No rain	N/A	ND
Countryside sample 2	Rain	N/A	ND
Average.		**ND**	**ND**

Table A12: Total UV Concentrations Associated with Particulate Material.

Location	Weather	Indoor Total UV	Outdoor Total UV
Non smokers houses		Filter 1 (ng/m^3)	Filter 1 (ng/m^3)
House 1	No rain	1663.1	1386.3
House 2	No rain	1046.2	437.5
House 3	No rain	442.4	67.3
House 4	No rain	941.7	1248.0
Average		**1023.32**	**784.78**
Smokers houses			
House 1	Rain	9334.0	1408.7
House 2	No rain	12054.2	1159.3
House 3	No rain	8831.1	1992.4
House 4	Rain	50769.0	5125.3
House 5	No rain	5783.3	3124.6
Average		**17354.32**	**2562.06**
Non smokers offices			
Office 1	No rain	2421.1	1860.4
Office 2	No rain	1556.7	1938.5
Office 3	Rain	1396.1	990.4
Office 4	Rain	578.3	1972.8
Average		**1488.06**	**1690.54**
Smokers offices			
Office 1	No rain	10964.5	2070.8
Office 2	No rain	3098.8	656.8
Office 3	Rain	5008.90	2736.2
Office 4	Rain	17995.6	2714.3
Average		**9266.95**	**2044.52**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	1153.8
Roadside sample 2	No rain	N/A	3698.5
Roadside sample 3	Rain	N/A	2053.8
Roadside sample 4	No rain	N/A	2139.0
Roadside sample 5	No rain	N/A	1279.8
Roadside sample 6	Rain	N/A	1804.1
Roadside sample 7	Rain	N/A	2597.9
Roadside sample 8	No rain	N/A	1560.4
Average			**2035.92**
Countryside samples			
Countryside sample 1	No rain	N/A	1235.4
Countryside sample 2	Rain	N/A	1738.3
Average			**1486.84**

Table A13: Total Fluorescence Concentrations Associated with Particulate Material.

Location Non smokers houses	Weather	Indoor Total fluorescence Filter 1 (ng/m^3)of Scopoletin	Outdoor Total fluorescence Filter 1 (ng/m^3)of Scopoletin
House 1	No rain	127.02	163.09
House 2	No rain	996.00	356.67
House 3	No rain	313.66	514.50
House 4	No rain	137.12	146.85
Average		**393.45**	**295.28**
Smokers houses			
House 1	Rain	676.68	118.10
House 2	No rain	1822.78	148.90
House 3	No rain	1231.40	73.38
House 4	Rain	6199.32	4.89
House 5	No rain	379.09	89.61
Average		**2061.85**	**86.98**
Non smokers offices			
Office 1	No rain	61.33	147.12
Office 2	No rain	286.66	278.55
Office 3	Rain	205.66	458.08
Office 4	Rain	78.40	91.30
Average		**158.01**	**243.76**
Smokers offices			
Office 1	No rain	3432.06	792.18
Office 2	No rain	488.41	119.84
Office 3	Rain	656.31	88.41
Office 4	Rain	1846.52	133.75
Average		**1605.82**	**283.54**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	48.96
Roadside sample 2	No rain	N/A	1035.36
Roadside sample 3	Rain	N/A	775.73
Roadside sample 4	No rain	N/A	63.52
Roadside sample 5	No rain	N/A	98.31
Roadside sample 6	Rain	N/A	129.14
Roadside sample 7	Rain	N/A	224.95
Roadside sample 8	No rain	N/A	55.64
Average			**303.95**
Countryside samples			
Countryside sample 1	No rain	N/A	205.07
Countryside sample 2	Rain	N/A	28.60
Average			**116.84**

Table A14: Solanesol Concentrations Associated with Particulate Material.

Location Non smokers houses	Weather	Indoor (ng/m^3)of Solanesol	Outdoor (ng/m^3)of Solanesol
House 1	No rain	0.0	0.0
House 2	No rain	0.0	0.0
House 3	No rain	0.0	0.0
House 4	No rain	0.0	0.0
Average.		**0.0**	**0.0**
Smokers houses			
House 1	Rain	383.38	0.0
House 2	No rain	509.94	0.0
House 3	No rain	301.20	0.0
House 4	Rain	3879.01	0.0
House 5	No rain	508.13	0.0
Average.		**1116.33**	**0.0**
Non smokers offices			
Office 1	No rain	0.0	0.0
Office 2	No rain	0.0	0.0
Office 3	Rain	0.0	0.0
Office 4	Rain	0.0	0.0
Average.		**0.0**	**0.0**
Smokers offices			
Office 1	No rain	984.84	0.0
Office 2	No rain	150.86	0.0
Office 3	Rain	424.60	0.0
Office 4	Rain	808.71	0.0
Average.		**592.25**	**0.0**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	0.0
Roadside sample 2	No rain	N/A	0.0
Roadside sample 3	Rain	N/A	0.0
Roadside sample 4	No rain	N/A	0.0
Roadside sample 5	No rain	N/A	0.0
Roadside sample 6	Rain	N/A	0.0
Roadside sample 7	Rain	N/A	0.0
Roadside sample 8	No rain	N/A	0.0
Average.			**0.0**
Countryside samples			
Countryside sample 1	No rain	N/A	0.0
Countryside sample 2	Rain	N/A	0.0
Average.			**0.0**

Table A15: Scopoletin Concentrations Associated with Particulate Material.

Location Non smokers houses	Weather	Indoor Filter 1 (ng/m^3)of Scopoletin	Outdoor Filter 1 (ng/m^3)of Scopoletin
House 1	No rain	0.000	0.000
House 2	No rain	0.000	0.000
House 3	No rain	0.000	0.000
House 4	No rain	0.000	0.000
Average.		**0.000**	**0.000**
Smokers houses			
House 1	Rain	25.329	0.000
House 2	No rain	173.972	0.000
House 3	No rain	64.878	0.000
House 4	Rain	289.481	0.000
House 5	No rain	8.861	0.000
Average.		**112.504**	**0.000**
Non smokers offices			
Office 1	No rain	0.000	0.000
Office 2	No rain	0.000	0.000
Office 3	Rain	0.000	0.000
Office 4	Rain	0.000	0.000
Average.		**0.000**	**0.000**
Smokers offices			
Office 1	No rain	78.417	0.000
Office 2	No rain	40.814	0.000
Office 3	Rain	53.036	0.000
Office 4	Rain	53.664	0.000
Average.		**56.483**	**0.000**
Roadside samples (outdoor)			
Roadside sample 1	Rain	N/A	0.000
Roadside sample 2	No rain	N/A	0.000
Roadside sample 3	Rain	N/A	0.000
Roadside sample 4	No rain	N/A	0.000
Roadside sample 5	No rain	N/A	0.000
Roadside sample 6	Rain	N/A	0.000
Roadside sample 7	Rain	N/A	0.000
Roadside sample 8	No rain	N/A	0.000
Average.			**0.000**
Countryside samples			
Countryside sample 1	No rain	N/A	0.000
Countryside sample 2	Rain	N/A	0.000
Average.			**0.000**

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Presentations Completed at Various Symposia/Meetings

Hewlett Packard. "GC-MS for the Chromatographer" and "MS Troubleshooting and Tips" training course days.
Jones Chromatography and IST. SPE Method Development Seminar.

Oral Presentations.

1. 24/September/97 Environmental Mass Spectrometry Special Interests Group, BMSS, at the University of Salford. "Attribution of Sources of Organic Micropollutants in Indoor and Outdoor Air Samples".
2. Other oral presentations have been completed both to my sponsors (Rothmans International), and in inter-departmental forums.

Poster Presentations.

1.. 21-26/May/95 Douce D.S. Clench M.R. and Cooke M., "Tree Bark as a Passive Sampler for Nitrated Polycyclic Aromatic Hydrocarbons". Proceedings of 43rd Annual Conference of the American Society for Mass Spectrometry Atlanta, Ga, USA.
2. 10-11/July/95. Royal Society of Chemistry (Analytical Division) R&D Topics at the University of Hull.
3. 5/Sept/95. Autumn Meeting & Pre-Doctoral Chemistry Symposium (Royal Society of Chemistry) at the University of Sheffield.
4. Yates PW, Douce D, Foss PW, Tidmarsh DH, Wilcock M, "The Determination of the Hydrocarbon Species Present in the Particle SOF from a Turbocharged Diesel Engine". The Automotive Technology event, Autotech; at the National Exhibition Centre, Birmingham, 7-9/Nov/95.
5. Yates PW, Bassett MD, Douce D, Foss PW, "The Measurement and Analysis of the Particulate Matter from a Turbo Charged Diesel Engine". Proceedings of the 14th National Conference on Internal Combustion Engines and Combustion. Institute of Armament Technology. Pune-411025, India, 8-10/Dec/95.
6. 5/March/96. Royal Society of Chemistry (Industrial Division) Young Environmental Chemists Meeting at Demontfort University.
7. Douce D.S. Clench M.R. Cooke M. "The Determination of Nitrated Polycyclic Aromatic Hydrocarbons in Vegetation and Diesel Emissions", 26th International Symposium on Environmental Analytical Chemistry, Vienna, Austria 9-12/April/96.
8. 16-18/April/96. The Scientific Instrument Association Conference, at Wembley Conference & Exhibition Centre, London.
9. 15/May/96. Royal Society of Chemistry (north-east Region) - Hot Topics in Environmental Analysis, at Sheffield Hallam University.
10. 22-23/July/96. Royal Society of Chemistry(Analytical Division) R&D Topics at Nottingham Trent University.
11. 18/March/97 Royal Society of Chemistry (Industrial Division) 2nd Young Environmental Chemists Meeting at Demontfort University.

Other Meetings Attended.

1. 13-16 September/1998. British Mass Spectrometry Society (BMSS) at the University of Warwick.

Journal Publications.

Douce. D.S. Clench. M.R. Cooke. M. and Wang. J. in Journal of Chromatography A, 786(1997) 275-283, "Evidence for the Adsorption of Nitrated Polycyclic Aromatic Hydrocarbons by Tree Bark".

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Journal of Chromatography A, 786 (1997) 275–283

JOURNAL OF CHROMATOGRAPHY A

Evidence for the adsorption of nitrated polycyclic aromatic hydrocarbons by tree bark

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Abstract

It has been previously demonstrated that polycyclic aromatic hydrocarbons (PAH) are adsorbed onto tree bark and that bark may in fact be used as a passive sampler for these compounds. It is now demonstrated that by suitable modification of this methodology nitrated polycyclic aromatic hydrocarbons (nitro-PAH) may also be detected in bark. Bark samples were taken from urban locations in Sheffield, South Yorkshire, UK. After soxhlet extraction using dichloromethane, the nitro-PAH fraction was isolated by solid-phase extraction using amino and alumina cartridges in series. Nitro-PAH were detected by gas chromatography with electron capture detection and gas chromatography–mass spectrometry in the negative chemical ionisation mode. A comparison is made with nitro-PAH found in diesel particulate extracts. © 1997 Elsevier Science B.V.

Keywords: Tree bark; Polynuclear aromatic hydrocarbons; Nitrated polynuclear aromatic hydrocarbons

1. Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) are one of the many families of organic compounds known to be produced as micropollutants from the combustion of organic materials including diesel [1–12], gasoline [2,3], and wood [2,3]. The release of these substituted polycyclic aromatic hydrocarbons (PAH) is however relatively small in comparison to other more common groups of compounds such as aliphatic hydrocarbons and PAH. However, their toxicity has been found to be far greater than that of unsubstituted PAH; they have been identified as direct acting mutagens and carcinogens to mammalian systems [13–15].

Nitro-PAH produced from combustion processes are predominantly formed by electrophilic aromatic substitution reactions. These yield isomers corresponding to the cationic (Wheland) intermediates that have the greatest resonance stabilisation. It has also been shown that nitro-PAH can be formed, alternatively, by the reaction of PAH with reactive species found in ambient air, i.e. dinitrogen pentoxide (N_2O_5) and oxygen radicals in the presence of NO_x. These gas-phase reactions have different mechanisms and produce different isomers to those formed in combustion processes. It can therefore be assumed that nitrated PAH isomers corresponding to the most stabilised cationic intermediates are formed almost entirely from the combustion of anthropogenic materials, and should therefore be a guide to the quantity of nitro-PAH released into the atmosphere

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from combustion sources. Examination of the literature on measured nitro-PAH confirms this and shows that the isomers expected from conventional electrophilic substitution (e.g. 1-nitropyrene, 1-nitronaphthalene, 3-nitrofluoranthene and 2-nitrofluorene) are detected in emissions from combustion sources (e.g. [1–12]) while the isomers due to gaseous reactions (e.g. 2-nitropyrene and 2-nitrofluoranthene) have only been found in ambient air [16] and emissions from an electrode factory [12].

The low levels of nitro-PAH released directly into the atmosphere dictates that a large sample of ambient air needs to be taken when conventional active sampling systems are employed in analyses. If a passive sampling system could be found readily available in the environment, costly sampling systems and sampling media would not be necessary. Many types of vegetation have been used as passive samplers for atmospheric pollutants. Reported systems have included pine needles for polychlorinated biphenyls (PCBs [17,18]) and pesticides, [18,19] and tree bark used for PCBs [20,21] and PAH [20,22,23] amongst others. As tree bark is ubiquitous throughout the environment, it was decided to examine this material for the presence of nitro-PAH. For comparison purposes diesel particulates were collected from the exhaust of a diesel engine running under controlled conditions.

The soluble organic extracts obtained from tree bark and diesel particulate exhaust filters are very complex mixtures. The extract may contain; aliphatics, simple aromatics, polycyclic aromatic hydrocarbons (PAH), nitrogen- and sulphur-containing derivatives of PAH along with polycyclic ketones, quinones, anhydrides, heterocyclic compounds and organometallics. Hence fractionation of this highly complex mixture is necessary prior to analysis. A variety of fractionation methods have been reported including; liquid–liquid partition [24,25], semi-preparative chromatography [4,26], low- and high-resolution chromatography [5–7,27] and chromatographic separation following a derivatisation step [8]. All these chromatographic fractionation methods have been applied to the pre-concentration of nitrated PAH from diesel exhaust particulates or air samples. More recently solid-phase extraction cartridges have been used as a possible method of pre-concentrating and fractionating nitrated PAH from complex matrices [28,29]. However, no methods were found in the literature which describe a comprehensive fractionation of complex samples obtained from tree bark. Therefore, as part of this work, a solid-phase extraction method for the fractionation of bark extracts was developed.

Many methods also exist for the analytical determination of nitro-PAH. These include; capillary gas chromatography using flame ionisation (FID) [4,8,26,30], electron capture (ECD) [8,30], nitrogen phosphorous (NPD) [1,8,11,26], chemiluminescent nitrogen detector (CLND) [5,7,31] and mass spectrometric detection [1,6,8–11,31,32].

High-performance liquid chromatography (HPLC) has also been used for the final determination of nitrated PAH. Ultra violet absorbance detection at 254 nm has been used [33], however better sensitivity has been obtained from fluorescence detection after reduction to their corresponding amine [34]. and in a recent paper this was carried out on-line using a zinc dust column [35].

In the work reported here we have employed gas chromatography with electron capture detection for qualitative and semi-quantitative determination of nitro-PAH in tree bark and diesel particulate extracts. The qualitative data have been confirmed and levels of nitro-PAH quantified by using gas chromatography–mass spectrometry with negative chemical ionisation and selected ion monitoring.

2. Experimental

2.1. Sampling

2.1.1. Tree bark

Tree bark was sampled from two different locations around the city of Sheffield. Maple trees (which have a smooth bark) were identified in each location and used for these experiments. The two locations were: (A) a tree situated in the central bus terminus of the city; (B) a tree situated in a park on the outskirts of Sheffield away from major roads and bus routes.

Samples of 1–3 g of bark were removed from the surface of each tree, 1–2 m above the ground. A surface area of approximately 15 cm^2 of bark was removed, with the depth of bark removed not

exceeding 2 mm. Samples were stored in amber screw-top vials at 0°C until they were extracted. Samples were taken on the following dates; 1/95, 7/95, 1/96.

2.1.2. Diesel samples

Diesel particulate exhaust samples from a four-cylinder, 4-l, non-inter-cooled direct-injection diesel engine with turbo charger in a controlled test environment were collected on glass fibre filter papers. The engine was run at 1600 rpm at full rated power. Samples were taken after the emissions were diluted and cooled to below 52°C using a dilution tunnel. This was carried out in order to reduce chemical reactions occurring on the filter surface. Sampling times of between 1 and 2 h were required to yield sufficient organic material to quantify the nitro-PAH of interest.

2.2. Solvents and standards

All solvents used in the following procedures were HPLC grade or better. All standards and solvents were purchased from Sigma-Aldrich Co. (Poole, Dorset, UK).

2.3. Extractions

A relevant quantity of the sample in question was finely chopped and placed into a cellulose extraction thimble in a soxhlet apparatus. The samples were then extracted with 80 ml of dichloromethane for 96 h. The soxhlet apparatus was wrapped in aluminium foil to minimize photochemical degradation of the desired analytes. This length of time was found to be necessary from earlier work [36] on the extraction of nitrated PAH spiked onto tree bark. In order to identify any contamination from the extraction process, clean thimbles were extracted and subjected to the same procedures as all other samples to produce reagent blanks.

2.4. Fractionation

2.4.1. Solid-phase extraction

Solid-phase extraction (SPE) was performed using a polypropylene cartridge containing amino-bonded phase (200 mg of sorbent with a 10-ml reservoir, obtained from International Sorbent Technology, Jones Chromatography, Mid Glamorgan, Wales, England) and alumina (500 mg of sorbent with a 6-ml reservoir obtained from J.T. Baker, UK, Milton Keynes, Bucks, UK) cartridges in series. The cartridges were initially cleaned with 30 ml of acetone to remove all adsorbed water. Fifteen ml of each eluting solvent were then passed through the cartridges, starting with methanol and continuing back through the solvents with reducing polarity to hexane, leaving a layer of 10 ml of hexane in the top cartridge reservoir. The sample extract was then loaded onto the cartridge using the smallest quantity of dichloromethane (often 50–100 μl) introduced directly into the 10 ml of hexane. Fractionation was achieved by elution of compounds with 10 ml of the following solvents of increasing polarity:

Solvent	Eluting compounds
Hexane	Aliphatics
Cyclohexane	2–4 ringed PAH (up to pyrene)
20% Dichloromethane in cyclohexane	Larger PAH and nitrated derivatives
Dichloromethane	Polar species
Acetonitrile	Polar species
Methanol	Polar species

The fractions were reduced to approximately 500 μl with a dry stream of nitrogen and transferred to pre-weighed amber vials. These were reduced to dryness once again by nitrogen to produce a residual weight. An internal standard (8-nitroquinaldine; obtained from Sigma-Aldrich Co., Poole, Dorset, UK, at 98% purity) and 100 μl of dichloromethane were added prior to analysis by GC–ECD and GC–NICIMS-SIM.

2.5. Instrumentation

2.5.1. Gas chromatography with electron capture detector (GC–ECD)

The instrument used in all cases was a Hewlett-Packard 5880 gas chromatograph using a 5% diphenyl wall-coated open tubular capillary column (Rtx-5, Restek, Thames Chromatography UK) (20 m×0.32 mm) with a film thickness of 0.25 μm. The carrier gas used was nitrogen, at a flow-rate of 1

ml/min, with nitrogen as the makeup gas yielding a total flow of 30 ml/min; 1 μl of each sample was injected splitless using a Hewlett-Packard 7673A autosampler. The injector temperature was set at 275°C with the detector at 300°C. The oven program temperature used was 40°C for 4 min, ramp 1; 25°C/min to 145°C hold for 1 min, ramp 2; 5°C/min to 280°C with a final hold time of 15 min.

2.5.2. Gas chromatography with negative-ion chemical-ionisation mass spectrometry working in selective ion-monitoring mode (GC–NICIMS-SIM)

This work was performed on two instruments due to the purchase of a more sensitive VG Trio III midway through the study. Initial work was completed on a Hewlett-Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 1 mass spectrometer (VG MassLab, Manchester, UK) with the MS working in the selective ion monitoring (SIM) mode.

The column used was a 30 m×0.32 mm I.D. 5% diphenyl wall-coated open tubular capillary column (Rtx-5 Thames Chromatography UK), with a film thickness of 0.25 μm. Helium was used as the carrier gas at a flow-rate of 1 ml/min. The injector temperature was set at 275°C with the oven temperature program being 40°C, held for 4 min then increased at 25°C/min to 175°C, held for 1 min; the temperature was then increased at 5°C/min to the final temperature of 280°C for 15 min. All samples (1 μl) were injected manually in splitless mode.

Later work was undertaken using a Hewlett-Packard 5890 (Series II) gas chromatograph coupled to a VG Trio 3 mass spectrometer working in SIM mode. In both cases the reagent gas used for chemical ionisation was methane with an ion source temperature of 125°C. The NICI conditions were optimised by injecting a small quantity of methyl iodide via the septum inlet and tuning the instrument via the peak at *m/z* 127. A SIM experiment was set up monitoring each of the $M^{-\cdot}$ ions for the nitrated PAH studied (Fig. 1). The column used was a 60 m×0.32 mm I.D. 5% diphenyl wall-coated open tubular capillary column (Rtx-5 Thames Chromatography UK) with a film thickness of 0.25 μm. The injector temperature was set at 275°C and the oven temperature program was as described earlier. The carrier gas was helium at a flow-rate of 1 ml/min; 1 μl of each sample was injected splitless.

3. Results and discussion

After soxhlet extraction, the residues obtained from the tree bark extracts were green/brown in colour. The diesel particulate extract was black in colour due to carbon particles extracted over the siphoning mechanism of the soxhlet.

3.1. Fractionation procedure

An amino cartridge was used as the initial sorbent of the SPE system. The bonded amino group strongly interacts with its nitrogen lone pair producing adsorption of nitrated compounds. The nitrated PAH can then be removed from the cartridge by a moderately polar eluent (i.e. 20% dichloromethane/80% cyclohexane). They then pass through the alumina cartridge with little retention whilst any other polar compounds that have been removed from the amino cartridge by the moderately polar eluent are retained by the alumina cartridge.

Table 1 shows the percent recoveries obtained from the tandem SPE fractionation of a standard containing seven nitro-PAH studied (Fig. 1). Complete separation into one fraction was achieved with four of the seven nitrated PAH having a percent recovery of greater than 94%. 9-Nitroanthracene and 1-nitropyrene have recoveries of 53 and 72%, respectively, with 1-nitronaphthalene having the lowest recovery at approximately 30%. This could possibly be due to irreversible adsorption to the alumina sorbent which occurred when alumina was used solely as the sorbent. A more likely reason for the losses of especially the volatile compounds could be attributed to the sample drying stage.

3.2. Tree bark

The quantitative results obtained from GC–NICI-SIM (Table 2, Fig. 2A (standards) and Fig. 2B (bark A)) indicate that the bus station sample, tree bark A. contained a larger quantity of nitrated PAH than tree bark B throughout the year. The exceptions to this were 5-nitroacenaphthene (Jan./96) and 1-nitronaph-

Table 1
Average percentage recovery and standard deviation data of amino/alumina fractionation method used to selectively pre-concentrate nitrated PAH

Compound	Hexane		Cyclohexane		20% Dichloromethane		Dichloromethane		Acetonitrile	
	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.	% recovery	S.D.
1-Nitronaphthalene	0	0	0	0	28.27	1.92	0	0	0	0
4-Nitrobiphenyl	0	0	0	0	105.25	6.78	0	0	0	0
5-Nitroacenaphthene	0	0	0	0	94.97	7.37	0	0	0	0
2-Nitrofluorene	0	0	0	0	106.15	1.02	0	0	0	0
9-Nitroanthracene	0	0	0	0	53.25	1.17	0	0	0	0
3-Nitrofluoranthene	0	0	0	0	72.15	2.24	0	0	0	0
1-Nitropyrene	0	0	0	0	108.31	10.2	0	0	0	0

thalene (July/95 and Jan./96) which were found to be higher in bark B than in bark A at these sampling times.

The semi-quantitative values obtained by GC–ECD (Table 3, Fig. 3A (standards), Fig. 3B (bark A)) show a similar trend to that in Table 2, with tree bark A consistently containing a larger amount of individual nitrated PAH compared to tree bark B. Here, the only exception is 4-nitrobiphenyl which is seen to have a greater amount in bark B than in the bark A (Jan./96).

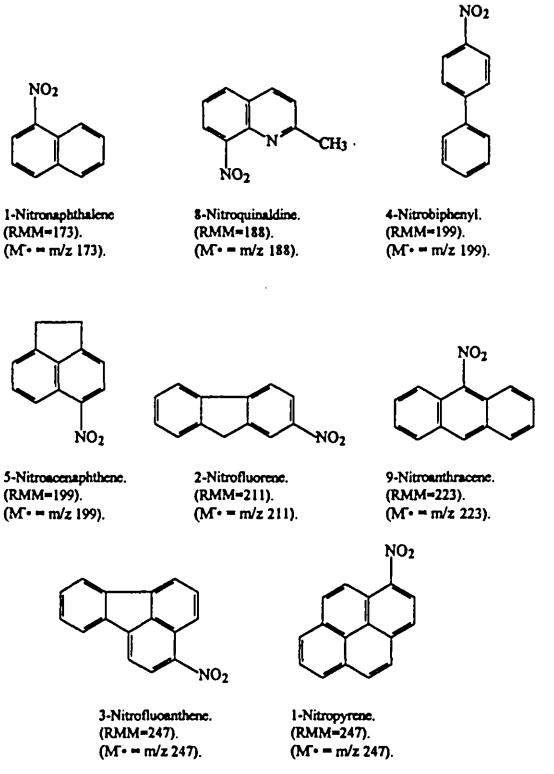

Fig. 1. Structures and molecular ions of all seven nitrated PAH and the internal standard.

Over the three sampling dates both the GC–NICI-SIM data (Table 2) and the GC–ECD data (Table 3), show higher levels of nitrated PAH in bark samples taken during January compared to July. The only compounds quantified in both trees during the summer sampling period were 1-nitronaphthalene and 4-nitrobiphenyl, with a further two nitrated PAH, 5-nitroacenaphthene and 2-nitrofluorene, being detected in the bus station bark (July/95). With the exception of 1-nitronaphthalene in bark B (Jan./95), all nitrated PAH were detected at higher concentrations in the January samples compared to the July 1995 sample. The reasons for this may be a combination of the following. (1) All nitrated PAH investigated in this study are found to some extent in the vapour phase at ambient temperatures. Average temperature and pressure will therefore have a great effect on the condensation of pollutants onto surfaces. For example, compounds will condense out during times of cold ambient temperatures (i.e. November–February in Britain) this is called the 'cold condensation effect'. (2) During warmer ambient temperatures, photodegradation of these vapour phase organic molecules is likely due to the higher levels of UV radiation and the presence of radicals capable of causing degradation i.e. $^{\cdot}OH$ [16]. (3) The cold winter months always induce an increase in the emissions of organic combustion material due to the extra use of vehicular transport by commuters and travellers. More organic fuel is also burnt due to the increased use of electricity for heating and lighting.

Table 2
GC–NICI-SIM quantitative results of specific nitrated PAH in tree bark A and B (three samples over a 1-year period) along with diesel particulate extracts: quantitative results are ng of compound in 1 g of bark or diesel particulates as appropriate

Compound	SIM molecular ion	Tree A Jan./95	Tree A July/95	Tree A Jan./96	Tree B Jan./95	Tree B July/95	Tree B Jan./96	Diesel particulates
1-Nitronaphthalene	173	70.48	2.48	22.11	0.71	8.07	26.53	1.64
Internal standard	188							
4-Nitrobiphenyl	199	37.99	16.42	37.26	8.19	6.23	16.59	6.14
5-Nitroacenaphthene	199	20.67	0.71	32.3	15.38	Trace	38.4	2.48
2-Nitrofluorene	211	11.79	1.79	45.62	1.28	N.D.	30.59	N.D.
9-Nitroanthracene	223	76.19	Trace	23.77	D.S.	N.D.	7.69	4.13
3-Nitrofluoranthene	247		Trace	45.3	—	N.D.	26.69	Trace
1-Nitropyrene	247		N.D.	52.91	—	N.D.	25.4	21.73

N.D., none determined. Trace, peak present but below limit of detection. D.S., nitrated PAH had degraded in sample.

(4) In winter, deciduous trees are without any foliage so any gaseous or particulate associated pollutants condensing out onto vegetation can only condense upon the bark. (5) Preferential adsorption of certain nitrated PAH could be a reason for the increased quantities of some compounds observed. The ambient temperature and the individual vapour pressures will determine whether the compound is predominantly in the gaseous phase or adsorbed onto a particulate surface. A variation in the degradation rate of certain compounds (e.g. 9-nitroanthracene, which is known to rapidly degrade to anthraquinone [37]), may also play a part.

However the small number of samples taken in this present study only allow us to present these ideas 'for discussion' rather than make any definitive conclusions.

3.3. Diesel particulates

The particulate extracts were fractionated using the previously described tandem amino/alumina SPE method. Nitrated PAH were only identified in the 20% dichloromethane/80% cyclohexane fraction. Samples were analysed by both the GC–NICI-SIM (Fig. 2C) and GC–ECD methods with the GC–NICI-SIM performed on the VG Trio III instrument.

These GC–NICI-SIM results (Fig. 2C, Table 2) show that, except for 2-nitrofluorene, all the nitrated PAH studied were present in the GC–NICI-SIM chromatogram (Fig. 2C). This is surprising as 2-nitrofluorene has previously been detected in diesel particulates [1]. 3-Nitrofluoranthene is present in the diesel particulates but only at a relatively low concentration. The tree bark sample (Fig. 2B), however, contains a large amount of 3-nitrofluoranthene. This could be due to preferential adsorption of 3-nitrofluoranthene on the surface of the bark or it could be due to co-elution with 2-nitrofluoranthene, which is known to be produced by atmospheric reactions [38]. The problem of separating these closely eluting isomers has been described in the literature [12]. The results obtained from the mass spectrometer using the SIM mode often contained several peaks in each mass chromatogram. These additional peaks could be isomers of the same nitrated PAH or compounds with the same empirical formula but a different structure, i.e., nitrofluoranthene and nitropyrene, produced from either polluting sources or atmospheric processes.

The semi-quantitative GC–ECD results (Table 3) also allowed identification and semi-quantification of five of the seven nitrated PAH. (3-Nitrofluoranthene was not quantifiable due to an impurity identified from the solvent or thimble in the blank experiments which obliterated the area of the chromatogram where 3-nitrofluoanthene would appear.) The quantities identified by the two methods are similar, however, with all the values being in the tens of ng per gram of diesel particulates. The GC–ECD results for the diesel particulates are consistently higher than the GC–NICI-SIM results (excluding 1-nitropyrene). This is probably due to the integration data from the GC–ECD being high due to incomplete baseline

ong with diesel

Diesel particulates
1.64
6.14
2.48
N.D.
4.13
Trace
21.73

resent in the latively low (Fig. 2B), nitrofluoran- dsorption of e bark or it fluoranthene, atmospheric rating these ribed in the m the mass ›n contained gram. These f the same e empirical nitrofluoran- ›ither pollut-

lts (Table 3) ntification of fluoranthene ty identified experiments romatogram .) The quan- are similar, e tens of ng ECD results higher than nitropyrene). ata from the lete baseline

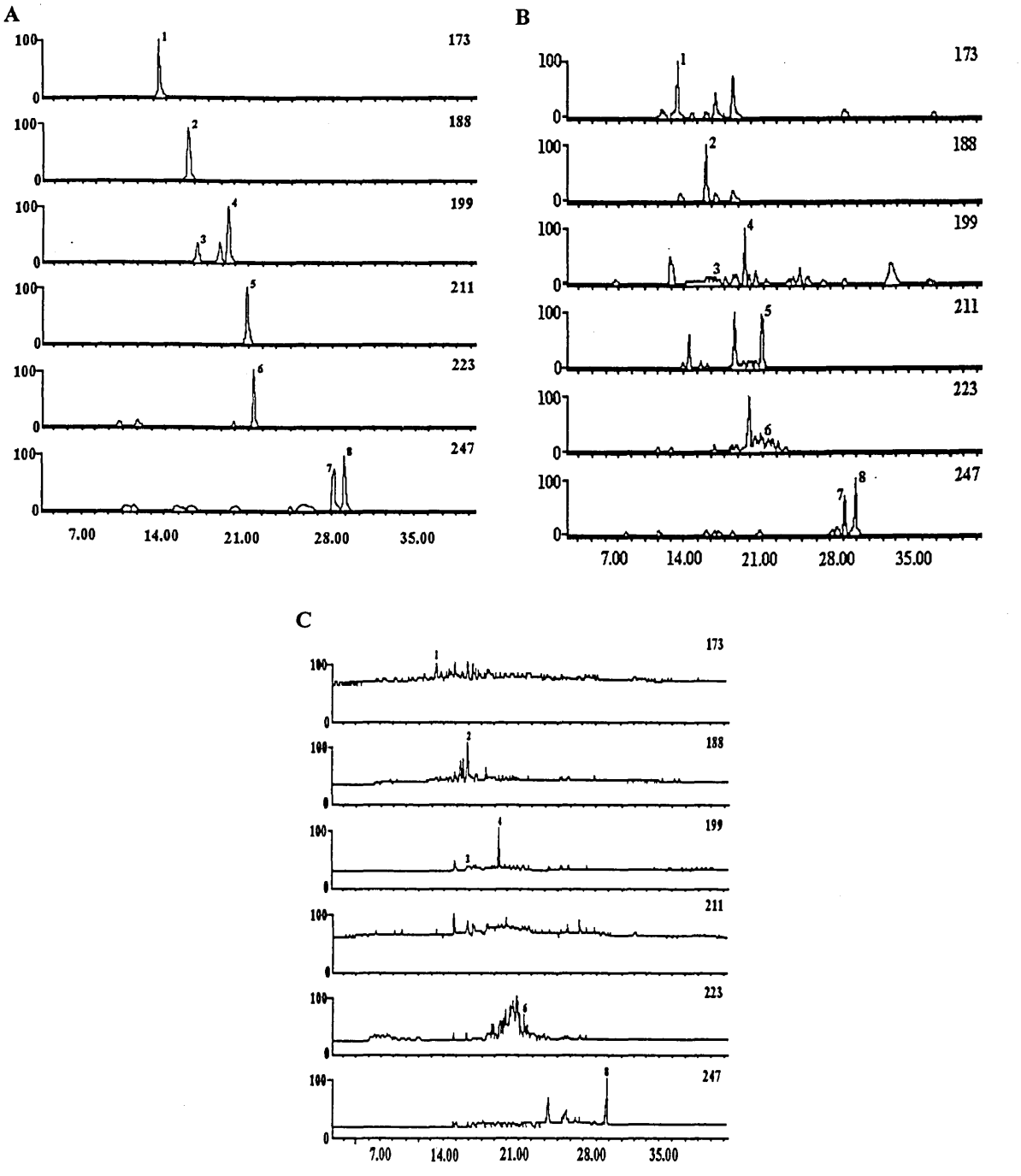

Fig. 2. (A) GC–NICI-SIM chromatograms of a standard containing seven nitrated PAH and an internal standard: (1) 1-nitronaphthalene, (2) Internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene. (B) GC–NICI-SIM chromatograms of tree bark A (2/96) after fractionation, identifying: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene. (C) GC–NICI-SIM chromatograms of diesel particulates (11/95) after fractionation, identifying: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (6) 9-nitroanthracene, (8) 1-nitropyrene.

Table 3
GC–ECD semi-quantitative results of specific nitrated PAH in tree bark A and B (three samples over a 1-year period) along with diesel particulate extracts: quantitative results are ng of compound in 1 g of bark or diesel particulates as appropriate

Compound	Tree A Jan./95	Tree A July/95	Tree A Jan./96	Tree B Jan./95	Tree B July/95	Tree B Jan./96	Diesel particulates
1-Nitronaphthalene Internal standard	48.52	6.33	39.37	3.43	4.17	28.9	2.5
4-Nitrobiphenyl	38.99	Trace	26.33	3.3	Trace	35.4	13.19
5-Nitroacenaphthene	20.67	N.D.	103.39	7.49	N.D.	71.09	12.43
2-Nitrofluorene	11.79	Trace	91.49	3.4	N.D.	43.94	N.D.
9-Nitroanthracene	N.D.	N.D.	57.49	Degraded	N.D.	11.09	9.79
3-Nitrofluoranthene		Obscured	Obscured		Obscured	Obscured	Obscured
1-Nitropyrene		N.D.	89.98		N.D.	73.63	18.39

N.D., none determined. Trace, peak present but below limit of detection. D.S., nitrated PAH had degraded in sample. Obscured, the relevant peak was obscured beneath a large contamination peak.

resolution of some of the relevant peaks. 1-Nitropyrene is often identified as being the major nitrated PAH present in diesel exhaust fumes, [1], and the data presented here supports this.

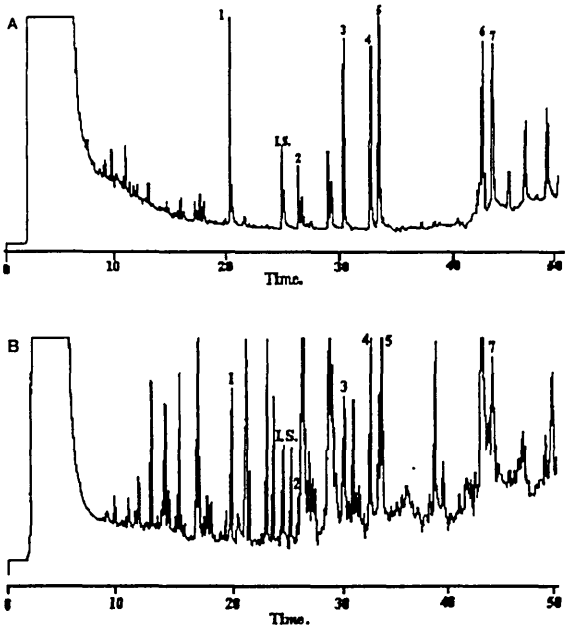

Fig. 3. (A) GC–ECD chromatogram of seven nitrated PAH with internal standard: (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene. (B) GC–ECD chromatogram of tree bark (1/96): (1) 1-nitronaphthalene, (2) internal standard, (3) 4-nitrobiphenyl, (4) 5-nitroacenaphthalene, (5) 2-nitrofluorene, (6) 9-nitroanthracene, (7) 3-nitrofluoranthene, (8) 1-nitropyrene.

4. Conclusions

The literature has shown that tree bark can act as a passive sampler for certain atmospheric pollutants. Here we have demonstrated the adsorption of nitrated PAH from the atmosphere by tree bark. The seven nitro-PAH studied (Fig. 1) were all from the most stable intermediate in electrophilic aromatic substitution and are, therefore, formed in combustion processes. Their major source in the centre of Sheffield is likely to be vehicular emissions. The presence of six out of the seven studied compounds was confirmed in separate experiments using a diesel engine under controlled test conditions. All nitrated PAH studied were found by GC–NICI-SIM in the January 1996 bark samples (Table 2) while four were found in both of the January 95 tree bark samples. (Note: 1-nitropyrene and 3-nitrofluoranthene were not analysed for in the Jan./95 samples.)

Nitrated PAH are produced in relatively large quantities with one route of removal from the environment being adsorption onto tree bark and/or other vegetation, especially during colder climatic periods. The extent to which this occurs, appears to be seasonally dependent since concentrations in the bark are lower in the summer than during the winter This has also been observed by Librando and Fazzino [5] who analysed air samples over a period of 1 year. Identification of the mechanism by which these pollutants are adsorbed onto vegetation (i.e either from the gas phase or directly from particulates) is required as the sampling method could be expanded to the analysis of nitrated PAH pro

duced in ambient air [16,39]. Then possible sources and routes to removal could be investigated with the result being a mass-balance model of nitrated PAH and their ultimate removal from the environment. The necessity for quick, robust methods for the determination of these compounds is important along with the identification of any other major sources. If the other sources of nitrated PAH are of little consequence, nitrated PAH could be used as markers to identify areas which are heavily polluted from diesel emissions.

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