

MONITORING AND ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

by

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LIST OF ABBREVIATIONS

s-VOC's:	Semi-volatile organic compounds
VOC's:	Volatile organic compounds
PAH's:	Polycyclic aromatic hydrocarbons
PCB's;	Polychlorinated biphenyls
POM:	Particulate organic matter
APM:	Atmospheric particulate matter
PTS:	Persistent toxic substances
HAP's:	Hazardous air pollutants
UNEP:	United Nation Environment Program
POP's:	Persistent organic pollutants
PCDD's:	Polychlorinated dibenzodioxins
PCDF's:	Polychlorinated dibenzofurans
TEF:	Toxic equivalent factor
TEQ:	Toxic equivalent quotient
EPA:	Environmental protection agency
PNA's:	Polynuclear aromatics
BaP:	Benzo(a)pyrene
US-EPA:	United States European Protection Agency
NATA:	National-Scale Air Toxic Assessment
PUF:	Polyurethane foam
K-D:	Kuderna-Danish
ADMS:	Atmospheric Dispersion Modelling System
EC:	European Commission
IARC:	International Agency for Research on Cancer
UK:	United Kingdom
GC/MS:	Gas Chromatography/Mass Spectrometer

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SUMMARY

The growing concern for environmental pollution indicates the importance of correctly predicting the fate of pollutants in ambient air. This study was conducted to predict the ambient levels of polycyclic aromatic hydrocarbons (PAH's) in the greater Sasolburg area and to better understand the distribution and the sources of PAH's in ambient air. PAH's are chemical compounds which consist of two or more fused benzene rings and made entirely from carbon and hydrogen. PAH's are widespread environmental pollutants which are mainly emitted from combustion sources, which includes automobiles, industrial processes and domestic heating systems. As a result of the ubiquitous presence of these combustion sources, PAH's are distributed throughout the atmosphere in both the gas and particulate phases. There is an international concern about human exposure to a number of PAH's, mainly benzo[a]pyrene and their associated health effects (carcinogenic and mutagenic). Human exposure to PAH's may occur via food, water, air and direct contact with materials containing PAH's.

In the case of PAH's, monitoring is difficult as these species have a very low ambient concentration. Advanced sampling techniques are necessary to collect adequate volumes of air samples. A high volume sampler equipped with polyurethane foam (PUF) and quartz filters were used to collect the air samples in the greater Sasolburg area. The polyurethane is used to collect gas-phase samples while the filter is used to collect the particle-phase samples.

Ambient air quality measurements for PAH's were conducted during the period of November to December 2005 at two sites in Sasolburg region (industrial and hospital area). Sixteen PAH species were targeted for this study and of the sixteen species; seven of them were identified as priority PAH's by US EPA; on basis of concern that they might cause cancer in animals and humans.

The measured results obtained showed anthracene to be one of the most predominant PAH species obtained in both the gas and particle phase. The total PAH emissions produced in the Sasolburg area were determined by using emission factors from the United State Environmental Protection Agency [39] for residential area and the emission factors from Environmental Protection Agency 42 [52] were used to determine the total emission produced for the industrial area.

The measured results were modelled using an Atmospheric Dispersion Modelling System developed by Cambridge Environmental Research Consultants to predict the ambient levels of PAH's. The results showed naphthalene, phenanthrene and fluoranthene to be the dominant PAH species at the industrial area. The accuracy of the model predicted concentrations performed best for the following PAH species: fluorene; fluoranthene and pyrene at both the Sasolburg hospital and industrial receptors. Conversely the accuracy of the model predicted concentrations consistently performed worst for the following PAH species: acenaphthene; acenaphthylene; naphthalene and phenanthrene at both the Sasolburg hospital and industrial receptors. The model predicted that the concentrations were significant overestimates of the actual measured concentrations, resulting in huge model deviations.

From the results obtained in this study, it is deduced that most of the PAH's were obtained in the gas-phase than in the particle phase. The highest PAH concentration in particle-phase was obtained at Sasolburg industrial area while the highest PAH concentration in gas-phase was observed at Sasolburg hospital area

OPSOMMING

Die groeiende toename in die gesteldheid op omgewingsbesoedeling wys daarop dat dit baie belangrik is dat die impak van lugbesoedelstowwe korrek voorspel moet kan word. Hierdie studie is gedoen om polisikliese aromatiese koolwaterstowwe (PAH's) in die groter Sasolburg area te meet en te voorspel asook om die verspreiding en bronne van PAH's in lug beter te verstaan. PAH's is chemiese verbindings wat uit twee of meer benseenringe bestaan en geheel en al uit kool- en waterstowwe saamgestel is. PAH's is omgewings-besoedelingstowwe wat wyd verspreid voorkom en hoofsaaklik in die lug vrygestel word deur verbrandingsprosesse vanaf motorvoertuie, nywerheidsprosesse en huishoudelike verwarmings sisteme. As gevolg van die alomteenwoordigheid van hierdie verbrandingsprosesse is PAH's regdeur die atmosfeer versprei in beide die gas- en partikel fases. Internasionale kommernis bestaan ook 'n oor die blootstelling van mense aan 'n aantal PAH's, hoofsaaklik benso[a]pireen asook hierdie PAH's se geassosieerde gesondheidsimpak (karsinogenies en mutagenies). Die mens word aan PAH's blootgestel deur voedsel, water, lug en direkte kontak met materiale wat PAH's bevat.

Monitering van PAH's is moeilik omdat hierdie spesies baie lae lug konsentrasies het. Gevorderde monsternemingstegnieke word benodig om genoegsame volumes lug te versamel. 'n Hoë volume monsternemer wat toegerus is met 'n poli-uretaan skuim (PUF) en 'n kwarts filter is gebruik om lugmonsters te versamel in die groter Sasolburg area. Die poli-uretaan word gebruik om die gasfase monsters te versamel en die kwarts filter is gebruik om partikels mee te versamel.

Metings vir PAH's is gedoen gedurende die periode van November tot Desember 2005 by twee monsternemingstasies in die Sasolburg area (industriële en hospitaal area). Daar is vir sestien PAH spesies geanaliseer in hierdie studie waarvan sewe as prioriteit PAH's deur die US EPA geklassifiseer is op die basis dat dit kankergewende PAH spesies is vir mens en dier.

Uit die gemete resultate blyk dit dat antraseen een van die mees algemeenste PAH spesies in beide die gas- en partikel fases is. Die totale PAH emissies wat in die Sasolburg area voorkom is bepaal deur van emissiefaktore gebruik te maak soos voorgeskryf deur die US EPA [39] vir residensiele areas. Die emissiefaktore van die "Environmental Protection Agency 42" [52] is gebruik om die totale emissies wat in die nywerheidsgebied gevorm word te bepaal.

Die gemete resultate is gemoduleer deur gebruik te maak van die Atmosferiese dispersie modelleringssisteem wat ontwikkel is deur die Cambridge Omgewings navorsings konsultante en gebruik word om vlakke van PAH's in die lug te voorspel. Die resultate wys dat naftaleen, fenantreen en fluoranteen die dominante PAH spesies in die industriële area is. Die akkuraatheid van die modelvoorspelde konsentrasies was die beste vir die volgende PAH spesies: fluoreen, fluoranteen en pireen, beide vir die Sasolburg hospitaal sowel as die industriële reseptor gebiede. Aan die ander kant het die akkuraatheid van die model voorspelde konsentrasies deurentyd swakker gevaar vir die volgende PAH spesies: asenafteen, asenaftileen, naftaleen en fenantreen vir by beide die Sasolburg hospitaal en industriële reseptors. Die modelvoorspelde konsentrasies is heelwat hoër as die gemete konsentrasies wat daartoe gelei het dat daar groot model afwyking voorkom.

Vanuit die resultate in hierdie studie is afgelei dat die meeste PAH's in die gasfase voorkom. Die hoogste totale PAH konsentrasie in die partikelfase het voorgekom by die Sasolburg industriële area terwyl die hoogste totale PAH konsentrasie in die gasfase voorgekom het by die Sasolburg hospitaal area.

CHAPTER 1

MOTIVATION AND GOALS

In this chapter the project motivation and goals are briefly discussed.

1.1 Project motivation

Industrial and human developments are accompanied by environmental impacts and are of particular concern in the case of emission of pollutants emitted into the atmosphere. These impacts are mainly associated with water-, land- and atmospheric pollutants. The impact on ambient air is specifically relevant for this study. There are several air pollutants emitted into the ambient air from biogenic and anthropogenic sources including sulphur dioxide, nitrogen oxides, trace elements, volatile organic compounds (VOC's) and semi-volatile organic compounds (s-VOC's) species [1]. These compounds may be present in the atmosphere in the gaseous or solid state, also known as particle matter or aerosols, before being deposited [1].

Atmospheric particulate matter (APM) is a complex mixture consisting of organic and inorganic compounds [2, 3, 4], where the organic fraction of aerosol generally contributes 30-60% of the total fine particulate matter in the atmosphere [4]. Atmospheric particulate matter are classified into fine (diameter $\leq 2\mu\text{m}$) and coarse (diameter $> 2\mu\text{m}$) fractions, which have a diverse origin, composition, lifetime and effect [5]. Sources of atmospheric particulates include various combustion processes (incomplete combustion of fossil fuels and wood), biogenic emissions and soil. These primary compounds may undergo several complex chemical reactions which produce secondary pollutants including aerosols [2,3].

The partitioning of organic compounds between particulate matter and gas phase is strongly influenced by temperature, water vapour concentration, the chemical composition of the particulate matter, amount of organic material in the particulate matter, and several atmospheric parameters [2, 3].

Atmospheric constituents follow a series of processes from the time of their introduction into the atmosphere until they are eventually removed from the atmosphere. The fate of air pollutants introduced into the atmosphere undergoes a series of main processes (pathways) including transformation (chemical reactions), transport and deposition. Understanding the atmospheric pathway of air pollutant species and quantifying the flux of material along these pathways are fundamental to the study of atmospheric chemistry [6]. This study aims to gain a better understanding of such a pathway associated with a group of pollutants known as semi-volatile organic compounds.

Semi-volatile organic compounds (s-VOC's) are a class of organic compounds with relative high boiling points and vapour pressures, thereby requiring temperatures well above room temperature ($>100^{\circ}\text{C}$) to be predominantly present in the gaseous state [7]. s-VOC's concentrations in ambient air results mainly from industrial wastewater-, incineration processes- and coal and biomass burning emissions [8].

Polycyclic aromatic hydrocarbons (PAH's) are an important group of s-VOC's, which are formed from combustion sources including emissions from industrial and residential processes, automobiles, waste incineration facilities and many other biogenic sources such as forest fires and volcanic eruptions. Exposure to humans may occur via air, food, water and direct contact with material containing PAH's. PAH's are quantified in air-, water-, sediments- and tissue samples due to the mutagenic and carcinogenic nature of some of these species [9].

Monitoring and analysis of PAH's will assist in determining the source strength, source profile, distribution pattern and effects they may have on humans, animals and the receiving environment.

A general classification of the different organic compounds in air is given in Figure 1.1.

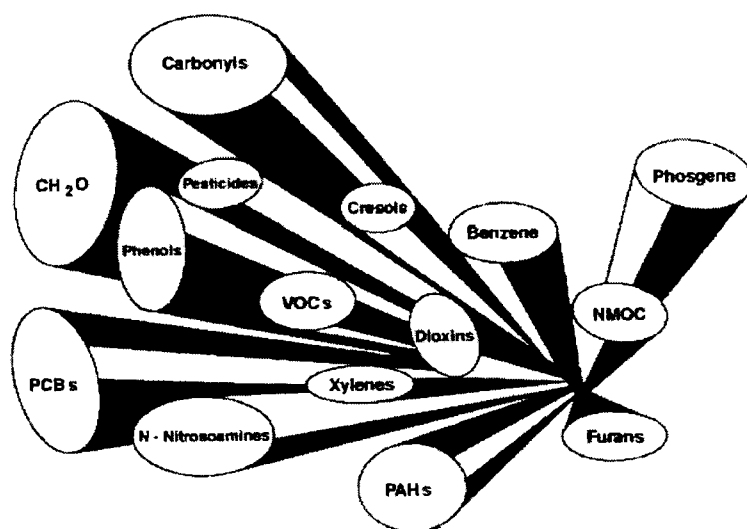


Figure 1.1: Different classes of organic compounds in ambient air [10]

The chemicals classified as s-VOC's in Figure 1.1 includes dioxins, furans, polycyclic aromatic hydrocarbons (PAH's), pesticides and polychlorinated biphenyls (PCB's). Details of these chemicals will be discussed in Chapter 2. PAH's, PCB's and pesticides are considered to be toxic, mutagenic and carcinogenic [11, 12, 13]. These compounds are also bio-accumulative and thus may cause serious environmental health problems such as chronic health effects; reproductive toxicity, birth defects and behavioural changes in animals including humans [12]. Therefore, monitoring the presence of these compounds in ambient air is important.

1.2 Project goals

This study is aimed at determining the concentrations of PAH's in ambient air focusing on the Vaal Triangle area (Greater Sasolburg Area) as it is one of the major industrial, mining and residential areas, and therefore experience major pollution impacts due to use of low-grade coal. The study is also aimed at determining emission loads, as well as predicting the impact on ambient air by means of dispersion modelling.

A suitable sampling collection protocol and analysis methodology for PAH's will also be adopted. The three main objectives of the study can thus be summarised as follows:

- to evaluate and implement monitoring and analysis methodologies for PAH's in ambient air
- to determine the concentration and presence of PAH species in ambient air
- to determine the link between source strength and ambient levels of PAH species in ambient air
- to model the results obtained and then compare the measured results to the modelled results

CHAPTER 2

LITERATURE SURVEY

This chapter will discuss in detail the background information of this study and in particular characteristics, sources and fate of polycyclic aromatic compounds belonging to a group of compounds known as the semi-volatile organic pollutant species which is the central focus of this study.

2.1 Introduction

Ambient air contains many potentially harmful substances. The introduction of these harmful air pollutants into the environment (ambient air, soil or water) has adverse effects on human health, productivity and natural ecosystems.

Pollution is defined as the introduction of substances or energy liable to cause hazards to human health, harm to the living resources and ecological systems, damage to the structures or amenity, or interferences with legitimate uses of the environment [6]. The difference between contamination and pollution can be made as follows; contamination is used for situations where a substance is present in the environment, but not causing any obvious harm, while pollution is used for cases where harmful effects are apparent [6].

2.1.1 Characterization of air pollutants

There are two categories of air pollutants defined, namely the criteria pollutants and air toxics. The criteria pollutants currently proposed for South Africa are carbon monoxide, nitrogen dioxide, ozone, sulfur dioxide, lead, particle matter smaller than 10 micron in diameter (PM₁₀) and fallout dust [14].

Air toxics are defined as gaseous-, aerosol- or particle pollutants that are present in the air at low concentrations and characterized as being toxic or persistent, so as to be a hazard to human health, plant or animal life [15].

In studying air pollution three main issues are of importance namely (1) source of pollution, (2) the transport medium (air, water or direct dumping onto land), and (3) the target, including ecosystems and individual organisms. Pollution can be classified according to the sources (example: biogenic (natural) and anthropogenic (human-made)), the media affected (example: air, soil or water pollution) or by the chemical nature of the pollutant (example: heavy metals, organic and inorganic) [6].

Ambient air contains a diversity of individual chemical species derived from anthropogenic emissions (fossil fuel, coal combustion), natural (biogenic and geochemical emissions) and secondary atmospheric chemical reaction products. The primary focus areas internationally for air pollutant characterization studies during the past few decades have included the speciation of gas-phase hydrocarbon emissions from combustion sources and its impact on photochemical processes as well as the impact of these air pollution species on human health. These organic species can be best described as existing in the volatile-(VOC's), semi volatile (s-VOC's) and particulate organic matter (POM) phases and is listed in Table 2.1 [16].

Table 2.1: Atmospheric phases of organic air pollutants

Air pollutants phase	Molecular weight range of carbon (C)
Volatile organic compounds (VOC's)	C ₁ -C ₁₁
Semi-volatile organic compounds (s-VOC's)	C ₁₀ -C ₁₇
Particulate organic matter (POM)	C ₁₅ -C ₆₀ ⁺

2.1.2 Atmospheric pollutant transport and chemistry

The atmosphere is an important pathway for the transport and the global distribution of many pollutants of toxicological relevance [17]. The distance and mean by which air pollutants can be transported depends on the weather conditions, type of pollutant, the phase of the pollutant (solid, liquid, condensed vapor or gaseous) and the size of the particle to which the pollutant is adsorbed. All these factors can also affect the removal rate of a pollutant from the atmosphere [18]. Once these chemicals are introduced into the atmosphere, chemical species in both the gas- and particle phases are subjected to several natural processes, including wet and dry deposition, air-water exchange, where PAH's may be adsorbed and conversely volatilized when facing large aquatic systems and air-soil interaction [19, 20].

The size of the airborne particle on which the compound of interest is bound will be determined by the rate of removal via dry and wet deposition. Particle size can also be used to determine the magnitude of human exposure of particle bound contaminants due to certain particle or aerosol size fraction's ability to remain in lung alveoli [21]. For example, the fine particles with diameter $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) are the greatest health concern because when inhaled they can be deposited more deeply in the lungs than the coarse particles [22]. All properties of a particle depend on their size; therefore knowledge of the particle-bound substance's distribution with respect to the particle size is essential for estimating their impact on the ecosystem via wet and dry deposition. It is therefore essential to measure both dry and wet deposition [17].

Dry deposition is associated with particles, whose transport is dependant on their various physical properties [18]. Dry deposition results from direct impaction of aerosols and particles with land- and water bodies and is not necessarily associated with rainfall events. Airborne PAH's are usually short lived in the atmosphere. PAH's removal rate is relatively rapid, in the order of tens of hours, and does not disperse over vast distances from the emission source [21].

During wet deposition processes, PAH's are associated with rain either by dissolving in the rain droplet or being incorporated as particles [19]. PAH's in the aqueous phase have a lifetime in the order of tens to hundreds of hours. Cloud droplets accumulate gaseous and particulate PAH's as they travel over long distances. In areas near to the urban or industrial areas, dry deposition is the prominent removal process, while in more remote areas, wet deposition become the prominent removal mechanism [23].

2.2 Semi-volatile organic compounds (s-VOC's)

2.2.1 Introduction

The term "semi-volatile organic compounds" is used to broadly describe organic compounds which are not volatile enough for thermal desorption from solid adsorbent at moderate temperatures [24]. The distribution of s-VOC's between the gaseous- and solid phase is the most important factor determining the removal mechanisms and residence time in the atmosphere [21]. Semi-volatile aerosols are ubiquitous and concentrations are higher in urban areas close to the source [24].

Semi-volatile organic compounds are generated as by-products from incomplete combustion of fossil fuels (coal, oil and natural gas) and are formed during photochemical reactions in the atmosphere reporting as secondary organic aerosols and biogenic emissions from natural sources. Many classes of chemical pollutants make-up the group commonly referred to as semi-volatile compounds. This group includes compounds such as alkanes, PCB's, PAH's, terpenes, quinines, nitrates and lipids [22].

Semi-volatile aerosols account for as much as 5-25% by mass in atmospheric particulate matter (APM). Many potential carcinogenic and mutagenic organic compounds found in the atmosphere are semi-volatile.

Semi-volatile organic compounds normally have vapour pressures between 10^{-4} and 10^{-11} atm over the normal ambient temperature range. These compounds may simultaneously exist as vapours or as sorbed species on airborne particulate matter [24].

As mentioned previously, s-VOC's are present in ambient air in the gaseous and particulate matter. The distribution of s-VOC's between the gas and particle phases controls their removal from the atmosphere by physical (e.g., wet and dry deposition), chemical and photochemical processes [24].

Semi-volatile organic compounds are also referred to as persistent toxic substances (PTS) according to the Global Report 2003 [25]. There is no formal or legal definition for PTS but the concept was developed during the project development phase to include chemicals that could be of concern due to their potential toxicity to ecosystems or humans. United Nation Environment Program (UNEP) Governing Council decided in 1997 that immediate international action should be taken to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve persistent organic pollutants (POP's). Semi-volatile organic compounds of interest include PCB's, PAH's, polychlorinated dibenzodioxins (PCDD's), polychlorinated dibenzofurans (PCDF's), organic pesticides (e.g., lindane, malathion) and the compounds which condense to form secondary organic aerosols [25].

2.2.2 Classes of semi-volatile organic compounds

There are four classes of s-VOC's which will be discussed, namely dioxins and furans, PCB's, PAH's and pesticides.

2.2.2.1 Dioxins and furans

Dioxins and furans are highly toxic chemical substances that are found in very small amounts in the environment, including air, water, and soil, and also in food [7]. The term dioxin refers to a group or family of toxic chemical compounds that share certain similar chemical structures, biological characteristics and a common mechanism of toxic actions [26]. Figure 2.1 gives the structures of a dioxin and furan.

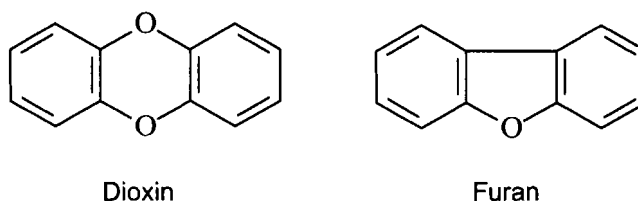


Figure 2.1: Structure of dioxin and furan

Because of their carcinogenic nature, analysis of dioxins is an important issue. Sources of dioxin emissions are mainly due to combustion processes such as waste incineration and steel industry [27]. Dioxin compounds include seven of the polychlorinated dibenzo dioxins (PCDD's), ten of the polychlorinated dibenzo furans (PCDF's) and twelve of the biphenyls (PCB's) [26]. Their chemical names are PCDD's ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDF's ($C_{12}H_{(8-n)}Cl_nO$) and they may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively [25]. The most dangerous are 17 members of this group characterized by the presence of a chlorine atom in the 2, 3, 7, and 8 positions (2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)) and this compound is used as reference for all other dioxins [7].

Each of those 2, 3, 7, 8-substituted congeners has been assigned a Toxic Equivalent Factor (TEF), which is used for computation of the Toxic Equivalent Quotient (TEQ). This scale is used in risk assessment studies to calculate the probability of causing cancer and other life threatening diseases in humans [7].

Dioxins such as CDD's, CDF's and PCB's were created intentionally for industrial purposes, but others are produced as unintentional by-products from processes such as the incineration of waste material from several industrial chemical processes, the burning of fossil fuels (including forest fires), combustion, the chlorine bleaching of pulp and paper and small amounts found in cigarette smoking [28].

Their solubility in water is in the range of 0.0002-0.43 ng/L at 25°C and they have vapour pressure of $0.007-2 \times 10^{-6}$ mmHg at 20°C. They are by-products from the production of other chemicals, from low temperature combustion and incineration processes and have no known use. PCDD/F's are characterized by their lipophilicity, semi-volatility and resistance to degradation (half-life of TCDD in soil is 10-12 years) and long-range transport. They are also known for their ability to bio-concentrate and bio-magnify under typical environmental conditions [25].

Dioxins and furans have the ability to travel long distances in the atmosphere, therefore may result in adverse effects far from the source. These compounds dissolve and remain stored in the body fat of animals and this will mean that more dioxins and furans are taken into living bodies through consumption of food than through air, water or soil [29]. In small doses, these substances do not appear to be a threat. However, large doses are known to cause serious health problems [7].

2.2.2.2 Polychlorinated biphenyls (PCB's)

PCB's were introduced in 1929 and refers to a class of manufactured chemicals (entirely man-made and do not occur naturally) that tend to last for many years. PCB's do not decompose easily (chemically stable) under normal environmental conditions.

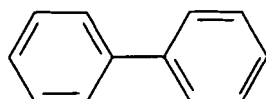


Figure 2.2: Basic structure of carbon-backbone of PCB's

PCB's consists of aromatic rings joined by a carbon-carbon bond. These two rings can be chlorinated at any position of each of the five remaining carbons on the two rings. Each possible combination of chlorination is a congener and different congeners are considered important by different regulatory bodies. Analytical methods are essential in separating and quantifying all relevant congeners to satisfy regulators [7]. Most PCB's congeners, particularly those lacking adjacent un-substituted positions on the biphenyl rings are extremely persistent in the environment. They are estimated to have half-lives ranging from three weeks to two years in air with the exception of mono- and di-chlorobiphenyls [25].

PCB's were widely used as ingredients in a number of industrial materials, such as sealing and caulking compounds, ink and paint additives from 1930 to 1970. They were also used to make coolants and lubricants for certain kinds of electrical equipment, such as transformers and capacitors. In 1977 concerns about the impact of PCB's on the environment led to a North American ban on the manufacturing and importation of PCB's, but the ban did not cover existing PCB's that were used in electrical applications. Little is known about the long-term effects of PCB's, so it is important to keep exposure to these chemicals as low as possible [30].

2.2.2.3 Pesticides

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pesticides are often misunderstood to refer only to insecticides, but the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests. A pesticide is also defined by United State law as any substance or mixture of substance intended to regulate, defoliate or desiccant [31].

Naturally, most pesticides create some risk of harm. Because they are designed to kill, they adversely affect living organisms and cause harm to humans or the environment. At the same time, pesticides are useful to society because they kill potential disease-causing organisms and control insects, weeds and other pests. Biologically based pesticides, such as pheromones and microbial pesticides, are becoming increasingly popular and are often safer than traditional chemical pesticides. In addition, the Environmental protection agency (EPA) is registering reduced-risk conventional pesticides in increasing number [31].

Just as pesticides are used to destroy an area of unwanted pests; an herbicide is a type of pesticide used to control or kill unwanted plants such as weeds, brush, unproductive bushes or trees, and other growths that takes nutrients away from the crops and other useful plants. Many herbicides are found to be synthetic therefore can be toxic to “good” plants, animals and humans. There are two main types of herbicides available, namely, the nonselective and selective herbicides. The nonselective herbicide is mainly used to kill all growth and it is generally reserved for agricultural use or for cleaning large or heavily overgrown areas. Nonselective herbicides are rarely required for the home gardens. A selective herbicide on the other hand is used to target certain types of plant life, for example, it works to curb growth through some type of hormone disruption and therefore should not effect other vegetation. Selective herbicides are suitable for maintaining grass and home gardens [32].

2.2.2.4 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH's), also known as polynuclear aromatics (PNA's), are a group of organic compounds consisting of two or more fused aromatic rings made entirely from carbon and hydrogen [33]. PAH's occur in both gaseous and particulate phase in the atmosphere and may come into contact with living beings either through the skin (externally) or through the lungs (internally). This makes some of the PAH's the major carcinogenic and mutagenic species [34]. The highest concentration of PAH's are found in places near urban environments due to industrial processes, vehicular traffic and other anthropogenic sources [33]. In urban areas, anthropogenic sources are the predominant source responsible for the presence of PAH's in the atmosphere and can be divided into stationary and mobile sources. PAH's have been identified mostly in stationary sources, which involves a variety of combustion processes such as residential furnace and heating supply using coal, oil, gas and wood, industrial processes, incineration and power generation [35].

PAH's can be formed by the thermal decomposition of any organic material containing carbon and hydrogen [36]. They are primarily released into the environment from anthropogenic sources such as combustion of fossil fuel, automobile exhaust fumes, domestic heating system, agricultural and industrial processes [22]. Automobile exhaust fume is the main source of urban PAH's emissions into the atmosphere. The PAH's emission profile varies with engine type, with diesel engines being the principal source of low molecular weight PAH's and petrol engines releasing the greatest amount of high molecular weight PAH's such as benzo(a)pyrene (BaP) and dibenzo(a,h)anthracene [34]. PAH's can also be formed naturally as a result of uncontrolled or accidental burning. More than 30 PAH compounds and several hundred PAH's derivatives have been identified since 1976 to have carcinogenic and mutagenic effects, making them the largest single class of chemical carcinogens known [36].

The semi-volatile property of some PAH's makes them highly mobile throughout the environment, deposition and re-volatilization distributing them between air, soil and water bodies. A small amount of PAH's are subjected to long-range atmospheric transport making them a global environmental problem [34]. The chemical structures of 14 selected PAH compounds are given in Figure 2.3.

PAH's solubility in water is 2.1-0.00014 mg/L at 25°C with vapour pressures of 0.0015×10^{-9} to 0.0051 mmHg at 25°C. Persistence of PAH's varies with their molecular weight. The low molecular weight PAH's are most easily degraded. The reported half-lives of naphthalene, anthracene and benzo(e)pyrene in sediments are 9, 43 and 83 hours, respectively, whereas for higher molecular PAH's, their half-lives are up to several years in soil and sediments. Due to their wide distribution, the environmental pollution by PAH's has global concern [25]. General properties of PAH's are given in the Table 2.2.

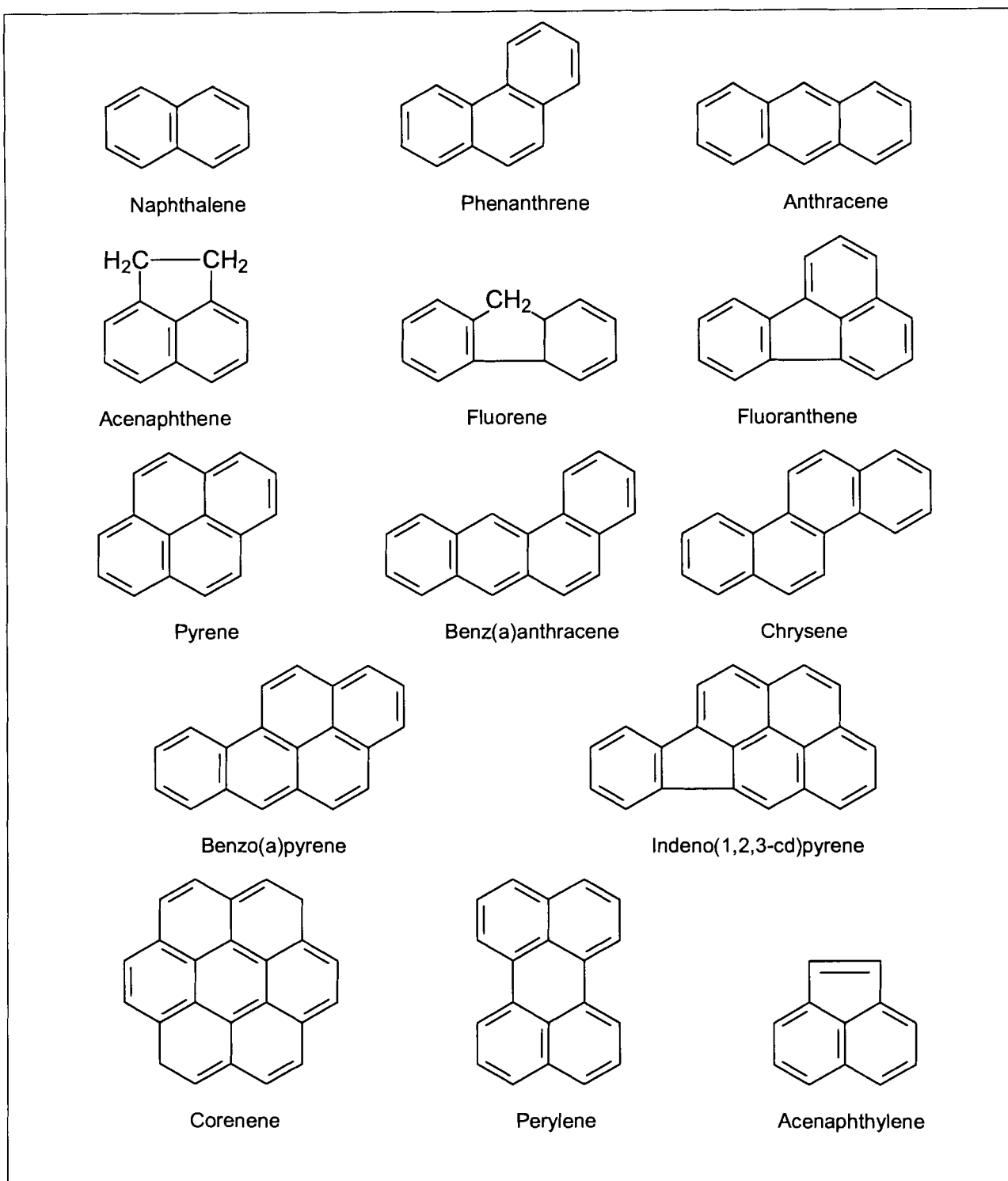


Figure 2.3: Chemical structures of selected PAH compounds

Table2.2: Physical and chemical properties of selected PAH species

Species	Chemical formula	Molecular weight (g/mol)	Boiling point (°C)	Melting point (°C)	Vapour pressure (kPa)
Acenaphthene	C ₁₂ H ₁₀	154,21	278-279	90-96	21
Acenaphthylene	C ₁₂ H ₈	152,20	265-280	92-93	39
Anthracene	C ₁₄ H ₁₀	178,24	340	216-219	36
Benzo(a)anthracene	C ₁₈ H ₁₂	228,30	435	157-167	15
Benzo(a)pyrene	C ₂₀ H ₁₂	252,32	493-496	177-179	73
Benzo(g,h,i)perylene	C ₂₂ H ₁₂	276,34	525	275-278	13
Chrysene	C ₁₈ H ₁₂	228,30	441-448	252-256	57
Fluoranthene	C ₁₆ H ₁₀	202,26	375-393	107-111	65
Fluorene	C ₁₃ H ₁₀	166,23	293-295	116-118	87
Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276,34		162-163	
Naphthalene	C ₁₀ H ₈	128,19	80-200	218	11
Phenanthrene	C ₁₄ H ₁₀	178,24	339-340	96-101	23
Pyrene	C ₁₆ H ₁₀	202,26	150-156	360-404	31
Coronene	C ₂₄ H ₁₂	300,36	525	438-440	20
Benzo(e)pyrene	C ₂₀ H ₁₂	252,32	493	178-179	74

2.2.3 Chemistry of selected PAH species

Atmospheric reactions ultimately determine the chemical composition of the atmosphere to which human populations are exposed to. Organic compounds are removed from the atmosphere by photolysis, deposition and reaction with hydroxyl radicals, nitrogen trioxide (NO₃) radicals, and ozone [37]. Chemical reaction leads to the formation of more polar products that can undergo gas-to-particle conversion, such as the formation of particle-phase nitro-PAH from reactions of gas-phase PAH's [16].

In the atmosphere, PAH's, comprises of 2 to 4 aromatic rings with partition between the gas and particulate phases [38]. PAH's are known to be distributed between the gas and particle phases according to their volatility [9, 39], as parameterized by their vapour pressure [39]. PAH's containing 5 or more rings (e.g. benzo(a)pyrene) are predominantly found in particulate phase (90% in filter/10% in adsorbent), those containing 2 or 3 rings (e.g. acenaphthene) are mostly present in the vapour phase (10% in filter/90% in adsorbent) and lastly, 4 ring (e.g. chrysene) compounds are particle-bound but have the greatest seasonal variability between all the phases (20% in filter/80% in adsorbent) [40, 41].

Therefore, it is very important to understand abundance, speciation, distribution and potential sources of PAH's in aerosols so that air pollution caused by particulate matter can be efficiently controlled [41].

There are a large number of PAH's, which differ in number of aromatic rings, position at which aromatic rings are fused to one another, chemistry and position of substituents on the basic ring system [42]. Naphthalene is one of the simplest and most abundant of all PAH's compounds found in polluted urban environments. Naphthalene has the lowest molecular weight of all PAH's and is formed when two benzene rings are fused together. Exposure to high concentration of naphthalene may have adverse health effects on human (mainly causing cancer).

In gas phase, naphthalene reacts with hydroxyl ($\text{HO}^\bullet$) and nitrate (NO_3) radicals through addition to an aromatic ring. In presence of NO_x , the OH-naphthalene and NO_3 -naphthalene adducts can further react with NO_2 or O_2 to yield a number of products, competing with the thermal decomposition of adducts to reform naphthalene [43]. The reaction of other PAH's with hydroxy radicals and gaseous nitrate radicals in the presence of NO_x leads to the formation of toxic-PAH's derivatives. Gas-phase atmospheric reaction a products of PAH species, with 3 and 4 rings, such as nitrofluoranthenes and nitropyrenes adsorbs onto particles in the atmosphere [40].

The nitro-PAH daughter product formed in the atmosphere, moves across environmental boundaries and partition the soil, sediment, water and biological organisms [40]. There is substantial evidence that many nitrated PAH compounds are mutagenic. Studies of ambient particulate organic matter (POM) collected in Southern California have shown that 10% of the mutagenic activity may be attributed to mutagenic nitro-polycyclic aromatic hydrocarbons (predominantly 2-nitrofluoranthene) formed by gas phase atmospheric reactions.

It is also evident that the majority of nitrated PAH's compounds observed in ambient atmospheric particulate matter are products of parent PAH compounds. In addition to being mutagenic, 2-nitrofluoranthene and 4-nitropyrene are two examples of transformation products that have been classified as carcinogens by the California Environmental Protection Agency [40].

PAH's can also be formed in the pyrolysis of aromatic and straight chain hydrocarbons and this can provide a logical mechanism for giving an explanation of PAH's formation. For example, the formation of phenanthrene, fluoranthene and benzo(a)pyrene are illustrated in Figure 2.4: [40].

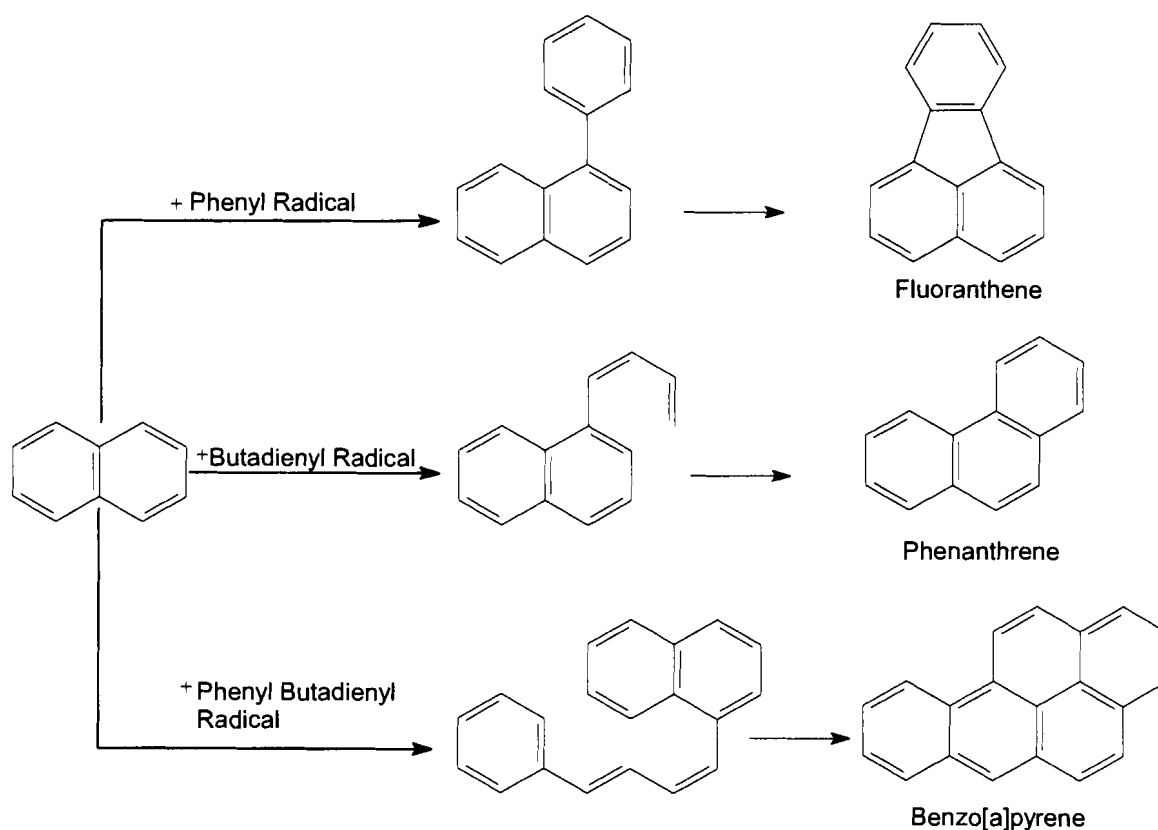


Figure 2.4: Formation of fluoranthene, phenanthrene and benzo(a)pyrene by pyrolysis of naphthalene

The example (Figure 2.4) offers an explanation of how phenyl-, butadienyl- and phenyl butadienyl radicals produced in pyrolysis of phenylbutadiene can react with naphthalene to produce the three PAH products which includes fluoranthene, phenanthrene and benzo(a)pyrene [40]. Phenanthrene, fluoranthene and pyrene, in contrast to benzo(a)pyrene are non carcinogenic, but give rise to radical attack to form nitro-PAH and nitro-PAH lactones responsible for most of the mutagenic and carcinogenic activity of atmospheric particulate products [44].

Most of the carcinogenic and mutagenic products are derived from the atmospheric reaction of gas-phase aromatic and PAH's and PAH's derivatives (e.g., methoxypyrene). Smog chamber experiments and ambient measurements performed suggested that atmospheric reaction products of 2- to 4-ring PAH's account for a substantial fraction of the mutagenic activity in urban air. These reaction products consist of various nitrated products. A major part of these PAH's reaction products remain unknown, and the potential health risks associated with these species are unidentified [38].

2.2.4 Characteristics of s-VOC's

There are many factors that influence partitioning behaviour between vapour and particulate phase. These factors include the compounds vapour pressure, the ambient air temperature and the concentration of the particulate matter in the atmosphere [18].

PAH's gas/particle partitioning is an important process that affects the long-range transport, chemical reactions, deposition, and impact on human and ecosystem health [45]. The gas/particle partitioning ratio is a measure of a semi-volatile organic compounds mass distribution for air pollutants [46].

Therefore, it is important to know the phase distribution of specific PAH species in order to assess the impact the species may have on visibility [46], atmospheric transport and deposition [24]. The distribution of s-VOC's is dependent on the compound's vapour pressure and the concentration of particles suspended in the air [47].

s-VOC's exist in both gas and particle phases in the atmosphere, due to their intermediate volatility [46]. The distribution of mass between both phases can be described at equilibrium by a partitioning coefficient, K_p ($\text{m}^3 \mu\text{g}^{-1}$) [48]:

$$K_p = \frac{[F]}{[A][TSP]} \quad (1)$$

where F is the particle-phase concentration of the compound of interest (s-VOC's) in ng/m^3 , A is the gas phase concentration (ng/m^3), and TSP is the amount of total suspended particulate matter ($\mu\text{g}/\text{m}^3$) [43, 48]. Gas-particle partition coefficients are used to model the formation, transport and fate of semi volatile compounds in the environment [24, 48]. By multiplying K_p with TSP, a ratio of the particle to gas-phase concentrations is obtained:

$$K_p \times [TSP] = \frac{[F]}{[A]} \quad (2)$$

When $K_p \times \text{TSP}$ is greater than one, the compound partitions mainly into particle phase and if $K_p \times \text{TSP}$ value is less than one, partitioning is mainly to the gas phase. For example, a compound with $K_p \times \text{TSP} = 100$ will partition 100 molecules to the particle phase for every one molecule to the gas phase.

Time-integrated measurements of gas and particle phase concentrations are commonly used to determine K_p . Unbiased measurements of K_p are difficult to make. There are numerous factors that can contribute to measurements being biased:

1. the gas-particle equilibrium is disturbed by the sampling method, thus causing mass transfer between phases during sampling,
2. the ambient conditions that governs the gas-particle equilibrium change while sampling (i.e. temperature shift) and they cause previously collected particles and gases to move between phases
3. the capture efficiency for particles or gases is greater than 100% for a given method
4. and, some of the collected compounds react during sampling (reactions with ozone for example) [48]

The gas-phase compounds can be incorrectly measured as particle-phase, or vice versa as a result. When gas-phase compounds are measured as being particle-phase, F is artificially increased, A is artificially decreased, and the sampling method overestimates K_p ; the opposite happens when particle-phase compounds are measured as being in the gas-phase [48].

2.2.5 Industrial emissions of PAH's

Industrial processes are believed to be the major source of PAH's found in the environment. Industrial boilers are widely used in manufacturing, processing, mining, and refining, primarily to generate process steam for electricity and space heating at the facility [40]. The four major sources of PAH species in industrial areas were identified to be, fossil fuel combustion (coal utilisation), biogenic emissions, refuse burning (both industrial and municipal incineration processes) and oil residue. Coal combustion (intensive coal burning) is one of the most important industrial processes and is believed to be the major contributor of PAH species released into the ambient air [49].

During combustion in power stations the coal structure undergoes chemical and physical changes where organic fragments are released leading to formation of PAH's. The concentration levels vary largely depending on the nature of fuel coal (Bituminous/Sub-bituminous coal) and combustion conditions. Bituminous coal is believed to emit higher concentrations of PAH's to the atmosphere [50].

2.2.6 Residential emissions of PAH's

In the absence of industrial and other sources of pollution, PAH's in the atmosphere are due to residential fuel burning and vehicle traffic [33]. Residential heating processes are believed to be one of the activities that are influence the concentration of PAH's present in ambient air. The residential sources of PAH's include furnaces, boilers burning coal, oil and natural gas/liquefied petroleum gas (paraffin); fireplaces burning wood and cooking [37, 40].

Residential wood combustion generally occurs in either stoves or fireplaces located inside the house. PAH's emitted during residential wood combustion are mainly the product of incomplete combustion. The emissions vary depending on how the processes are operated and how the emissions are measured [41]. PAH emissions due to solid fuels combustion in residential areas make a significant contribution to the total PAH emissions. In Sweden, wood combustion has been estimated to contribute 430 kg of benzo(a)pyrene in 1994 whereas gasoline and diesel vehicles together were estimated to contribute a maximum of 320 kg of benzo(a)pyrene together. The coal and wood in fireplaces are often hand fed, of low thermal efficiency and potentially have high PAH emissions. Benzo(a)pyrene from these processes is associated with particle size $<2.5\ \mu\text{m}$ fraction [37].

2.2.7 Emission factors for PAH species

Emission factors and emission inventories are fundamental tools for air quality management. Emission estimates are important for developing emission control strategies and for determining source apportionment. Emission inventories are also important in ambient dispersion modelling and analysis, control strategy development and for screening sources for compliance investigation.

Emission factors are representative values used to calculate the degree to which a particular source contributes to the total emission of pollutants emitted into the atmosphere. Emission factors can also be used in facilitating the estimation of emission from various sources of air pollution. Emission factors are expressed as weight of pollutant divided by a unit weight, volume, distance or duration of the process/activity emitting the pollutant. The equation for emission estimate is given below:

$$E = A \times EF \times \left(\frac{1-ER}{100} \right) \quad (3)$$

where E is emissions, A is activity rate, EF is an emission factor and ER is the overall emission reduction efficiency (%). These factors are simply averages of all available data of acceptable quality and are assumed to be representative of long-term averages of all facilities in the source category [51]. The factors often shows a wide range of values, therefore their use can lead to widely differing estimates of emissions from the same type of processes (e.g. coal combustion). The US-EPA has published the measured emission factor of the most abundant PAH's found in the atmosphere [52]. Table 2.3 and 2.4 shows the industrial and residential PAH emission factors respectively.

Table 2.3: Industrial emission factors for PAH's from controlled coal combustion [53]

Species	Emission Factor (kg/ton)
Biphenyl	$7,72 \times 10^{-7}$
Acenaphthene	$2,32 \times 10^{-7}$
Acenaphthylene	$1,14 \times 10^{-7}$
Anthracene	$9,53 \times 10^{-8}$
Benzo(a)anthracene	$3,63 \times 10^{-8}$
Benzo(a)pyrene	$1,73 \times 10^{-8}$
Benzo(b,j,k)fluoranthene	$4,99 \times 10^{-8}$
Benzo(g,h,i)perylene	$1,23 \times 10^{-8}$
Chrysene	$4,54 \times 10^{-8}$
Fluoranthene	$3,22 \times 10^{-7}$
Fluorene	$4,13 \times 10^{-7}$
Indeno(1,2,3-cd)pyrene	$2,77 \times 10^{-8}$
Naphthalene	$5,90 \times 10^{-6}$
Phenanthrene	$1,23 \times 10^{-6}$
Pyrene	$1,50 \times 10^{-7}$
5-Methyl Chrysene	$9,99 \times 10^{-9}$

Table 2.4: PAH emission factors for residential coal stoves [40]

Species	Emission Factor (kg/ton)
Acenaphthylene	$1,20 \times 10^{-2}$
Anthracene	$3,10 \times 10^{-3}$
Benzo(a)anthracene	$3,00 \times 10^{-3}$
Benzo(a)pyrene	$2,60 \times 10^{-3}$
Chrysene	$2,80 \times 10^{-3}$
Phenanthrene	$1,10 \times 10^{-2}$
Benzo(e)pyrene	$2,00 \times 10^{-3}$

2.2.8 Atmospheric abundance of PAH species

PAH's are ubiquitous in the atmosphere and believed to be mutagenic and carcinogenic; therefore this makes them important atmospheric pollutants. Concentration of PAH's increase in winter because of the frequent inversion layers in winter than in summer.

Polycyclic organic matter is one of the hazardous air pollutants (HAP's) that were regulated by US-EPA. Benzo(a)anthracene, benzo(e)fluoranthene, benzo[a]pyrene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene are the most important human carcinogens.

The outdoor concentration of these seven PAH species in across United State in 1990 were estimated as part of the cumulative exposure project, and was updated in 1996 as the results of National-Scale Air Toxic Assessment (NATA), both conducted by US-EPA. The total concentration of the seven PAH species were found to be $0.13 \mu\text{g}/\text{m}^3$ at New Jersey by a dispersion model and this ambient concentration far exceeding the benchmark concentration ($0.018 \mu\text{g}/\text{m}^3$) according to the NATA report of New Jersey. Table 2.5 below gives the annual ambient concentration of 5 PAH's in a study conducted in Philadelphia, US, 2000 [35].

Table 2.5: Annual ambient concentration of PAH's in fine particles

Species	Annual concentration (ng/m^3)
Benzo(b)fluoranthene	1,0
Benzo(k)fluoranthene	0,8
Benzo(e)pyrene	0,7
Indeno(1,2,3-cd)pyrene	0,3
Indeno(1,2,3-cd)fluoranthene	0,0

In a study conducted by University of California, the total PAH's concentration ranged from $3\text{-}132 \text{ ng}/\text{m}^3$. In the individual PAH's distribution, phenanthrene was found to have the highest concentration averaging $11 \text{ ng}/\text{m}^3$ of the total 24 PAH compounds analyzed, naphthalene, methyl naphthalene and fluorene averaged $\geq 2 \text{ ng}/\text{m}^3$ and the other fifteen PAH compounds averaged $< 1 \text{ ng}/\text{m}^3$ [54].

In another study to evaluate dry deposition of PAH's and PCB's from San Francisco Estuary detected the concentration of PAH's in ambient air to be in a range from $8\text{-}37 \text{ ng}/\text{m}^3$ for the total PAH's. PAH's and PCB's in ambient air samples were predominantly in the gaseous phase, ranging from 83-99% of the organic compounds in the gaseous and particulate phase combined in the total concentration in the atmosphere. PAH's concentration in the ambient air showed high seasonal variation with the highest concentration detected in November, being five times than the concentration detected in August [18].

Table 2.6 below shows the typical ranges of most targeted PAH compounds at remote, rural and urban location in the United Kingdom (UK) in 1996. Table 2.6 shows that the sites differ substantially in PAH concentrations and represent a range along an urban, rural and remote gradient. Table 2.6 is also a “dilution” of ambient air concentrations at sites further away from the major source region.

The PAH concentration at the Scandinavian sites (Pallas and Rörvik) is 1-2 orders of magnitude lower than the urban UK ones, whilst Alert concentrations are almost a thousand times lower. At semi-rural Hazelrigg, high concentrations of some light PAH's (most notably phenanthrene) are shown. The sources are investigated, but may be due to the proximity to major highway (motorway). Table 2.6 suggests that the proximity to the source region drives the PAH air concentrations [55]. N/a and N/d in the Table 2.6 below, means not analysed and not detected respectively.

Table 2.6: Ranges of the PAH's air concentrations (gas and particle) at selected sites (ng/m³)

Species	London	Manchester	Hazelrigg	Rörvik	Pallas	Alert
Acenaphthene	0,7-1,5	1,0-4,0	0,50-2,00	N/a	N/a	0,001-0,02
Fluorene	3,0-90	4,0-20	5,00-20,0	N/a	N/a	0,01-0,30
Phenanthrene	20-22	20-50	70,0-160	0,80-3,00	0,20-0,80	0,02-0,08
Anthracene	1,0-2,0	1,0-4,0	5,00-15,0	0,01-0,10	0,002-0,01	0,002-0,003
Fluoranthene	4,0-6,0	5,0-10	5,00-10,0	0,30-1,70	0,10-0,30	0,005-0,07
Pyrene	2,5-5,0	3,5-8,0	5,00-10,0	0,10-1,00	0,05-0,2	0,004-0,05
Benzo(a)anthracene	0,2-0,9	0,2-1,6	0,30-0,70	0,01-0,20	0,005-0,02	N/d-0,020
Chrysene	0,5-2,0	0,4-6,0	0,25-1,00	0,05-0,50	0,03-0,04	N/d-0,050
Benzo(b)fluoranthene	0,2-1,5	0,2-1,5	0,05-1,00	0,04-0,80	0,02-0,05	N/d-0,012
Benzo(k)fluoranthene	0,1-1,0	0,1-1,0	0,02-0,40	0,01-0,30	0,01-0,02	N/d-0,010
Benzo(a)pyrene	0,1-1,0	0,1-1,0	N/a	0,01-0,20	0,01-0,03	N/d-0,004
Benzo(g,h,i)pyrene	0,3-10	0,2-0,8	0,02-0,50	0,02-0,15	0,01-0,04	N/d-0,013

NOTE: NA = not analysed & ND = not detected

In other recent studies of PAH concentrations in ambient aerosol in Ahmadabad, Mumbai, Nagpur and Kanpur shows that the total PAH concentrations in Indian cities are 10-50 times than those reported internationally and ranges from 23-190 ng/m³ [56].

In Mumbai, the total PAH concentration at Saki Naka (Training center) was 38.8 ng/m³ and PAH concentrations at Indian institute of technology (IIT) was found to be 24.5 ng/m³ [56]. These concentrations are at the lower end of the range of reported PAH concentrations (23-190 ng/m³) in Indian cities. PAH profiles were also developed and for example, coal showed predominance of pyrene, benzo(a)pyrene, dibenz-anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene, wood burning in cooking stoves showed predominance of benzo(a)pyrene and the diesel emissions PAH profile showed large predominance of phenanthrene (60%) along with small amounts of chrysene and benzo(e)pyrene [56].

2.2.9 Modelling

Modelling is used for predicting the long-range dispersion and chemical reactions of air pollutants in the atmosphere (e.g. photochemical reactions to form ozone). Dispersion models are used to predict how pollutants are transported in the atmosphere from point of pollutant release (emission source) to a distant receptor area. The pollutant concentration is calculated and expressed in mass per unit mass in the distant receptor. Dispersion models can be used effectively in investigating pollutants both for local (within 10-50 km of emission source) and regional (across hundred/thousands of kilometres) scale. Dispersion models also offer a number of benefits to the process of air quality management:

1. Dispersion model are used to predict the pollutant concentrations at a number of ground level receptors, therefore this predictions are used to produce pollutant concentration isopleths, which effectively identify difficult areas.

2. Can be used to predict concentration in the future, for example scenario testing, taking into account different pollutant reduction measurement [52]

PAH's can travel long distances in the atmosphere and modelling these compounds could result in a better understanding of how these compounds behave [35]. There are a number of limitations to the application of dispersion models for PAH's at ground level:

1. PAH's emission estimates, even for benzo(a)pyrene alone, have a high degree of uncertainty, therefore this uncertainty will be transferred to PAH's concentration predictions.
2. Important processes (dry deposition and degradation) for long range transport modelling (regional/national level) are not well known for PAH's.
3. Emission estimates for the future are uncertain.
4. Validation of models is difficult due to a lack of long term ambient concentration data.

All these factors combined cast a doubt over the ability of dispersion model studies to accurately predict ground level PAH concentrations, especially from fugitive emissions sources such as residential fuel burning. Despite these limitations, it is expected that dispersion models will play an important role in providing broad estimates of potential non-attainment areas [37].

2.3 Closing remarks

In this chapter, the characterisation of air pollution has been discussed. Emphasis has been placed on discussing atmospheric processes and pathways including dry and wet deposition as well as gas-particle partitioning. Semi-volatile organic pollutant species, being the focus of this study, has been discussed including the different classes and behaviour of these species under atmospheric conditions. The chemistry, characteristic, emission sources, emission calculation methods and dispersion modelling of Polycyclic aromatic hydrocarbon species has also been discussed in broad terms.

The next chapter will be discussion the experimental methodology followed in studying PAH species in ambient air, as well as the methodologies followed to determine the source strength and dispersion of the species over the greater Sasolburg area.

CHAPTER 3

METHODOLOGY

In this chapter an overview of the sampling-, laboratory- and analysis procedure for PAH's are discussed, as well as the methodologies used to determine the source strengths and dispersion potential.

3.1 Introduction

Difficulties associated with sampling s-VOC's includes their low ambient air concentration, difficulty to isolate, complex mixture, high boiling points and their phase distribution between vapour and particulate matter.

A good sampling method provides a sample that accurately reflects the level (concentration) of the chosen compounds and may also provide sufficient sample for the purpose of the study by also taking into account the sensitivity of the analytical instrumentation. Contamination must be minimized by thoroughly cleaning all the glassware used. [57].

The relative low concentration of s-VOC's (PAH's in particular) in the environment requires the use of high volume sampling techniques to acquire sufficient samples for analysis. A high volume sampler provides for lower detection limit. A high volume sampler for sampling s-VOC's involves the use of a combination of both quartz fibre filter (allow total suspended particulate (TSP) to collect on filter) and sorbent cartridge (polyurethane foam (PUF) plugs, collects vapour/gases which might be stripped from the particulates on the filter) [58].

The use of quartz fibre filter is advantageous as they can be baked at temperatures between 400-500°C to remove any contaminants (organic impurities) prior to its use. It is important that filters are stored in a plastic jar (lined with aluminium foil) when transported from the field to the laboratory.

Because we were dealing with low concentration samples, caution was taken to prevent contamination, therefore it was important that all glassware used should be adequately cleaned and gloves must be worn at all times whenever PUF and filters are handled. High purity chemicals and distilled water was used to prepare standards [59].

EPA-compendium method TO-13A was followed. This method describes sampling of PAH's in ambient air [59].

3.2 Field procedure

3.2.1 Apparatus

High volume sampler (Figure 3.1) manufactured by Tisch Environmental, Village of Cleves OH, was used as it is capable of sucking ambient air through the Quartz micro fibre filter cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) ($0.25 \text{ std m}^3/\text{min}$) to obtain sample volume of over 300 m^3 over 24 hours. Sample module given in Figure 3.2, manufactured by Tisch Environmental, Village of Cleves, OH was used. It is a metal holder capable of holding 102 mm circular particle filter supported by 16 mesh stainless steel screen and attaching to a metal cylinder capable of holding a $6 \text{ cm} \times 7.6 \text{ cm}$ large PUF cartridge. The filter holder is equipped with inert sealing gaskets placed on either side of the filter. Similarly, inert pliable gaskets are used to provide an air-tight seal at each end of the glass sorbent cartridge.

Large PUF cartridges (6 cm × 7.6 cm) with density of 0.022 g/cm³ from Supelco were used and quartz microfibre filter sheets (20.3 × 25.4 cm) from Whatman Inc were cut to size 102 mm for the experiment. A cooler box was used to hold samples at 4°C from the field to the laboratory.

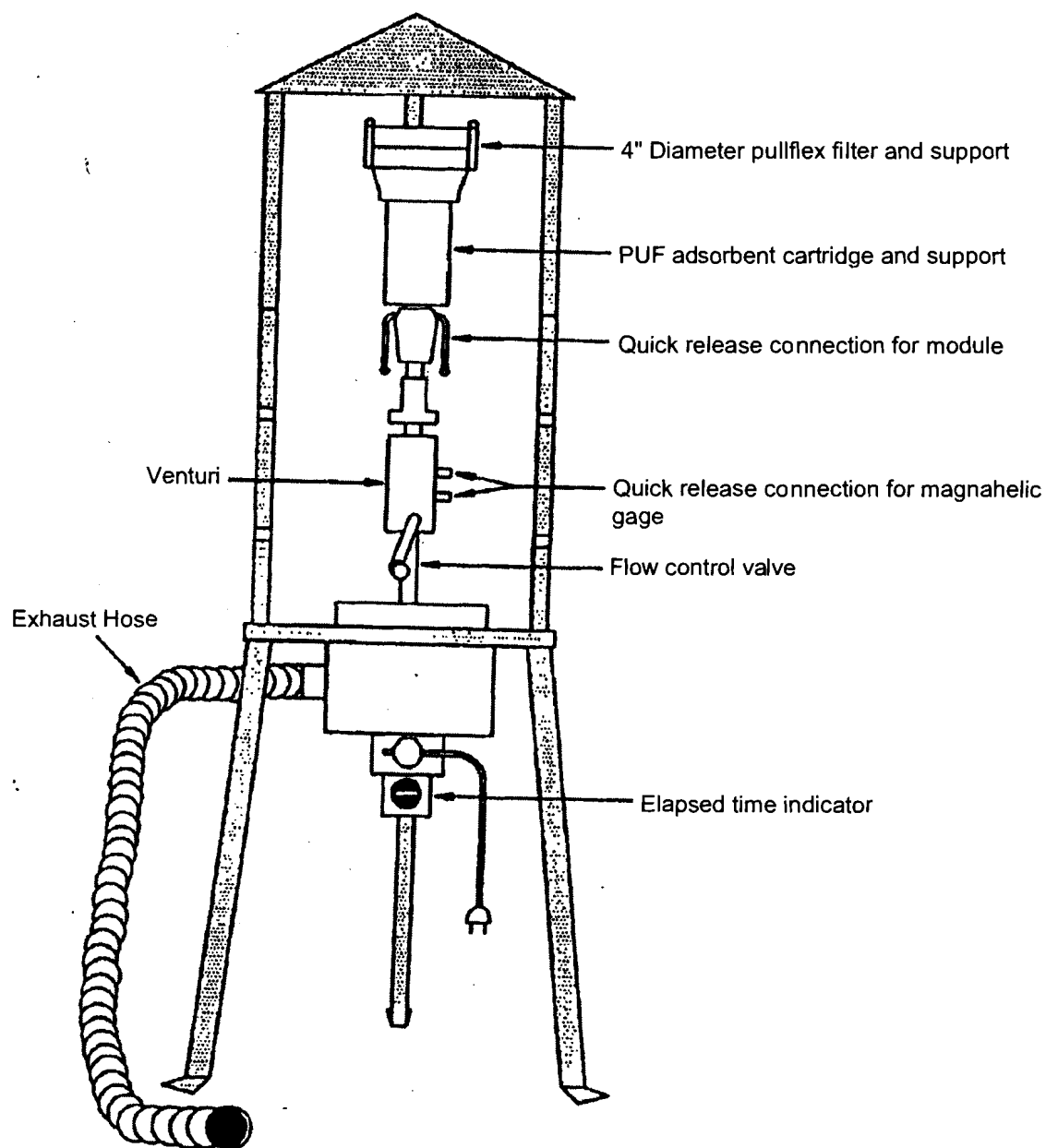


Figure 3.1: Structure of high volume sampler developed by EPA [59]

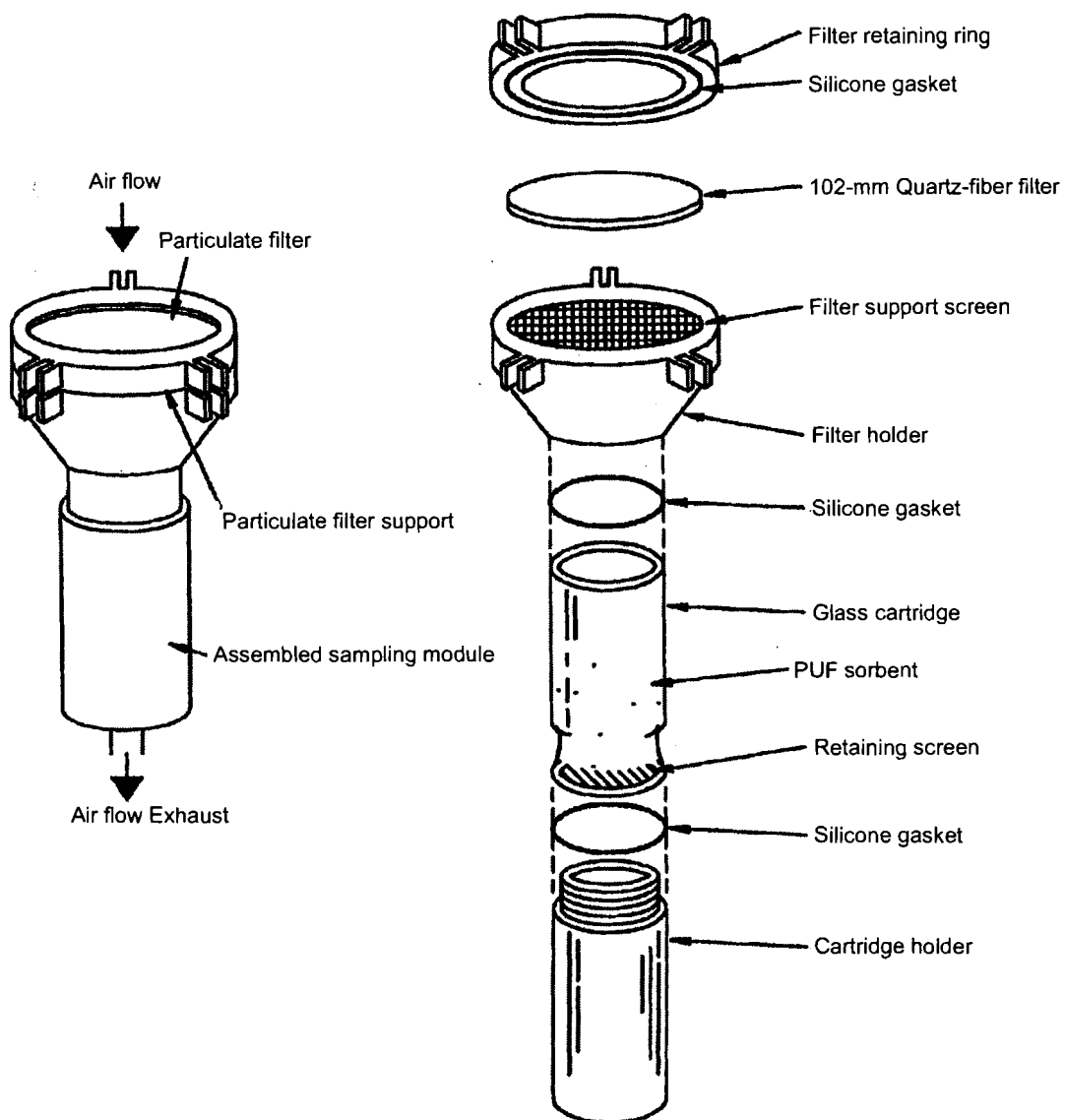


Figure 3.2: Typical adsorbent cartridge assembly for sampling PAH's (Sampling module) [59]

3.2.2 Sampling Procedure

Prior to sampling, filters were baked at 400°C for 24 hours and after cooling down at room temperature and was wrapped in an aluminium foil and stored in a foil-lined container and kept in the refrigerator until date of use in the field sampling.

Samples were collected using a high volume sampler equipped with a quartz fibre filter (to collect particle phase compounds) followed by a PUF plugs (to collect gaseous/vapour phase) which was held in place by a glass sleeve. A high-volume pump was used to drawn large quantities of air, ~30 cfm, through a quartz fibre filter that captured airborne particulate matter with nearly 100% efficiency. A PUF captured gas phase organic immediately downstream of the filter. A sample flow rate of 0.25 m³/min was used over a period of 24 hours. After each sampling period, the high volume sampler was turned off and filter and PUF were removed from the sample head wrapped with aluminium foil and placed into their original aluminium foiled containers and kept in the fridge. Filters were kept in a cooler box (temperature maintained at 4°C) during transport from the field to the laboratory and prior analysis.

3.3 Laboratory procedure

3.3.1 Apparatus

- Soxhlet extraction with Cellulose Extraction Thimbles (35 mm × 85 mm), 500 ml flask and condenser.
- Erlenmeyer flasks.
- Non-Sterile latex examination gloves from Medtex.
- Minivials, 2 ml clear crimp vials with marking spot, from Supelco.
- Macro Kuderna-Danish concentrator manufactured by Supelco, with ground joint that includes a 310 mm 3-ball Macro Synder column (24/40), 500 ml evaporation flask (top 24/40, bottom 19/22) and a 15 ml receiving vessel flask with top 24/40 and bottom 19/22 ground glass joint, Springs,

Teflon full length sleeves (19/22 and 24/40) and Plastic clips (19/22 and 24/40).

- Roto-evaporator system manufactured by Heidolph VV 2000.
- Nitrogen cylinder (UHP).
- Glass wool.

3.3.2 Chemicals

- Toluene, assay 99.8%, Rochelle chemicals
- Hexane, assay 99%, Saarchem (Merck chemicals).
- Sodium sulphate-Anhydrous, Assay 99%
- Diethyl-ether, 99%, Saarchem (Merck chemicals).
- Pentane (n-Pentane), 99%, Labchem
- Boiling chips
- Silica gel, High purity, type 60, 70-230 mesh ASTM, Particle size 0.063-0.200 mm.

3.3.3 Glassware clean-up

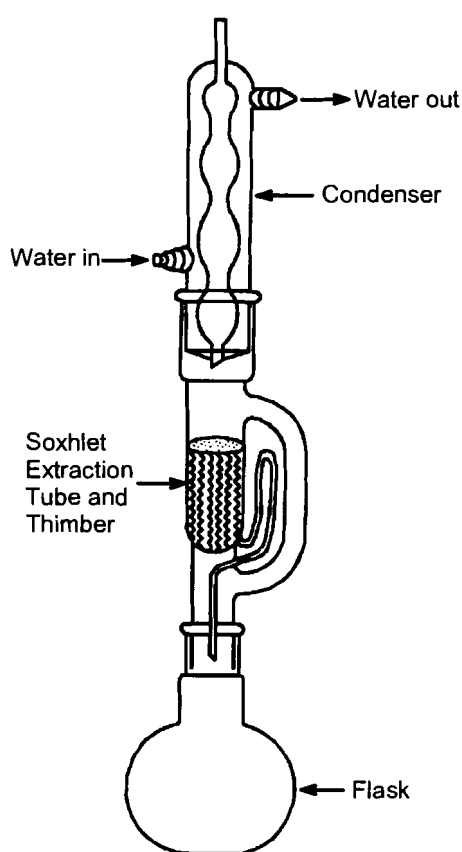
All glassware were washed with hot water and detergent and rinsed two times with water from the tap. Then distilled water was used to rinse the glassware, followed by rinsing with acetone. Hexane was then used to rinse all the glassware to remove contaminants and then lastly rinsed with distilled water. All glassware were dried in a 400°C oven for four hours and stored in a clean environment to prevent accumulation of dust and contamination. Before use of any glassware, it was rinsed with solvent that is to be used for the experiment.

3.3.4 Soxhlet extraction

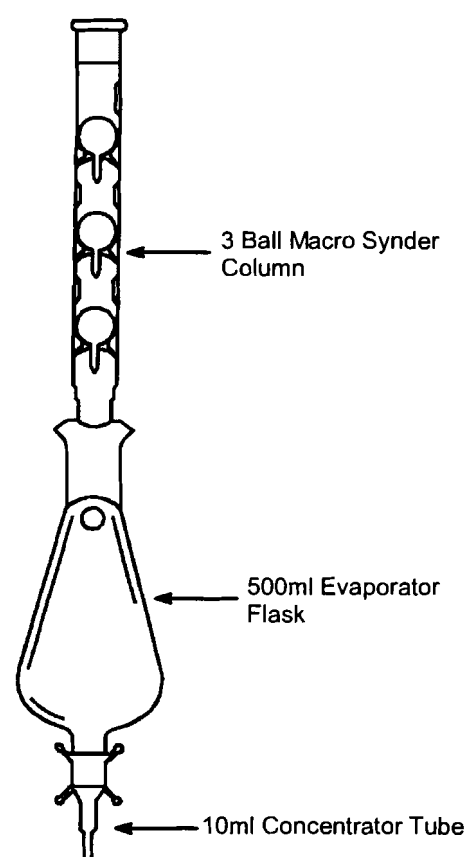
After sampling, PUF cartridge were returned to their original container and safely stored. PUF cartridge was taken to the laboratory where they were cut into small pieces using stainless steel scissors, placed into the extraction thimble and into the soxhlet tube given in Figure 3.3 (a). PUF cartridge was extracted with 275 ml of toluene in a 500 ml round bottom flask for twelve hours.

After extraction with toluene, the PUF cartridge was extracted with 275 ml of a 10% diethyl ether/hexane mixture for another twelve hours. The two extracts were combined and concentrated to 25 ml using a roto-evaporator at a temperature of $\pm 70^{\circ}\text{C}$ and a pressure of 0.60 bar.

The same procedure was performed for filter extraction, where the filter was cut into smaller pieces and placed inside the extraction thimble.



(a) Soxhlet Extraction Apparatus with a Condenser



(b) Kuderna Danish Evaporator with a Macro Synder Column

Figure 3.3: Soxhlet extraction and Kuderna-Danish evaporator

3.3.5 Kuderna-Danish concentration

2 ml of 10% diethyl ether/hexane mixture was used to wet the 3-Ball Macro Synder to prevent any loss of the sample. Kuderna-Danish (K-D) evaporator is given in Figure 3.3 (b). 25 ml of concentrated extract from the soxhlet extraction was poured into the 500 ml evaporator flask with a 10 ml concentrator tube. Boiling chips were added into the flask and placed over a warm water bath (50°C). The water level in the bath was maintained just below the lower joint on the flask and the apparatus mounted so that the rounded surface of the flask was bathed under steam. Reflux was done until the final 2 ml concentrate was collected in the lower tube.

It was sometimes very difficult to concentrate samples using K-D. In this case, the extract can be concentrated to 2 ml by carefully controlling evaporation under an inert atmosphere. Kuderna-Danish concentrator tube was placed in water bath and under nitrogen blow down (analytical evaporator). The nitrogen should also be very clean. The nitrogen flow was adjusted through a tube to provide gentle stream. This was done by lowering a tube of nitrogen to about 1 cm above the liquid level and adjustment was continued as the level of sample decreased. This was done until the 2 ml of concentrated sample was obtained.

3.3.6 Column preparation

Using a clean glass rod, a small piece of glass wool was placed in the bottom of a pipette. 5 g of dry silica gel was poured into the pipette, followed by addition of and 0.5 g of sodium sulphate. 250 ml of 10% diethyl ether in pentane was poured into the pipette to obtain a packed column. The solution was allowed to go through the pipette until all air bubbles were removed. The column was then pre-eluted with 40ml of pentane to remove contaminates. Pentane pre-elute was allowed to elute through the column and when small amount of pentane covered the top layer of sodium sulphate, 2 ml of the sample extract was poured into the column and this was followed by addition of 2 ml of hexane to complete the transfer.

The elute was allowed to go through the column and prior sodium sulphate layer exposed to air, 25 ml of pentane was poured into the column and elution continued. The column was finally eluted with 25 ml of 10% diethyl ether in pentane and was collected in a K-D flask equipped with 10ml concentrator. The extract in the flask (water bath of 50°C) was concentrated to 2 ml under gentle nitrogen blow. A schematic representation of sample preparation is given in Figure 3.4:

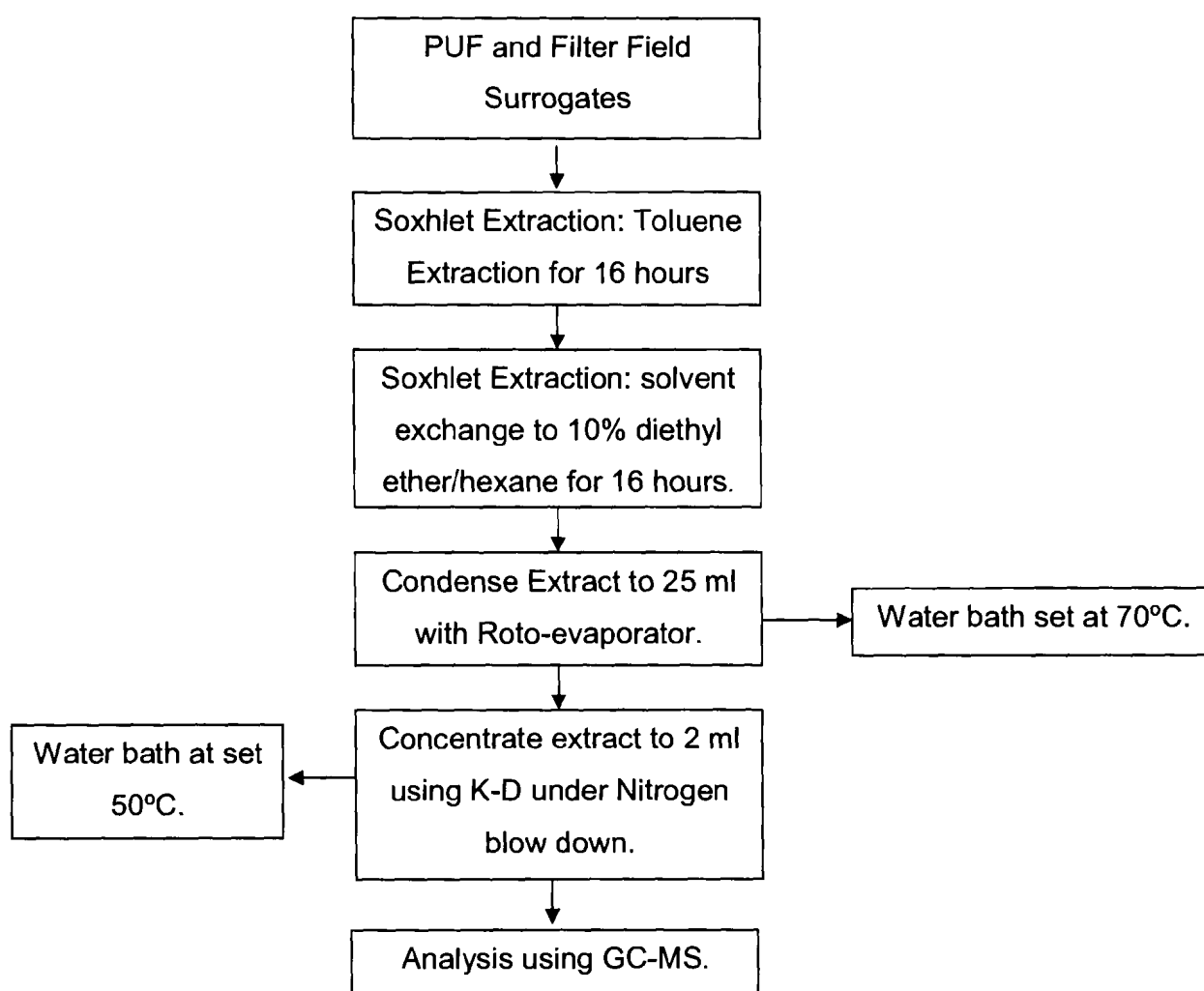


Figure 3.4: Sampling preparation and analysis scheme for ambient air monitoring for PAH's

3.4 Analytical procedure

3.4.1 Chemicals

- 1ml Semi-volatile Internal Standard Mix, 2000 µg/ml in methylene chloride from Supelco.
- 1ml TCL Polycyclic aromatic hydrocarbons mix, 20-1000 µg/ml in ACN: MeOH (90:10) from Supelco.
- Dichloromethane

3.4.2 Analysis

All samples were analyzed using a Hewlett Packard 6890/5972 GC-MS from Agilent Technology. The extracts were spiked with 0.2 µl of the internal standards (IS) before analysis. The following internal standards indicated in Table 3.1 were used successfully in PAH analysis by GC/MSD:

Table 3.1: Internal standard mix

Internal standard mix (Analyte)
Acenaphthene-D10
Chrysene-D12
Naphthalene-D8
Perylene-D12
1,4-Dichlorobenzene-D4

To prepare a mixed stock solution for PAH internal standard, 0.25 ml from 1 ml PAH internal standard was transferred into a 10 ml volumetric flask and diluted to the mark with dichloromethane (DCM).

Calibration PAH's standards were generated from the stock PAH standard using series of dilution and the following equation was used:

$$C_1V_1 = C_2V_2$$

where:

C_1 = concentration of stock PAH's standard, ng/ μ L

V_1 = volume of the stock PAH's standard solution taken to make calibration
PAH's standard, μ L

V_2 = volume diluted to generate calibration PAH's standard, μ L

C_2 = final concentration of calibration PAH's standard, ng/ μ L

The equation above was used to prepare a series of calibration standards which includes surrogate compounds, (i.e. 2.50, 1.25, 0.50, 0.25 and 0.10 ng/ μ L) and description is given below [59];

- CAL 5, 1.00 ml of PAH calibration mix was transferred to a 10 ml volumetric flask and diluted to the mark with hexane. This was used as PAH stock solution. The resulting concentration was 2.5 ng/ μ L for PAH analytes.
- CAL 4, 500 μ L (0.5 ml) of PAH stock solution (CAL 5) was transferred to a 10ml volumetric flask and diluted to the mark with hexane. The resulting concentration was 1.25 ng/ μ L for PAH analytes.
- CAL 3, 200 μ L (0.2 ml) of PAH stock solution (CAL 5) was transferred to a 10ml volumetric flask and diluted to the mark with hexane. The resulting concentration was 0.50 ng/ μ L for PAH analytes.
- CAL 2, 100 μ L (0.1 ml) of PAH stock solution (CAL 5) was transferred to a 10 ml volumetric flask and diluted to the mark with hexane. The resulting concentration was 0.25 ng/ μ L for PAH analytes.

- CAL 1, 40 μL (0.04ml) of PAH stock solution (CAL 5) was transferred to a 10 ml volumetric flask and diluted to the mark with hexane. The resulting concentration was 0.10 ng/ μL for PAH analytes [59].

A Hewlett Packard 6890/5972 GC/MSD was used to quantify the results and the conditions of the analysis are given in Table 3.2:

Table 3.2: GC/MS operating conditions

Activity	Conditions
<u>Gas Chromatography</u>	
Column	HP-5 MS (30.0 m $\times$ 250 μm $\times$ 0.25 μm film thickness)
Carrier Gas	Helium, velocity between 28-30 cm^3/sec at 250°C
Injection Volume	2 μL , Grob-type, splitless
Injection Temperature	290°C
<u>Temperature Program</u>	
Initial Column Temperature	70°C
Initial Hold Time	4 $\pm$ 0.1 min
Program	10°C/min to 300°C and hold 10 min
Final Temperature	300°C
Final Hold time	10 min
<u>Mass Spectrometer</u>	
Transfer Line Temperature	250°C
Source Temperature	230°C
Electron Energy	70 volts
Ionization Mode	EI
Mass Range	50-550 amu, full data acquisition (SCAN) mode
Scan time	5 scans per peak, not to exceed 1.5 second per scan.

3.5 Dispersion modelling methodology

3.5.1 Introduction

Numerical "models" are used to describe complex systems of interacting physical, chemical, and biological processes. These models consist of sets of mathematical equations that attempt to describe processes observed in nature, allowing scientists to create replicas of natural systems with a computer, so that the causes and effects of system behaviour may be better understood.

3.5.2 Modelling domain

The greater Sasolburg area is situated within the drainage basin of the Vaal River, and is at an elevation of ~1480 m above sea level. The area hosts both large industrial and agricultural sectors. Informal housing associated with residential coal burning is situated to the south of the central business district, with industry located between the electrified and non-electrified (informal housing) suburbs. Figure 3.5 shows a map of the greater Sasolburg area including the Industrial and Hospital area as the main receptors for this study. The suburb indicated as Zamdela consists mainly of informal to semi-informal housing, while A.J. Jacobs and Vaalpark are considered electrified residential suburbs. Industry lies to the North and East of Zamdela, to the east of A.J. Jacobs and to the south of Vaalpark. The predominant wind-direction is from the Northwest.

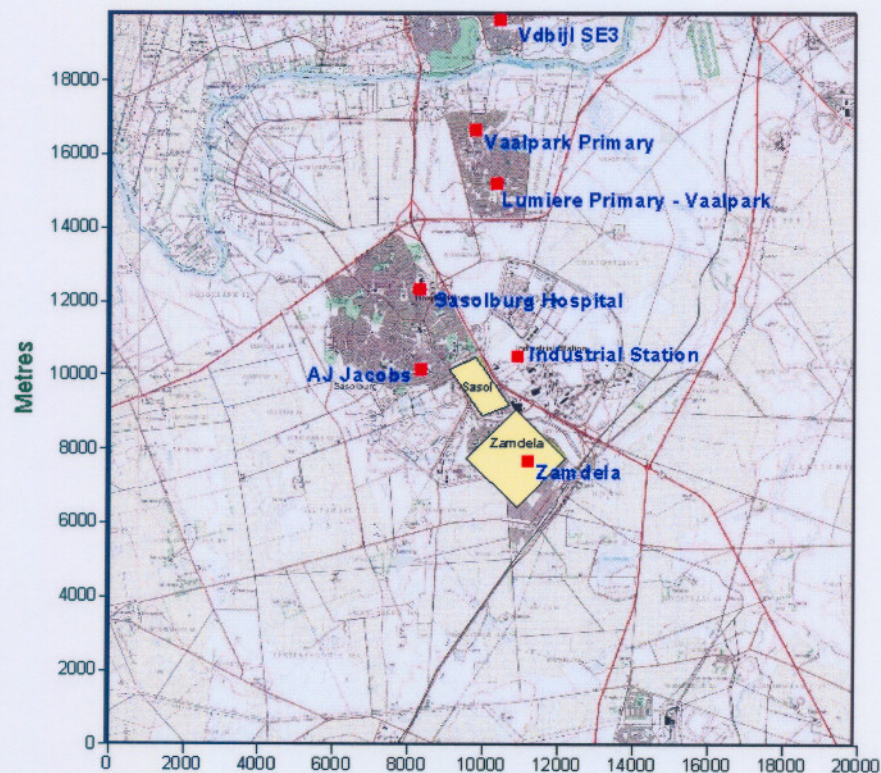


Figure 3.5: The modelling domain for the footprint, indicating the discrete receptors in greater Sasolburg areas

3.5.3 Methodology

The simulation of PAH species were undertaken through the application of the Atmospheric Dispersion Modelling System (ADMS-3). Input data types required for the ADMS-3 model include: source data, meteorological data and information on the nature of the receptor grid. A flat terrain was assumed during the baseline. Hourly average meteorological data as input is needed and includes wind speed, wind direction, ambient air temperature, precipitation and cloud cover. Hourly meteorological data recorded at Vereeniging, was provided by the South African Weather Service for the period 01/01/2002 to 31/12/2002 (1 year). This information was used in the dispersion simulations. All meteorological calculations (i.e., mixing heights and atmospheric stability) are performed by the ADMS-3 model. Simulation results that were generated have predicted concentrations at a height of 1 meter above ground level for each pollutant. This information provides the predicted ambient concentrations due to release of PAH species from industrial and residential coal burning. Sectorial contributions have been obtained by utilizing US-EPA emission factors. Model results were compared with actual ambient measurements taken in Zamdela.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the measured results of this study are reported and discussed based on the reported emission factors, the PAH source strength was calculated and the measured results are modelled, and a comparison between the measured results and modelled results is given. A conclusion of the results is given at the end of the section.

4.1 Introduction

The low concentrations of PAH species, their high boiling points and the difficulty to isolate in ambient air makes these species very difficult to sample and therefore this study was very complex. There were numerous laboratory trial experiments undertaken in this study, where the first sampling of PAH's was conducted in the greater Sasolburg areas during April 2004 and the results obtained were lower than the detection limit (on GC/MS analysis) and this campaign was declared not successful. Therefore, another field campaign was conducted during November to December 2005 and from this campaign positive results were obtained. The results of the trial experiments are not reported in this section, but the results rather focus on only the successful field campaign.

The major sources contributing to PAH's emissions obtained is mainly due to the industrial processes, vehicular traffic and other anthropogenic sources such as fossil fuel and coal combustion. It should also be noted that PAH's are highly mobile throughout the environment, therefore the PAH's emissions measured at the days of sampling may be due to other sources not in vicinity to the sampling

site. A small amount of PAH's emissions are subjected to long range atmospheric transport.

4.2 PAH source strength determination

The US-EPA emission factors (Table 2.3, Chapter 2) from controlled coal combustion (Bituminous coal) were used to calculate the total emissions of PAH's in the greater Sasolburg area (industry). The total industrial coal usage in this area per annum is 2.25×10^7 tons. The equation below was used to calculate the emissions produced at Sasolburg industrial area and Table 4.1 gives the total emission of PAH's produced by Sasolburg industries:

$$\text{Emission factor} \times \text{Quantity used (Sasolburg)} = \text{Emission Produced}$$

Table 4.1: PAH emissions from coal combustion in the greater Sasolburg industrial area

Species	Emission Factor (kg/ton)	Coal usage /annum(10^7 tons)	kg/annum
Biphenyl	$7,72 \times 10^{-7}$	2,25	17,37
Acenaphthene	$2,32 \times 10^{-7}$	2,25	5,210
Acenaphthylene	$1,14 \times 10^{-7}$	2,25	2,550
Anthracene	$9,53 \times 10^{-8}$	2,25	2,150
Benzo(a)anthracene	$3,63 \times 10^{-8}$	2,25	0,820
Benzo(a)pyrene	$1,73 \times 10^{-8}$	2,25	0,390
Benzo(b,j,k)fluoranthene	$4,99 \times 10^{-8}$	2,25	1,120
Benzo(g,h,i)perylene	$1,23 \times 10^{-8}$	2,25	0,280
Chrysene	$4,54 \times 10^{-8}$	2,25	1,020
Fluoranthene	$3,22 \times 10^{-7}$	2,25	7,250
Fluorene	$4,13 \times 10^{-7}$	2,25	9,300
Indeno(1,2,3-cd)pyrene	$2,77 \times 10^{-8}$	2,25	0,620
Naphthalene	$5,90 \times 10^{-6}$	2,25	132,80
Phenanthrene	$1,23 \times 10^{-6}$	2,25	27,58
Pyrene	$1,50 \times 10^{-7}$	2,25	3,370
5-Methyl Chrysene	$9,99 \times 10^{-9}$	2,25	0,220

Residential emission factors for PAH's (Table 2.4, Chapter 2) were used to calculate the total emissions produced in Zamdela (residential area in Sasolburg area). The total coal usage for Zamdela per annum is 5×10^5 tons. Table 4.2 gives the total emissions produced by coal usage in Zamdela:

Table 4.2: Residential: PAH's emission from coal combustion in Zamdela

Species	Emission Factor	Coal usage/annum(tons)	kg/annum
Acenaphthylene	$1,20 \times 10^{-2}$	$5,00 \times 10^5$	$6,00 \times 10^3$
Anthracene	$3,10 \times 10^{-3}$	$5,00 \times 10^5$	$1,55 \times 10^3$
Benzo(a)anthracene	$3,00 \times 10^{-3}$	$5,00 \times 10^5$	$1,55 \times 10^3$
Benzo(a)pyrene	$2,60 \times 10^{-3}$	$5,00 \times 10^5$	$1,30 \times 10^3$
Chrysene	$2,80 \times 10^{-3}$	$5,00 \times 10^5$	$1,40 \times 10^3$
Phenanthrene	$1,10 \times 10^{-2}$	$5,00 \times 10^5$	$5,50 \times 10^3$
0Benzo(e)pyrene	$2,00 \times 10^{-3}$	$5,00 \times 10^5$	$1,00 \times 10^3$

4.3 Overview of results

The objective of this study was to identify the ambient PAH's and the atmospheric concentrations in both the gas- and particle-phase in the greater Sasolburg area. The samples were taken from two locations in Sasolburg, namely the industrial and hospital area. Determination of PAH's concentration was difficult due to the very low concentration level of these compounds in ambient air samples as it will be shown in the results obtained from Sasolburg area. Concentration of 16 PAH species were measured in both gas and particle phase during November-December 2005 period in Sasolburg.

Eight samples (each in pair containing a filter and a PUF) were obtained using a high volume sampler, during the period 28 November 2005 to 01 December 2005 and a control experiment to collect information was taken on the 09 December 2005 at North-West University (Potchefstroom). The sample on the 28th and 29th of November was taken at Sasolburg industrial area while the samples taken on the 30th of November and 01 December were taken at Sasolburg hospital area. On each day, a sample was taken for 24 hours at flow rate of $0.25 \text{ m}^3/\text{min}$ (360 m^3 of air through the high volume sampler), assuming that the flow remained constant through-out the 24 hours. The sample that was taken on the 28 November 2005 was not detected due to the fault experienced during the preparation of the sample. Therefore the results obtained on the 28 November 2005 are left out in this report.

Of the sixteen PAH species targeted in this study, seven species have been identified as priority PAH's by the US-EPA on the basis of concern that they cause cancer in animals and humans as indicated in Table 4.3 [60]. There are no international recognised ambient air quality standards for PAH's, the UK and European Commission (EC) recommended benzo(a)pyrene (BaP) as surrogate for the total PAH and for the development of BaP ambient air quality guideline. The EC has adopted an annual BaP ambient air guideline of 1.0 ng/m³ measured in the PM₁₀ fraction.

Table 4.3: Priority PAH's identified by the US-EPA (1988)

PAH species contributing to total PAH	US-EPA priority PAH	IARC ²	US-EPA ³
Benzo(a)anthracene	Yes	2A	B2
Benzo(a)pyrene	Yes	2A	B2
Benzo(b)fluoranthene	Yes	2B	B2
Benzo(e)pyrene	No	3	
Benzo(g,h,i)pyrene	Yes	3	D
Benzo(k)fluoranthene	Yes	2B	B2
Chrysene	Yes	3	B2
Coronene	No	3	
Dibenz(a,h)anthracene	Yes	2A	B2
Indeno(1,2,3-c,d)pyrene	Yes	2B	B2
Pyrene	No		
PAH species occurring predominantly in the vapour phase			
Acenaphthene	Yes		-
Acenaphthylene	Yes		D
Anthracene	Yes	3	D
Fluoranthene	Yes	3	D
Fluorene	Yes	3	D
Naphthalene	Yes	2B	
Phenanthrene	Yes	3	D
Pyrene	Yes	3	D

² Carcinogenic classifications of the International Agency for Research on Cancer [61]

- Group 1, carcinogenic to humans;
- Group 2A, probably carcinogenic to humans;
- Group 2B, possibly carcinogenic to humans;
- Group 3, not classifiable as to its carcinogenicity to humans.

³ US EPA carcinogenic classifications [62 and 63]

- Group A, human carcinogen;
- Group B1, probable human carcinogen, limited human data available;
- Group B2, probable human carcinogen, sufficient evidence in animals and inadequate or no evidence in humans;
- Group C, possible human carcinogen;
- Group D, not classifiable as to human carcinogenicity (insufficient evidence, or no data available, in animals and humans).

4.4 Calculations

The concentration of the PAH species were obtained using the following equation:

$$\text{Concentration}(\text{ng}/\text{m}^3) = \frac{A_x \times I_s \times V_t \times D_f}{A_{is} \times V_i \times \text{RRF}}$$

where:

A_x : area response for the PAH compounds to be measured, counts

A_{is} : area response for the internal standard, counts

I_s : amount of internal standard, ng/ μ l

RRF: the mean RRF from the most initial calibration, dimensionless

V_i : volume of air sampled, std m^3

V_t : volume of the final extract, μ l

D_f : Dilution factor for the extract: if there is no dilution $D_f = 1$ and if the sample was diluted, D_f is greater than 1

There was no dilution in the experiments performed and therefore D_f was one. The concentration calculated in ng/m^3 was converted to ppbv for general reference, using the following equation:

$$C_A(\text{ppbv}) = C_p(\text{ng}/\text{m}^3 \times 24.4 \text{MW}_A$$

where:

C_P : concentration of analyte calculated, ng/stdm³

MW_A : molecular weight of analyte, g/mol

24.4: molar volume occupied by ideal gas at std temperature and pressure
(25°C and 760 mmHg)

4.5 Measured results

Table 4.4 and 4.5 gives the measured ambient PAH concentrations, as per sampled in the greater Sasolburg region.

Table 4.4: Results of gas-phase and particle-phase PAH concentration at the Sasolburg industrial area on the 29/11/05

Species	PUF (ng/m ³)	Filter (ng/m ³)
Acenaphthene	$3,05 \times 10^{-6}$	$9,25 \times 10^{-4}$
Acenaphthylene	$4,69 \times 10^{-6}$	$1,80 \times 10^{-3}$
Anthracene	$2,74 \times 10^{-2}$	$7,07 \times 10^{-2}$
Benzo(a)anthracene	ND	$2,76 \times 10^{-2}$
Benzo(a)pyrene	ND	$2,47 \times 10^{-2}$
Benzo(b)fluoranthene	ND	$8,55 \times 10^{-2}$
Benzo(g,h,i)perylene	ND	$1,92 \times 10^{-2}$
Benzo(k)fluoranthene	ND	$6,26 \times 10^{-2}$
Chrysene	ND	$2,54 \times 10^{-2}$
Dibenz(a,h)anthracene	ND	$3,24 \times 10^{-3}$
Fluoranthene	$9,96 \times 10^{-4}$	$1,29 \times 10^{-2}$
Fluorene	$1,42 \times 10^{-3}$	$1,18 \times 10^{-2}$
Indeno(1,2,3-CD)pyrene	ND	$6,69 \times 10^{-2}$
Naphthalene	$3,36 \times 10^{-4}$	$2,25 \times 10^{-3}$
Phenanthrene	$1,54 \times 10^{-3}$	$3,25 \times 10^{-2}$
Pyrene	$4,44 \times 10^{-4}$	$1,10 \times 10^{-2}$

NOTE: ND = compounds not detected; below detection limit

The results in Table 4.4 shows that the highest concentration PAH's were obtained from the particle-phase (filter). The filter contained all the 16 PAH's that were analysed with benzo(b)fluoranthene ($8.55E-02$ ng/m³), anthracene ($7.07E-02$ ng/m³), indeno(1,2,3-CD)pyrene ($6.69E-02$ ng/m³) and benzo(k)fluoranthene ($6.26E-02$ ng/m³) having the highest concentrations of all PAH species sampled. The most carcinogenic PAH species (namely Benzo(a)pyrene) was not detected in the gaseous phase but was detected in the particle-phase as illustrated in the

Table 4.4. Figure 4.1 illustrate the comparison of particle-phase on the 29/11/05. Although BaP was detected in the particle-phase, its concentration was found to be much lower than that proposed by the United Kingdom (the 0.25 ng/m³ annually averaged standard for BaP).

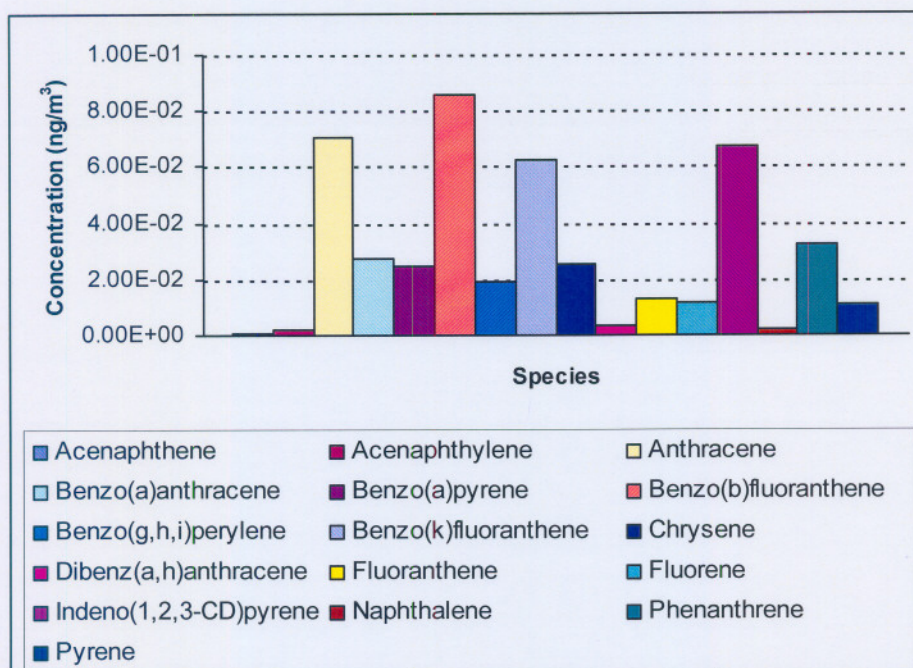


Figure 4.1: Comparison of the PAH 24hr average particle-phase concentrations on 29/11/05 at the Sasolburg area

The gas-phase distribution is shown to be dominated by low-medium molecular weight species (naphthalene-pyrene) and with higher molecular PAH compounds (such as benzo(a)anthracene- dibenz(a,h)anthracene) not detected within the analytical detection limit. Anthracene ($2.74\text{E-}02 \text{ ng/m}^3$), phenanthrene ($1.54\text{E-}03 \text{ ng/m}^3$) and fluorene ($1.42\text{E-}03 \text{ ng/m}^3$) were the dominant PAH species in gas phase. Figure 4.2 show a comparison of gas-phase PAH concentrations on the 29/11/05.

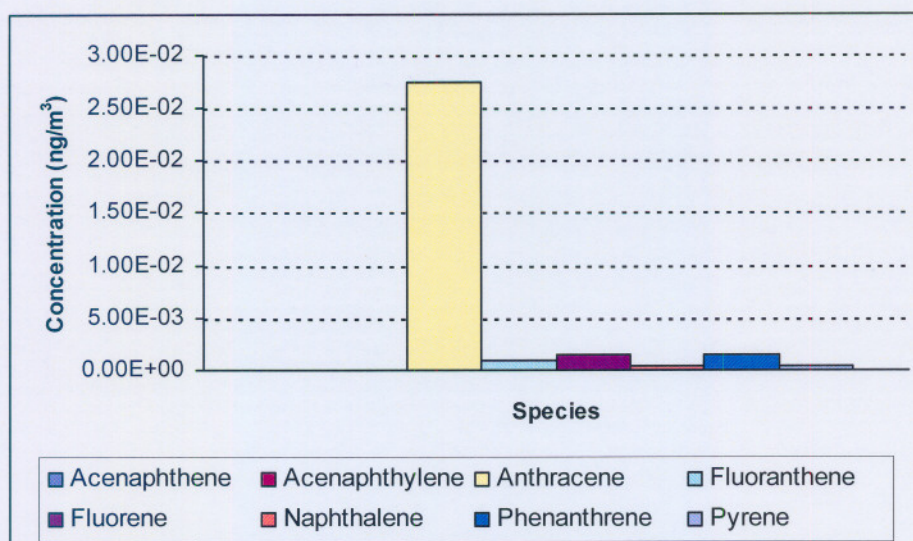


Figure 4.2: Comparison of the PAH 24hr average gas-phase concentrations on 29/11/05 at the Sasolburg industrial area

The results in Table 4.4 above is in agreement with the study that was performed by Guo *et al* [41], in which it was reported that high molecular weight PAH's (such as benzo(a)pyrene) are predominantly found in particulate phase and lower molecular weight PAH's (such as acenaphthylene) are mostly present in gas/vapour phase. The sources contributing to the concentrations at the industrial area are mainly due to the different industrial processes (such as petroleum refining, combustion of fossil fuel) and the automobile emissions.

Table 4.5 shows the PAH concentrations found at the hospital area in the Sasolburg region on the 30/11/05 and 01/12/05. Anthracene is shown to be predominant in both gas and particle-phase on these two days. The results of 01/12/05 are slightly lower than that of 30/11/05 and this may be due to the rainy weather that was experienced on the 01/12/05 when the sampling was performed. Some of the PAH's might have been washed away by rain droplets and therefore not captured by either the PUF or filter. Higher molecular weight PAH's were not detected for both the PUF and filter, only lower-medium molecular weight PAH's compounds were detected at this site on these days.

Table 4.5: The gas-phase and particle-phase at the Sasolburg hospital area on 30/11/05 and 01/11/05

Species	30/11/05		01/12/05	
	PUF (ng/m ³)	Filter (ng/m ³)	PUF (ng/m ³)	Filter (ng/m ³)
Acenaphthene	$4,85 \times 10^{-6}$	ND	$1,52 \times 10^{-6}$	$7,84 \times 10^{-7}$
Acenaphthylene	$7,05 \times 10^{-6}$	ND	$4,32 \times 10^{-6}$	$1,22 \times 10^{-6}$
Anthracene	$6,18 \times 10^{-2}$	$4,37 \times 10^{-3}$	$2,53 \times 10^{-2}$	$2,60 \times 10^{-3}$
Benzo(a)anthracene	ND	$2,37 \times 10^{-4}$	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND
Benzo(k)fluoranthene	ND	ND	ND	ND
Chrysene	ND	$4,18 \times 10^{-4}$	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND
Fluoranthene	$2,26 \times 10^{-3}$	$3,87 \times 10^{-4}$	$7,38 \times 10^{-4}$	$1,47 \times 10^{-4}$
Fluorene	$1,72 \times 10^{-3}$	$2,53 \times 10^{-4}$	$8,13 \times 10^{-4}$	$1,67 \times 10^{-4}$
Indeno(1,2,3-CD)pyrene	ND	ND	ND	ND
Naphthalene	$4,83 \times 10^{-4}$	$2,26 \times 10^{-4}$	$7,58 \times 10^{-5}$	$6,92 \times 10^{-5}$
Phenanthrene	$4,84 \times 10^{-3}$	$7,16 \times 10^{-4}$	ND	$3,26 \times 10^{-4}$
Pyrene	$9,14 \times 10^{-4}$	$2,35 \times 10^{-4}$	$2,52 \times 10^{-4}$	8.55E-05

NOTE: ND = compounds not detected; below detection limit

Figures 4.3 and 4.4 illustrates the comparison of gas-phase and particle-phase PAH's concentrations on the 30/11/05 respectively and Figures 4.5 and 4.6 gives a comparison of the gas- and particle-phase PAH concentrations on the 01/12/05. The sources contributing to the PAH concentrations at the hospital area in Sasolburg are mainly due to the automobiles.

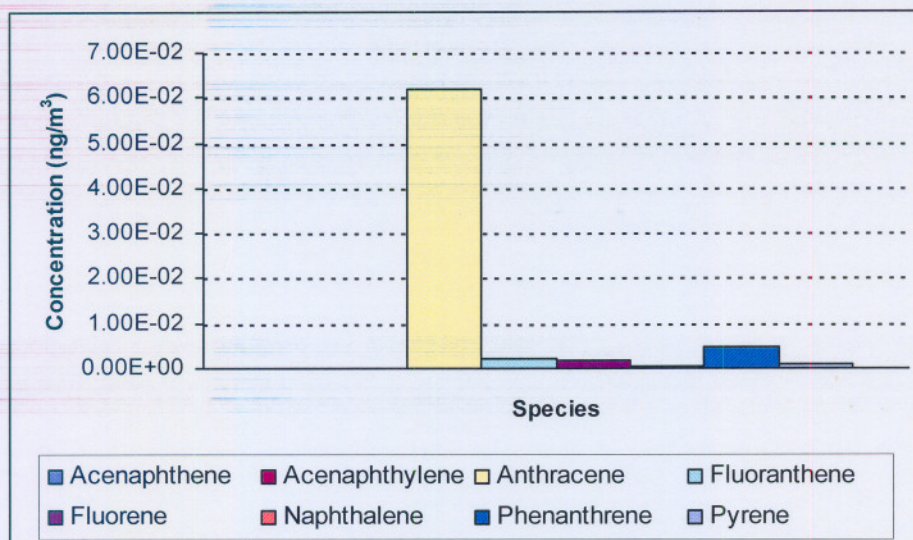


Figure 4.3: Comparison of PAH 24hr average gas-phase concentrations on 30/11/05 at the hospital area in Sasolburg

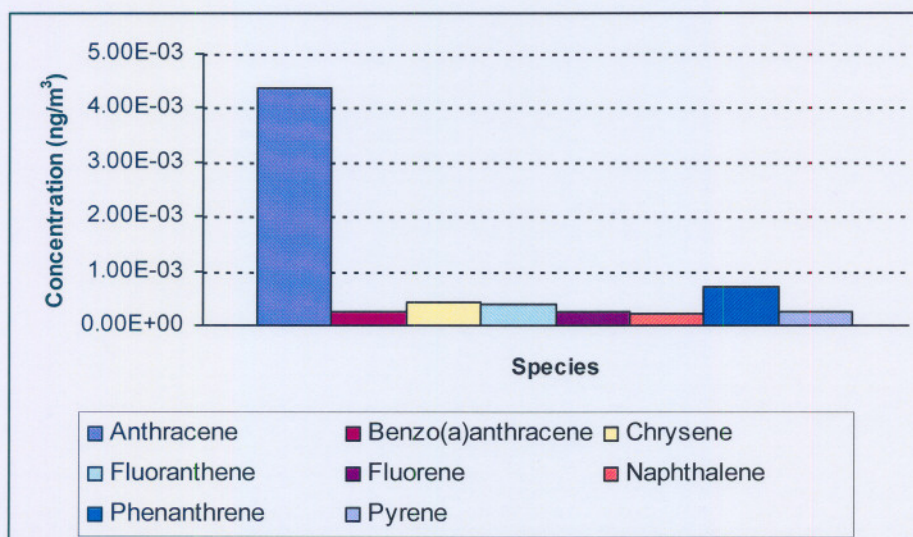


Figure 4.4: Comparison of PAH 24hr average particle-phase concentrations on 30/11/05 at the hospital area in Sasolburg

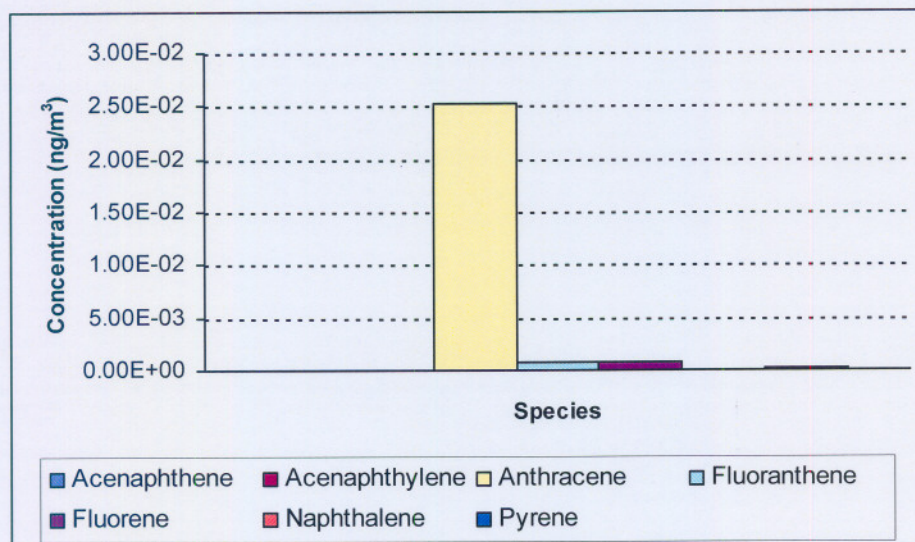


Figure 4.5: Comparison of PAH 24hr average gas-phase concentrations on 01/12/05 at the hospital area in Sasolburg

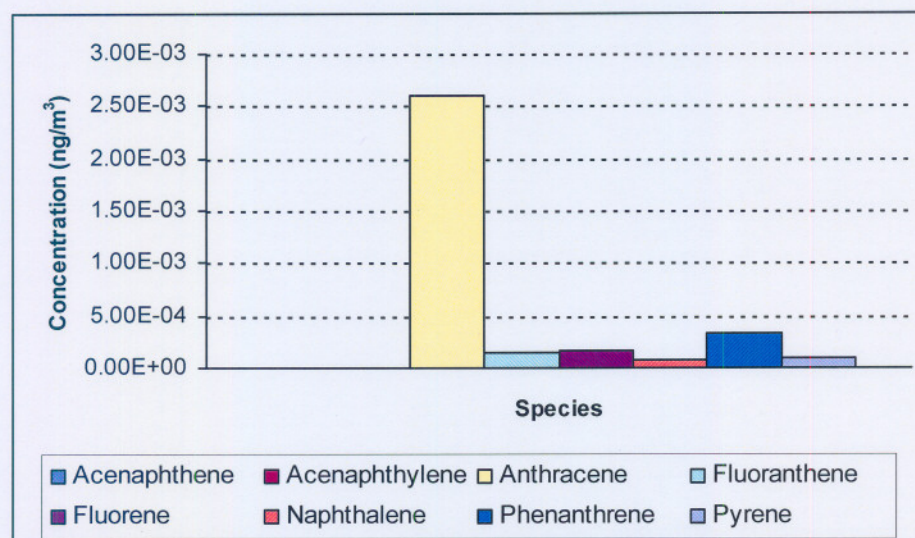


Figure 4.6: Comparison of PAH 24hr average particle-phase concentrations on 01/12/05 at the hospital area in Sasolburg

In Table 4.6, the result of a control experiment that was conducted to collect background information at the North-West University in Potchefstroom is given. The results obtained shows that anthracene is predominant with the highest concentration in both the PUF and the filter at this site.

Table 4.6: Results of gas-phase and particle-phase PAH concentrations at the North-West University (Potchefstroom campus) on the 09/12/05

Species	PUF (ng/m ³)	Filter (ng/m ³)
Acenaphthene	ND	$8,33 \times 10^{-7}$
Acenaphthylene	ND	$1,25 \times 10^{-6}$
Anthracene	$2,81 \times 10^{-2}$	$2,86 \times 10^{-3}$
Benzo(a)anthracene	ND	ND
Benzo(a)pyrene	ND	ND
Benzo(b)fluoranthene	ND	ND
Benzo(g,h,i)perylene	ND	ND
Benzo(k)fluoranthene	ND	ND
Chrysene	ND	ND
Dibenz(a,h)anthracene	ND	ND
Fluoranthene	$7,30 \times 10^{-4}$	$1,50 \times 10^{-4}$
Fluorine	$2,30 \times 10^{-3}$	$1,26 \times 10^{-4}$
Indeno(1,2,3-CD)pyrene	ND	ND
Naphthalene	$7,23 \times 10^{-5}$	$7,32 \times 10^{-5}$
Phenanthrene	$1,96 \times 10^{-3}$	$2,82 \times 10^{-4}$
Pyrene	$2,48 \times 10^{-4}$	$9,77 \times 10^{-5}$

NOTE: ND = compounds not detected; below detection limit

Figures 4.7 and 4.8 illustrate the comparison of gas- and particle-phase PAH of the 09/12/05. From this results, it can be seen that the samples taken at the North-West University (Potchefstroom campus) contains low concentrations of PAH's. It is not clear what sources contribute to these concentrations at this site but traffic in and around the campus are suspected.

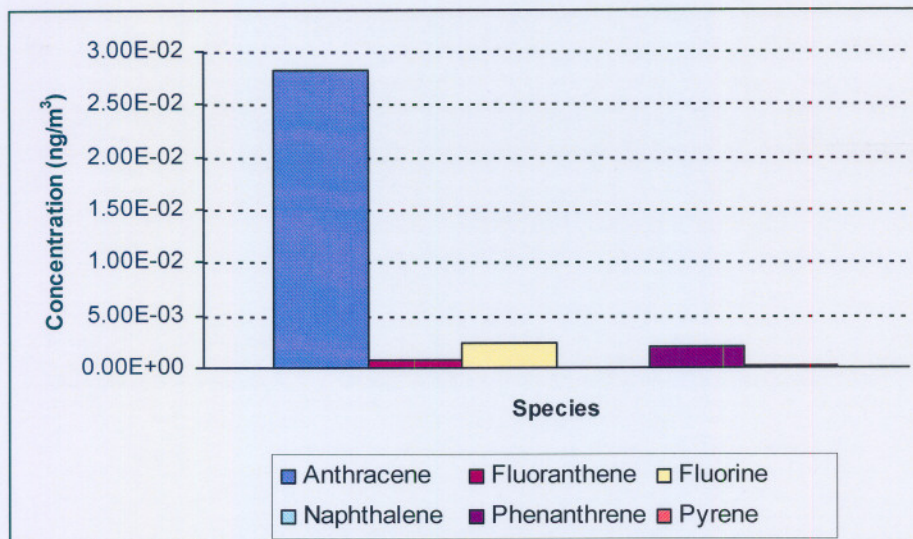


Figure 4.7: Comparison of PAH 24hr average gas-phase concentrations on 09/12/05 in North-West University (Potchefstroom campus)

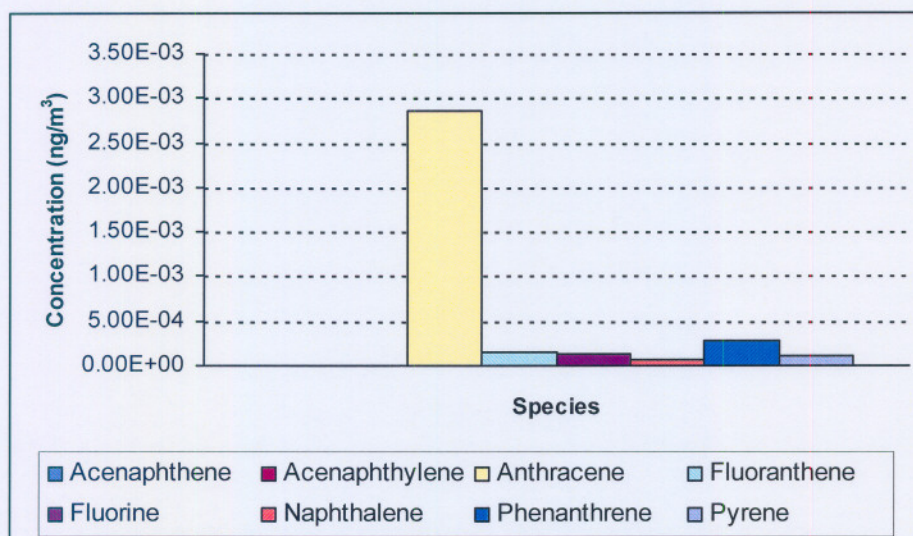


Figure 4.8: Comparison of PAH 24hr average particle-phase concentrations on 09/12/05 in North-West University (Potchefstroom campus)

In Table 4.7, the sum of the ambient PAH concentrations of all the 16 PAH species is given. The total concentration ranges from 0.00272-0.072 and 0.0034-0.459 ng/m³ for the gas and particulate phases respectively on all the days that sampling was performed. The concentrations of the particle-phase PAH compounds obtained in the Sasolburg Industrial area on 29/11/05 is shown to be the highest (0.459 ng/m³), while the highest concentration in the gas-phase was obtained in the hospital area (0.072 ng/m³) on the 30/11/05.

Table 4.7: Sum of PAH's in gas and particle-phase on each day of sampling

Date	Total concentration of gas-phase (ng/m ³)	Total concentration of particle-phase (ng/m ³)
29/11/05	$3,21 \times 10^{-2}$	$4,59 \times 10^{-1}$
30/11/05	$7,20 \times 10^{-2}$	$6,84 \times 10^{-3}$
01/12/05	$2,72 \times 10^{-2}$	$3,40 \times 10^{-3}$
09/12/05	$3,34 \times 10^{-2}$	$3,59 \times 10^{-3}$

Figures 4.9 and 4.10 give a comparison of the sum of gas and particle-phase PAH on all the sampling days.

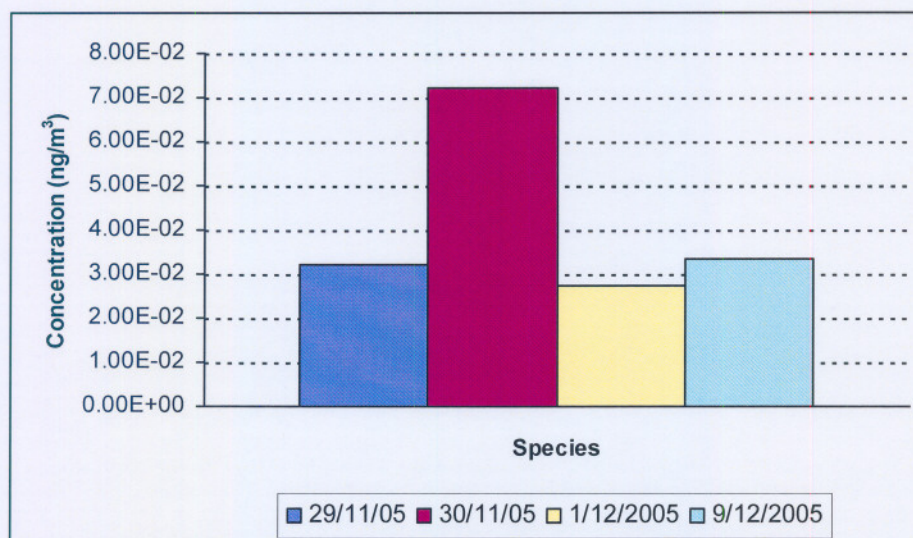


Figure 4.9: Comparison of the sum of the PAH concentrations in the gas-phase on the four days of sampling

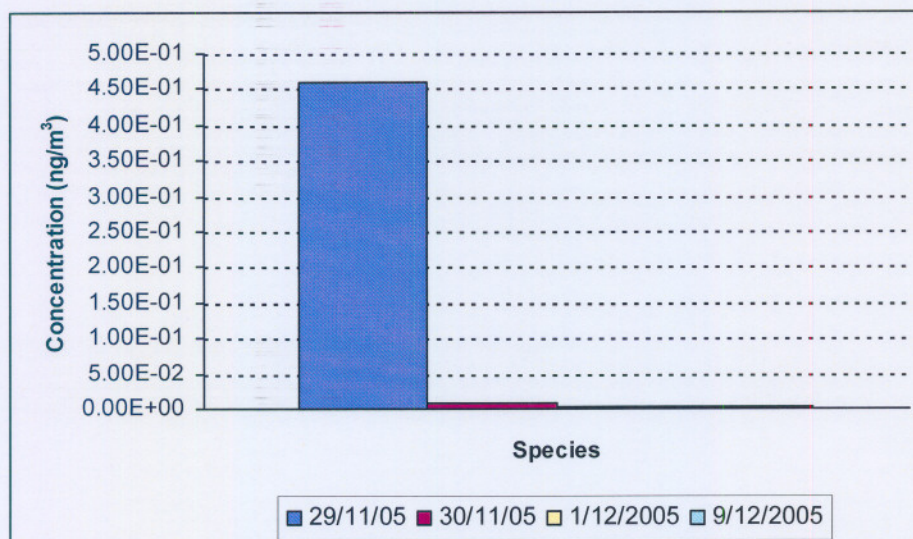


Figure 4.10: Comparison of the sum of the concentration in the particle-phase on the four days of sampling

From the results obtained in all sites, the analysis of PAH's in both gas and particle-phases has shown that the concentration of PAH's may be underestimated if only the particle-phase concentration from ambient air are measured. Therefore, it is important to measure PAH's in both the gas and particle-phases.

4.6 Individual PAH Distribution

Lower molecular weight PAH compounds were detected in all the samples collected. They are believed not to be carcinogenic but PAH's such as phenanthrene, fluoranthene and pyrene may give rise to radical attack to form nitro-PAH and nitro-PAH lactose which are believed to be responsible for the mutagenic and carcinogenic activity of atmospheric particulate product [44].

Anthracene has been shown to have the highest concentration of the all 16 PAH compounds quantified. In Figures 4.11 and 4.12, anthracene concentrations obtained in the four days of sampling are compared in both the gas and particle-phases.

Figure 4.11, shows that the highest concentration of anthracene was obtained on 30/11/05 at hospital area while Figure 4.12 shows that the highest concentration of anthracene in particle-phase was obtained on the 29/11/05 at Sasolburg industrial area. The major difference in the concentrations reported on the 01/12/05 might be due to the rain on the day and some of the particle-phase might have been washed away by rain droplets (wet scavenging).

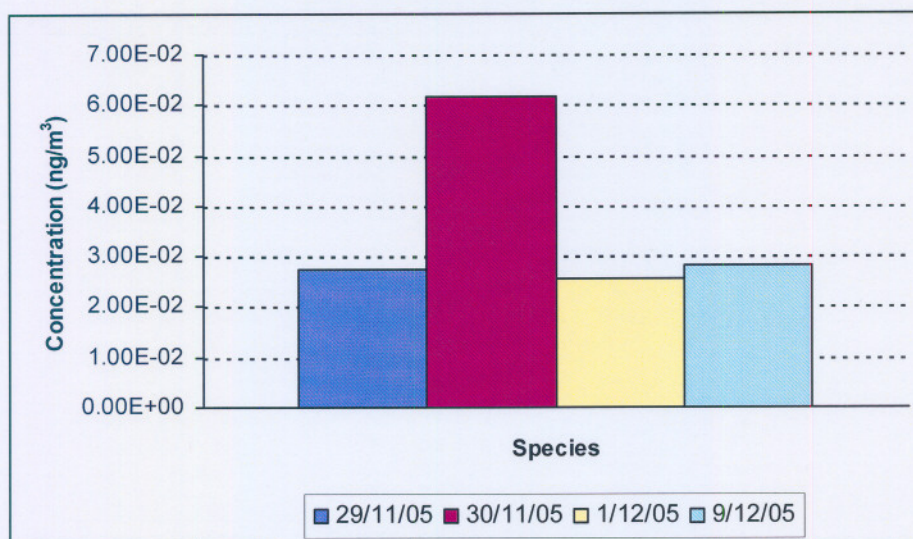


Figure 4.11: Comparison of gas-phase anthracene concentrations obtained during the field campaigns

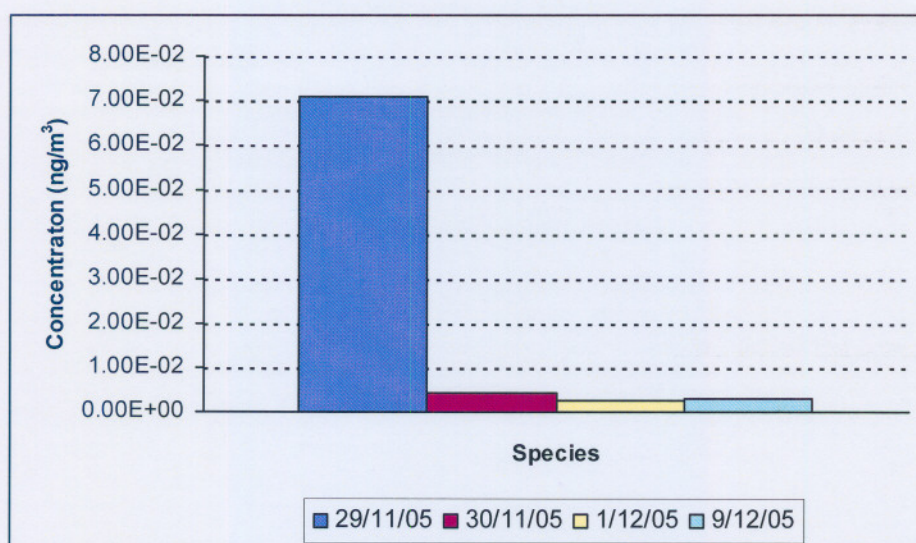


Figure 4.12: Comparison of particle-phase anthracene concentrations obtained during the field campaign

4.7 Comparison of the Sasolburg results with literature data

Concentrations of PAH's (anthracene in particular) obtained from the greater Sasolburg area, are compared to the results from United Kingdom (Table 2.6, Chapter 2) [55]. PAH concentrations from rural (Rörvik, Pallas and Alert) and urban areas (London and Manchester) of the UK were also compared to the measured results. Figures 4.13 to 4.16, illustrates the comparison of anthracene concentrations (in both gas and particle phase) obtained in greater Sasolburg area and in the UK in the mentioned studies.

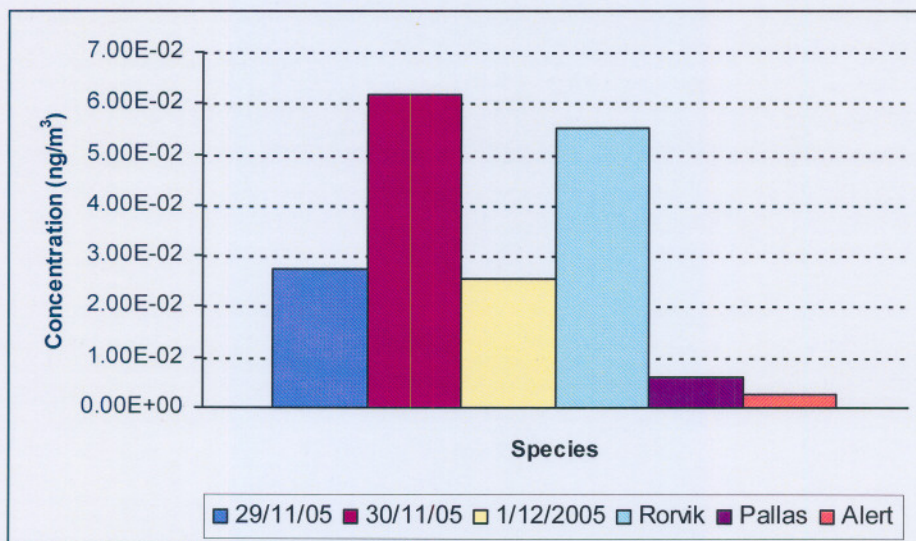


Figure 4.13: Comparison of gas-phase anthracene concentration in the greater Sasolburg and the UK rural areas

In Figures 4.13 and 4.14, anthracene concentrations (both in gas and particle phase) obtained in greater Sasolburg areas are compared to the rural area in the UK in 1996. Both these figures show that the concentrations obtained in the greater Sasolburg area are of similar magnitude to that reported for the rural areas in the UK. The anthracene concentration in gas-phase obtained on the 30/11/05 was the highest and the highest anthracene concentration in particle-phase was on the 29/11/05. The concentrations obtained in the urban areas (as illustrated in Figures 4.15 and 4.16) in the UK were higher than the ones obtained in the greater Sasolburg area.

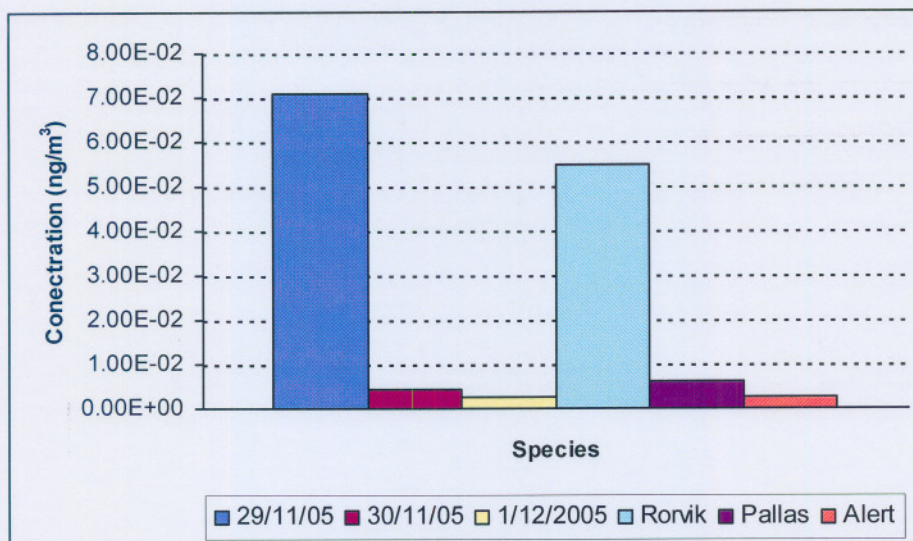


Figure 4.14: Comparison of particle-phase anthracene concentrations in the greater Sasolburg and the UK rural areas

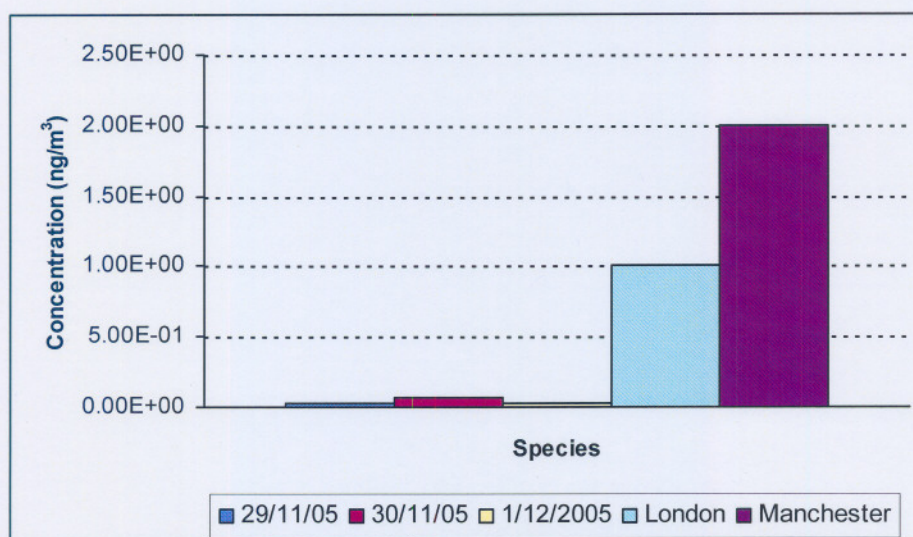


Figure 4.15: Comparison of gas-phase anthracene concentrations in the greater Sasolburg and the UK urban areas

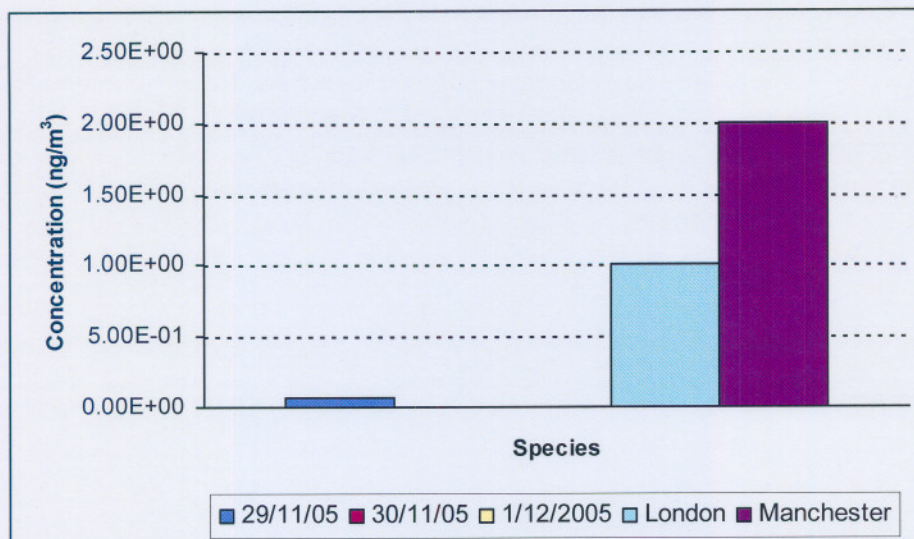


Figure 4.16: Comparison of particle-phase anthracene concentrations in the greater Sasolburg and the UK urban areas

4.8 Atmospheric dispersion modelling

4.8.1 Background

The aim of this section of the study was to determine whether it is possible to predict the ambient levels of PAH's at different receptors in the greater Sasolburg area by utilizing dispersion modelling. The modelled results were compared to the PAH concentrations that were measured. The atmospheric dispersion modelling system (ADMS) was utilized for this purpose in this study. A 24 hours (daily) averaging period of PAH's emission was simulated for both Sasolburg industrial and hospital areas.

It is important to note that any dispersion model will have an associated degree of error in the predictions due to simplifications in the model algorithms, which are used to describe complex (and inherently random) atmospheric dispersion processes. The US EPA 42 emissions factors that were applied in determining the emissions are assumed to be representative US site-specific conditions and may not necessarily be applicable to the South African conditions.

Thus the accuracy of the emissions data which are used as input to the model have a significant effect upon the accuracy of the predicted concentrations, for example the PAH emissions estimates (even for [BaP] alone) have a high degree of uncertainty. This level of uncertainty will be transferred to any PAH concentration predictions. Predictions of annual average concentrations are at best +/- 50% of the true value; this may be improved if extensive validation trials are carried out.

Since the predominant wind direction over the greater Sasolburg area is in a northerly and north north easterly direction, the emissions from both the Sasolburg industrial area and Zamdela residential area will be dispersed in a southerly, south south easterly direction and as a result the Zamdela receptor will experience the greatest downwind impact of the resultant PAH concentrations.

4.8.2 Modelling Parameters

The modelling includes calculation of the total PAH emission loads from coal utilization in the greater Sasolburg area and making use of known emission factors for these species. Tables 4.8 to 4.9 are summary of the modelling parameters used to simulate the sources in this study.

Table 4.8: Sasolburg Industrial area source parameters

Area source	Sasolburg Industrial area
Pollutants	Refer to Table 4.9
Emission Rate	Refer to Table 4.9
Release Height (m)	2
Exit Velocity (m.s ⁻¹)	10
Exit Temperature (°C)	25
Area (m ²)	1120000

Table 4.9: Sasolburg industrial area pollutant emission rates

Species	kg/annum	g/annum	g/s	Emission rate (g/m ² s ⁻¹)
Biphenyl	$1,74 \times 10^1$	$1,74 \times 10^4$	$5,51 \times 10^{-4}$	$4,92 \times 10^{-10}$
Acenaphthene	$5,21 \times 10^0$	$5,21 \times 10^3$	$1,65 \times 10^{-4}$	$1,48 \times 10^{-10}$
Acenaphthylene	$2,55 \times 10^0$	$2,55 \times 10^3$	$8,09 \times 10^{-5}$	$7,22 \times 10^{-11}$
Anthracene	$2,15 \times 10^0$	$2,15 \times 10^3$	$6,82 \times 10^{-5}$	$6,09 \times 10^{-11}$
Benzo(a)anthracene	$8,20 \times 10^{-1}$	$8,20 \times 10^2$	$2,60 \times 10^{-5}$	$2,32 \times 10^{-11}$
Benzo(a)pyrene	$3,90 \times 10^{-1}$	$3,90 \times 10^2$	$1,24 \times 10^{-5}$	$1,10 \times 10^{-11}$
Benzo(b,j,k)fluoranthene	$1,12 \times 10^0$	$1,12 \times 10^3$	$3,55 \times 10^{-5}$	$3,17 \times 10^{-11}$
Benzo(g,h,i) perylene	$2,80 \times 10^{-1}$	$2,80 \times 10^2$	$8,88 \times 10^{-6}$	$7,93 \times 10^{-12}$
Chrysene	$1,02 \times 10^0$	$1,02 \times 10^3$	$3,23 \times 10^{-5}$	$2,89 \times 10^{-11}$
Fluoranthene	$7,25 \times 10^0$	$7,25 \times 10^3$	$2,30 \times 10^{-4}$	$2,05 \times 10^{-10}$
Fluorene	$9,30 \times 10^0$	$9,30 \times 10^3$	$2,95 \times 10^{-4}$	$2,63 \times 10^{-10}$
Indeno(1,2,3-cd) pyrene	$6,20 \times 10^{-1}$	$6,20 \times 10^2$	$1,97 \times 10^{-5}$	$1,76 \times 10^{-11}$
Naphthalene	$1,33 \times 10^2$	$1,33 \times 10^5$	$4,21 \times 10^{-3}$	$3,76 \times 10^{-9}$
Phenanthrene	$2,76 \times 10^1$	$2,76 \times 10^4$	$8,75 \times 10^{-4}$	$7,81 \times 10^{-10}$
Pyrene	$3,37 \times 10^0$	$3,37 \times 10^3$	$1,07 \times 10^{-4}$	$9,54 \times 10^{-11}$
5-Methyl Chrysene	$2,20 \times 10^{-1}$	$2,20 \times 10^2$	$6,98 \times 10^{-6}$	$6,23 \times 10^{-12}$

The following assumptions were made during the simulation:

- No chemical transformation of the PAH's occurred during the dispersion period;
- No wet or dry deposition of the PAH's occurred.

4.8.3 Simulation Conditions

A 24hour (daily) and a 1hour (annual) averaging period of PAH's emissions was simulated for both the Sasolburg industrial and Zamdela residential areas. The dispersion of the PAH species was simulated using the prevailing meteorological conditions that was available which covered the period 1 January 2002 to 31 December 2004 (A 3 year sequential meteorological period). A windrose depicting the predominant wind directions and wind speeds over the modelling domain is illustrated in Figure 4.17. The output PAH's concentrations were simulated at a height of 1 meter above ground level which is in agreement with the sampling height.

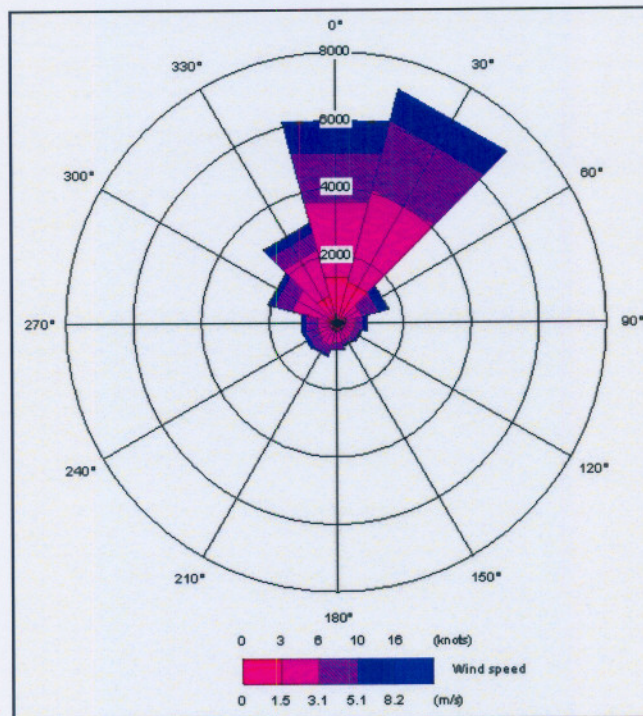


Figure 4.17: Windrose for the period: 1 January 2002 to 31 December 2004

4.8.4 Dispersion modelled results of PAH's emissions

The modelled results of a 24 hours (daily) averaging period of PAH's emission from greater Sasolburg area is presented in this section. Six discrete receptor points residing in residential areas and another receptor located in the industrial area of modelling region were used to calculate specific concentrations during the simulation. The modelling results of the industrial and hospital areas are summarized in Tables 4.10 to 4.12. Tables 4.10 and 4.11 are a summary of the mean daily PAH concentrations experienced at the discrete receptors during the period of simulation, while Table 4.13 indicate the source appointment of PAH's calculated at the discrete receptors from the greater Sasolburg area emissions.

Table 4.10: Mean concentrations in ng/m³, calculated at discrete receptors from the Sasolburg industrial area emissions

Species	Sasolburg Hospital	Industrial Station
Biphenyl	$1,88 \times 10^{-2}$	$2,54 \times 10^{-2}$
Acenaphthene	$5,65 \times 10^{-3}$	$7,63 \times 10^{-3}$
Acenaphthylene	$2,77 \times 10^{-3}$	$3,73 \times 10^{-3}$
Anthracene	$2,33 \times 10^{-3}$	$3,15 \times 10^{-3}$
Benzo(a)anthracene	$8,90 \times 10^{-4}$	$1,20 \times 10^{-3}$
Benzo(a)pyrene	$4,23 \times 10^{-4}$	$5,71 \times 10^{-4}$
Benzo(b,j,k) fluoranthene	$1,22 \times 10^{-3}$	$1,64 \times 10^{-3}$
Benzo(g,h,i) perylene	$3,04 \times 10^{-4}$	$4,10 \times 10^{-4}$
Chrysene	$1,11 \times 10^{-3}$	$1,49 \times 10^{-3}$
Fluoranthene	$7,87 \times 10^{-3}$	$1,06 \times 10^{-2}$
Fluorene	$1,01 \times 10^{-2}$	$1,36 \times 10^{-2}$
Indeno(1,2,3-cd) pyrene	$6,73 \times 10^{-4}$	$9,07 \times 10^{-4}$
Naphthalene	$1,44 \times 10^{-1}$	$1,94 \times 10^{-1}$
Phenanthrene	$2,99 \times 10^{-2}$	$4,04 \times 10^{-2}$
Pyrene	$3,66 \times 10^{-3}$	$4,93 \times 10^{-3}$
5-Methyl Chrysene	$2,39 \times 10^{-4}$	$3,22 \times 10^{-4}$

From Table 4.10, it is evident that naphthalene, phenanthrene and then fluoranthene are the dominant PAH species contributing to the total PAH concentrations calculated at each of the discrete receptors. The highest mean daily naphthalene concentration of 4.10×10^{-2} ng/m³, phenanthrene concentration of 8×10^{-3} ng/m³ and fluoranthene concentration of 2×10^{-3} ng/m³ occur at the Zamdela receptor. Consequently the industrial station regions respectively were most impacted on due to the PAH emissions released from the Sasolburg industrial area.

4.8.5 Comparison of the modelled results and the measured PAH's results

The model predicted concentrations of PAH species at the Sasolburg hospital and industrial station receptors and the results were compared to the ambient PAH's air quality measurements of Table 4.4 and 4.5. Tables 4.11 to 4.16 are a comparison of the mean daily PAH's measured and modelled concentrations experienced at the receptors.

Tables 4.11 and 4.12 indicate the mean daily PAH's gas and particle phase results experienced at the Sasolburg industrial area on the 29/11/05, whilst Tables 4.13 to 4.14 and Tables 4.15 to 4.16 indicate the mean daily PAH's gas and particle phase results experienced at Sasolburg hospital area on the 30/11/05 and 1/12/05 respectively.

Table 4.11: Comparison of the measured and modelled gas-phase concentrations at the Sasolburg industrial area on the 29/11/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	$3,05 \times 10^{-6}$	$8,76 \times 10^{-4}$	$2,86 \times 10^4$
Acenaphthylene	$4,69 \times 10^{-6}$	$3,67 \times 10^{-1}$	$7,82 \times 10^6$
Anthracene	$2,74 \times 10^{-2}$	$9,52 \times 10^{-2}$	$2,47 \times 10^2$
Benzo(a)anthracene	ND	$9,48 \times 10^{-2}$	ND
Benzo(a)pyrene	ND	$7,94 \times 10^{-2}$	ND
Benzo(b)fluoranthene	ND	$1,88 \times 10^{-4}$	ND
Benzo(g,h,i)perylene	ND	$4,71 \times 10^{-5}$	ND
Benzo(k)fluoranthene	ND	ND	ND
Chrysene	ND	$8,57 \times 10^{-2}$	ND
Dibenz(a,h)anthracene	ND	ND	ND
Fluoranthene	$9,96 \times 10^{-4}$	$1,22 \times 10^{-3}$	$2,23 \times 10^1$
Fluorene	$1,42 \times 10^{-3}$	$1,56 \times 10^{-3}$	$1,01 \times 10^1$
Indeno(1,2,3-CD)pyrene	ND	$1,04 \times 10^{-4}$	ND
Naphthalene	$3,36 \times 10^{-4}$	$2,23 \times 10^{-2}$	$6,54 \times 10^3$
Phenanthrene	$1,54 \times 10^{-3}$	$3,45 \times 10^{-1}$	$2,23 \times 10^4$
Pyrene	$4,44 \times 10^{-4}$	$5,66 \times 10^{-4}$	$2,76 \times 10^1$

As indicated by Table 4.11, the PAH's gas-phase modelled estimates were much higher than the measured ambient values. The model deviation from the measured values performed the best for the following species: fluorene (10% overestimate); fluoranthene (22% overestimate) and pyrene (28% overestimate) as illustrated by Figures 4.18 and 4.19. For the other species, large estimates were observed and this may be due to the fact that the emission point sources are not well characterised and/or that most of the emission factors calculated for coal usage are not applicable for Sasolburg industrial and hospital areas. A large percentage of emissions are released at high stack levels which may also results in different dispersion patterns.

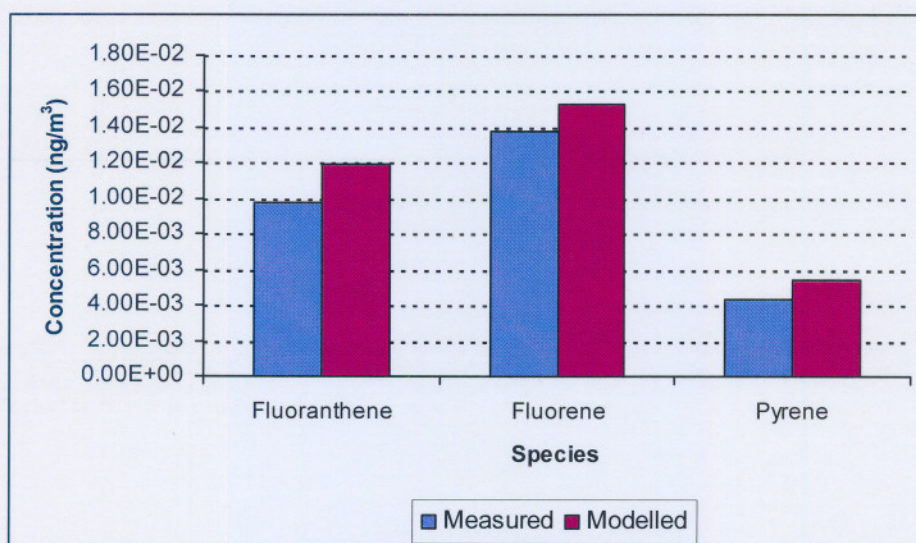


Figure 4.18: Comparison of PAH 24hr average gas-phase concentrations on the 29/11/05 at Sasolburg industrial area

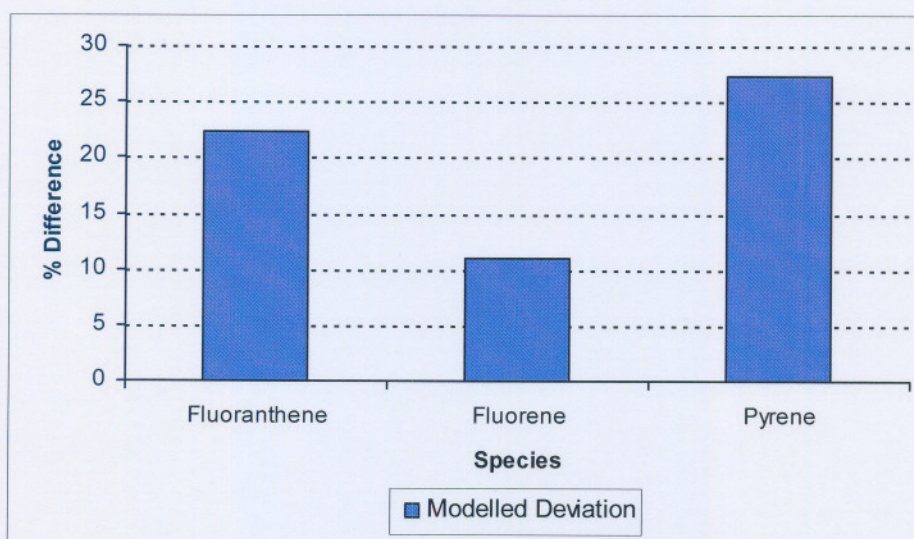


Figure 4.19: Percentage deviation of the modelled gas-phase concentrations on 29/11/05 at Sasolburg industrial area

Table 4.12: Comparison of the measured and modelled particle-phase concentrations at the Sasolburg industrial area on the 29/11/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	$9,25 \times 10^{-4}$	$8,76 \times 10^{-4}$	$-5,35 \times 10^0$
Acenaphthylene	$1,80 \times 10^{-3}$	$3,67 \times 10^1$	$2,03 \times 10^4$
Anthracene	$7,07 \times 10^{-2}$	$9,52 \times 10^{-2}$	$3,47 \times 10^1$
Benzo(a)anthracene	$2,76 \times 10^{-2}$	$9,48 \times 10^{-2}$	$2,43 \times 10^2$
Benzo(a)pyrene	$2,47 \times 10^{-2}$	$7,94 \times 10^{-2}$	$2,21 \times 10^2$
Benzo(b)fluoranthene	$8,55 \times 10^{-2}$	$1,88 \times 10^{-4}$	$-9,98 \times 10^1$
Benzo(g,h,i)perylene	$1,92 \times 10^{-2}$	$4,71 \times 10^{-5}$	$-9,98 \times 10^1$
Benzo(k)fluoranthene	$6,26 \times 10^{-2}$		ND
Chrysene	$2,54 \times 10^{-2}$	$8,57 \times 10^{-2}$	$2,37 \times 10^2$
Dibenz(a,h)anthracene	$3,24 \times 10^{-3}$		ND
Fluoranthene	$1,29 \times 10^{-2}$	$1,22 \times 10^{-3}$	$-9,06 \times 10^1$
Fluorene	$1,18 \times 10^{-2}$	$1,56 \times 10^{-3}$	$-8,68 \times 10^1$
Indeno(1,2,3-CD)pyrene	$6,69 \times 10^{-2}$	$1,04 \times 10^{-4}$	$-9,98 \times 10^1$
Naphthalene	$2,25 \times 10^{-3}$	$2,23 \times 10^{-2}$	$8,92 \times 10^2$
Phenanthrene	$3,25 \times 10^{-2}$	$3,45 \times 10^{-1}$	$9,60 \times 10^2$
Pyrene	$1,10 \times 10^{-2}$	$5,66 \times 10^{-4}$	$-9,49 \times 10^1$

NOTE: ND = compounds not detected; below detection limit

According to Table 4.12, the particle-phase modelled estimates were in some cases higher and in other cases lower than the measured ambient values. The model deviation from the measured values performed the following species, acenaphthene (5% underestimated), anthracene (35% overestimated) and fluorine (87% underestimated) as illustrated in Figures 4.20 and 4.21.

In contrast to the gas-phase emissions, a more even, over and under estimations were observed in the case of particulate concentrations. The fact that the surrounding informal usage of coal contributes significantly to the particulates may explain this improved agreement. The measured and modelled values are in this case reasonably in agreement.

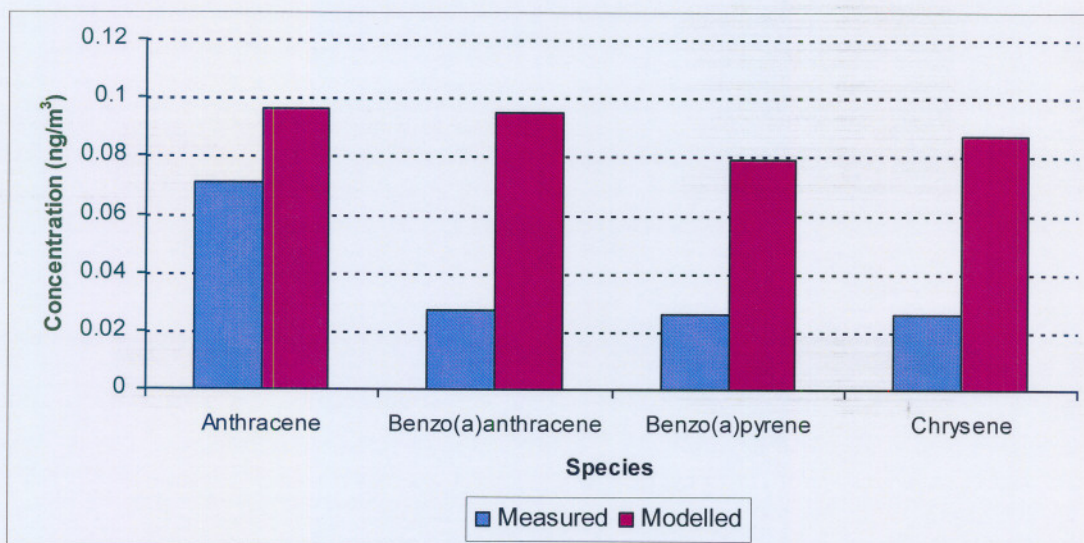


Figure 4.20: Comparison of PAH 24hr average particle-phase results on the 29/11/05 at Sasolburg industrial area

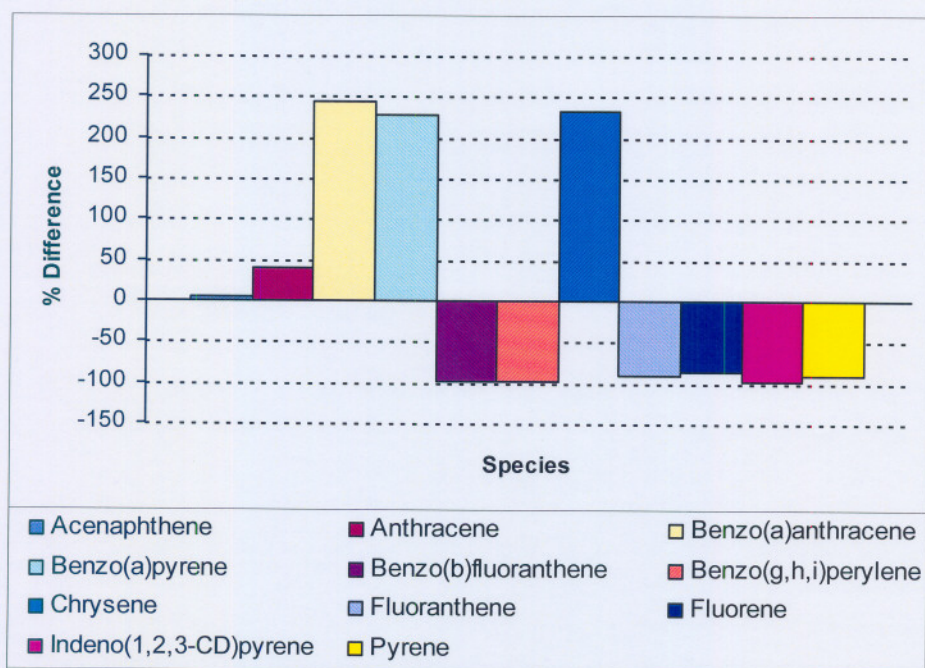


Figure 4.21: Percentage deviation of the modelled particle-phase results on 29/11/05 at Sasolburg industrial area

Table 4.13: Comparison of the measured and modelled gas-phase concentrations at Sasolburg hospital area on the 30/11/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	$4,85 \times 10^{-6}$	$2,65 \times 10^{-4}$	$5,37 \times 10^3$
Acenaphthylene	$7,05 \times 10^{-6}$	$1,53 \times 10^{-5}$	$2,18 \times 10^6$
Anthracene	$6,18 \times 10^{-2}$	$3,98 \times 10^{-2}$	$-3,56 \times 10^1$
Benzo(a)anthracene	ND	$3,96 \times 10^{-2}$	ND
Benzo(a)pyrene	ND	$3,32 \times 10^{-2}$	ND
Benzo(b)fluoranthene	ND	$5,70 \times 10^{-5}$	ND
Benzo(g,h,i)perylene	ND	$1,43 \times 10^{-5}$	ND
Benzo(k)fluoranthene	ND		ND
Chrysene	ND	$3,58 \times 10^{-2}$	ND
Dibenz(a,h)anthracene	ND		ND
Fluoranthene	$2,26 \times 10^{-3}$	$3,69 \times 10^{-4}$	$-8,37 \times 10^1$
Fluorene	$1,72 \times 10^{-3}$	$4,74 \times 10^{-4}$	$-7,25 \times 10^1$
Indeno(1,2,3-CD)pyrene	ND	$3,16 \times 10^{-5}$	ND
Naphthalene	$4,83 \times 10^{-4}$	$6,76 \times 10^{-3}$	$1,30 \times 10^3$
Phenanthrene	$4,84 \times 10^{-3}$	$1,43 \times 10^{-1}$	$2,86 \times 10^3$
Pyrene	$9,14 \times 10^{-4}$	$1,72 \times 10^{-4}$	$-8,12 \times 10^1$

NOTE: ND = compounds not detected; below detection limit

As indicated by Table 4.13, the PAH's gas-phase modelled estimates were in some cases lower than the measured ambient values. The model deviation from the measured values performed the best for the following species: anthracene (36% underestimate); fluorene (72% underestimate); pyrene (81% underestimate) and fluoranthene (84% underestimate).

The overestimates between the measured and modelled results may be due to the fact that the measured concentrations were obtained from the samples, which were taken from ground level while the modelled results included emissions released at high stack levels.

Table 4.14: Comparison of the measured and modelled particle-phase concentrations at Sasolburg hospital area on the 30/11/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	ND	$2,65 \times 10^{-4}$	ND
Acenaphthylene	ND	$1,53 \times 10^{-1}$	ND
Anthracene	$4,37 \times 10^{-3}$	$3,98 \times 10^{-2}$	$8,10 \times 10^2$
Benzo(a)anthracene	$2,37 \times 10^{-4}$	$3,96 \times 10^{-2}$	$1,66 \times 10^4$
Benzo(a)pyrene	ND	$3,32 \times 10^{-2}$	ND
Benzo(b)fluoranthene	ND	$5,70 \times 10^{-5}$	ND
Benzo(g,h,i)perylene	ND	$1,43 \times 10^{-5}$	ND
Benzo(k)fluoranthene	ND		ND
Chrysene	$4,18 \times 10^{-4}$	$3,58 \times 10^{-2}$	$8,47 \times 10^3$
Dibenz(a,h)anthracene	ND		ND
Fluoranthene	$3,87 \times 10^{-4}$	$3,69 \times 10^{-4}$	$-4,59 \times 10^0$
Fluorene	$2,53 \times 10^{-4}$	$4,74 \times 10^{-4}$	$8,72 \times 10^1$
Indeno(1,2,3-CD)pyrene	ND	$3,16 \times 10^{-5}$	ND
Naphthalene	$2,26 \times 10^{-4}$	$6,76 \times 10^{-3}$	$2,89 \times 10^3$
Phenanthrene	$7,16 \times 10^{-4}$	$1,43 \times 10^{-1}$	$1,99 \times 10^4$
Pyrene	$2,35 \times 10^{-4}$	$1,72 \times 10^{-4}$	$-2,70 \times 10^1$

NOTE: ND = compounds not detected; below detection limit

According to Table 4.14, the PAH's particle-phase modelled estimates were in some cases higher and other cases lower than the measured ambient values. The model deviation from the measured values performed the best for the following species: fluoranthene (5% underestimate); pyrene (27% underestimate) and fluorene (87% overestimate).

Table 4.15: Comparison of the measured and modelled gas-phase concentrations at Sasolburg hospital area on the 01/12/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	$1,52 \times 10^{-6}$	$2,65 \times 10^{-4}$	$1,74 \times 10^4$
Acenaphthylene	$4,32 \times 10^{-6}$	$1,53 \times 10^{-1}$	$3,55 \times 10^6$
Anthracene	$2,53 \times 10^{-2}$	$3,98 \times 10^{-2}$	$5,72 \times 10^1$
Benzo(a)anthracene	ND	$3,96 \times 10^{-2}$	ND
Benzo(a)pyrene	ND	$3,32 \times 10^{-2}$	ND
Benzo(b)fluoranthene	ND	$5,70 \times 10^{-5}$	ND
Benzo(g,h,i)perylene	ND	$1,43 \times 10^{-5}$	ND
Benzo(k)fluoranthene	ND		ND
Chrysene	ND	$3,58 \times 10^{-2}$	ND
Dibenz(a,h)anthracene	ND		ND
Fluoranthene	$7,38 \times 10^{-4}$	$3,69 \times 10^{-4}$	$-5,00 \times 10^1$
Fluorene	$8,13 \times 10^{-4}$	$4,74 \times 10^{-4}$	$-4,17 \times 10^1$
Indeno(1,2,3-CD)pyrene	ND	$3,16 \times 10^{-5}$	ND
Naphthalene	$7,58 \times 10^{-5}$	$6,76 \times 10^{-3}$	$8,82 \times 10^3$
Phenanthrene	ND	$1,43 \times 10^{-1}$	ND
Pyrene	$2,52 \times 10^{-4}$	$1,72 \times 10^{-4}$	$-3,19 \times 10^1$

NOTE: ND = compounds not detected; below detection limit

As indicated by Table 4.15, the PAH's gas-phase modelled estimates were in some cases higher and other cases lower than the measured ambient values. The model deviation from the measured values performed the best for the following species: pyrene (32% underestimate); fluorene (42% underestimate) and fluoranthene (50% underestimate).

Table 4.16: Comparison of the measured and modelled particle-phase concentrations at Sasolburg hospital area on the 01/12/05

Species	Measured PUF (ng/m ³)	Modelled PUF (ng/m ³)	%Difference
Acenaphthene	$7,84 \times 10^{-7}$	$2,65 \times 10^{-4}$	ND
Acenaphthylene	$1,22 \times 10^{-6}$	$1,53 \times 10^{-1}$	ND
Anthracene	$2,60 \times 10^{-3}$	$3,98 \times 10^{-2}$	$1,43 \times 10^3$
Benzo(a)anthracene	ND	$3,96 \times 10^{-2}$	ND
Benzo(a)pyrene	ND	$3,32 \times 10^{-2}$	ND
Benzo(b)fluoranthene	ND	$5,70 \times 10^{-5}$	ND
Benzo(g,h,i)perylene	ND	$1,43 \times 10^{-5}$	ND
Benzo(k)fluoranthene	ND		ND
Chrysene	ND	$3,58 \times 10^{-2}$	ND
Dibenz(a,h)anthracene	ND		ND
Fluoranthene	$1,47 \times 10^{-4}$	$3,69 \times 10^{-4}$	$1,51 \times 10^2$
Fluorene	$1,67 \times 10^{-4}$	$4,74 \times 10^{-4}$	$1,84 \times 10^2$
Indeno(1,2,3-CD)pyrene	ND	$3,16 \times 10^{-5}$	ND
Naphthalene	$6,92 \times 10^{-5}$	$6,76 \times 10^{-3}$	$9,67 \times 10^3$
Phenanthrene	$3,26 \times 10^{-4}$	$1,43 \times 10^{-1}$	$4,38 \times 10^4$
Pyrene	$8,55 \times 10^{-5}$	$1,72 \times 10^{-4}$	$1,01 \times 10^2$

NOTE: ND = compounds not detected; below detection limit

As indicated by Table 4.16, the PAH's particle-phase modelled estimates were higher than the measured ambient values. The model deviation from the measured values performed the best for the following species: pyrene (101% overestimate); fluoranthene (151% overestimate) fluorene (184% overestimate).

4.8.6 Benzo(a)pyrene Dispersion Results

The mean annual BaP concentrations (based on European Commission annual ambient air guideline) [64] experienced at the industrial and hospital receptors during the period of simulation was found to be 6.5×10^{-5} ng/m³ and 2.0×10^{-5} ng/m³ respectively. The source apportionment of BaP emission calculated at the discrete receptors from the Sasolburg areas shows that the industrial area contributes 0.08%, while the hospital area contributes 0.06% to the overall BaP emissions. The mean daily measured concentration of BaP was found to be 2.47×10^{-2} ng/m³ and the modelled concentrations was 7.71×10^{-2} ng/m³ at the Sasolburg Industrial receptor on the 29/11/05.

The measured and modelled concentrations were compared and the modelled gas-phase BaP estimates were higher than the measured ambient value. The model deviation from the measured concentration of BaP was an overestimate (% difference of 212).

The benzo(a)pyrene toxic equivalent quotient (TEQ) annual average concentration was calculated for the industrial and hospital area. The BaP TEQ for hospital area was 0.038 ng/m^3 and BaP TEQ for industrial area was 0.090 ng/m^3 . The BaP TEQ concentrations were compared to the BaP annual average for industrial (0.077 ng/m^3) and hospital area (0.034 ng/m^3), these values compares very well and Figure 4.23 illustrates the annual BaP concentrations emitted from the Sasolburg industrial area.

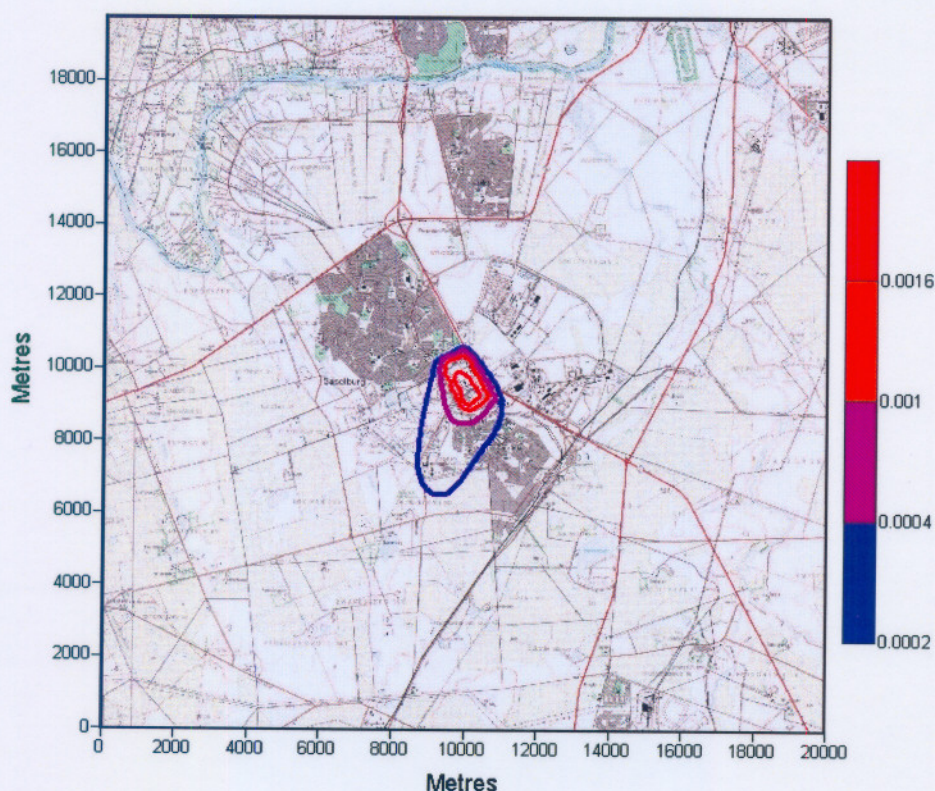


Figure 4.23: Mean annual BaP concentration isopleths (ng/m^3) emitted from Sasolburg industrial area

Table 4.17 indicates the average contribution from the seven PAH species to the TEQ.

Table 4.17: Average contribution from the seven PAH species to TEQ

Species	Percentage contribution	
	Sasolburg Hospital	Industrial Station
Benzo(a)anthracene	11	11
Benzo(a)pyrene	88	88
Benzo(b,j,k)fluoranthene	0	0
Chrysene	1	1
Indeno(1,2,3-cd)pyrene	0	0
5-Methyl Chrysene	0	0
Total Percentage	100	100

4.9 Conclusion

4.9.1 Measured results

From Table 4.4 (results from the industrial area, 29/11/05), it is evident that anthracene, fluorene and phenanthrene in gas-phase were found to be highest respectively (also shown in Figure 4.2), while in the particle-phase benzo(b)fluoranthene, anthracene and indeno(1,2,3-cd)pyrene were found to be the highest respectively (also shown in Figure 4.1). The sources related to the PAH's concentrations obtained in the Sasolburg industrial area may be due to industrial processes (such as fossil fuel and coal combustion) and the emissions from automobiles.

Table 4.5 gives the results of 30/11/05 and 01/12/06 obtained from the Hospital area. On the 30/11/05 in gas-phase (Figure 4.3), the highest concentration obtained was anthracene, phenanthrene, and fluoranthene respectively. The same finding was found for the particle-phase as illustrated in Figure 4.4. Table 4.5 also shows the results obtained on the 01/12/06. The gas-phase results obtained shows that anthracene, fluorene and fluorenthene are found to be the highest respectively. In the particle-phase, the highest concentration was obtained in anthracene, phenanthrene, and fluorene respectively.

The PAH's concentrations obtained from hospital area may be due to the vehicular traffic experienced in vicinity to the area.

4.9.2 Comparison of modelled and measured PAH dispersion results

The results obtained during this modelling assessment of PAH's will contribute to the understanding and managing of the risks associated with the emissions of these species. PAH's are carcinogenic and believed to pose a threat to the environment. The concentrations of PAH's in ambient air must be monitored in order to determine whether the PAH's concentrations are within the regulated specification. South Africa does not have regulated specifications and in this case the US-EPA and EC information was used as benchmarks. Benzo(a)pyrene (the most carcinogenic PAH); the largest contributor to the overall toxicity was obtained only in the particle-phase on the 29/11/05, but its concentration was below the BaP annual limit guideline of 1.0 ng/m^3 measured in the PM_{10} fraction.

The modelled results were overestimates of the actual measured results and this could be due the different dispersion parameters. The measured results were taken from the ground level while the modelled results takes account for PAH's in high stack levels. The accuracy of the model predicted concentrations performed best for the following PAH species: fluorene; fluoranthene and pyrene at both the Sasolburg hospital and industrial receptors. In particular the PAH's gas-phase modelled estimates for these PAH species were lower than the measured ambient PAH's values at the Sasolburg hospital receptor and conversely higher than the measured ambient PAH's values at the Sasolburg industrial receptor.

However the accuracy of the model predicted concentrations consistently performed worst for the following PAH species: acenaphthene; acenaphthylene; naphthalene and phenanthrene at both the Sasolburg hospital and industrial receptors. The model predicted concentrations were significant overestimates of the actual measured concentrations resulting in huge model deviations.

For the Sasolburg industrial area PAH emissions, the dominant species contributing to the total PAH concentrations calculated at each of the discrete receptors were found to be naphthalene, phenanthrene and fluoranthene.

4.9.3 BaP and BaP TEQ Results

The industrial station was the most impacted on due to the BaP emissions released from the Sasolburg industrial processes. The BaP annual average obtained in the industrial area was found to be 0.074 ng/m^3 and did not exceed the European Commission's BaP annual limit of 1.0 ng/m^3 .

The benzo(a)pyrene toxic equivalent quotient (TEQ) annual average concentrations are higher than the BaP annual average concentrations calculated at the industrial and hospital receptors. Benzo(a)pyrene dominates the TEQ since the BaP contributes 88%, while benzo(a)anthracene and chrysene contributes 11% and 1% respectively. Thus BaP is consistent with findings used in the development of the UK goal, where BaP was also found to be the largest contributor to the overall toxicity.

CHAPTER 5

PROJECT EVALUATION

In this chapter, the entire study is critically evaluated in terms of the goals that were set at Chapter1 and in terms of the results obtained. Shortcomings and remaining challenges identified during the study are also pointed out.

5.1 Successes of the study

In this study, useful information concerning the methodology for sampling PAH's in ambient air, analysis methodology, presence of PAH species in ambient air, the link between source strength and the levels of PAH species (concentration) in ambient air were successfully obtained.

The evaluation of the study in terms of the goals stated in Chapter 1 gives a good idea of the success of the study. This evaluation can also help in understanding the PAH species and their sources in ambient air. The points listed below correlates with the goals stated in Section 1.2 in Chapter 1:

- PAH's in the atmosphere have a low ambient air concentration, therefore a high volume sampler (which provides for low detection limit) was used to successfully collect the samples in both gaseous and particulate phase in the greater Sasolburg area. Although the concentrations of PAH's in ambient air are very low, the high volume sampler could effectively acquire sufficient samples for analysis.
- GC/MS technique was used to identify and quantify the different PAH species from the samples obtained.

- The different types of PAH's were obtained, their concentrations were calculated and the levels obtained.
- The link between the source strength and ambient levels of PAH's were determined
- The results were modelled and compared to the measured results of ambient PAH emissions.

By considering the goals stated and fulfilment of these goals, this study was seen as successful. There are however still a lot of research opportunities in this specific study.

5.2 Shortcomings of the study

A high volume sampler was used for acquiring samples. A high volume sampler is however a rather a complex and very expensive sampling technique and has a drawback of needing electrical connection in order to work and this is a limiting factor when sampling in remote areas. The other problem experienced in this study, is that samples obtained requires being concentrated and cleanup procedure prior chromatography analysis. Soxhlet extraction; a technique used to concentrate the PUF and filter, requires large volumes of solvents and is time consuming. In most cases, the sample pre-treatment procedure is the critical step in achieving reliable quantitative results. The major concern was, there are only a few countries with legal basis requiring the measurements of PAH's. A high-resolution Mass spectrometer (MS) was needed for this action and the available MS performance needed to be first enhanced. This proves that the availability of suitable instrumentation is a prerequisite for this type of analysis.

To better understand the regional distribution of PAH's in different locations and to elucidate the source and fate of these compounds in the environment, more convenient and powerful sampling techniques are needed that should be preferably cheaper, easy to handle and that can be used to sample over period of time at many locations concurrently.

5.3 Future challenges

Higher winter concentrations of particulate PAH's have been reported elsewhere by Harrison *et al.* [65]. Menichini *et al.* [66] also reported that concentrations of PAHs measured at a site in Rome, Italy, tended to be about one order of magnitude higher in winter than in summer.

Factors contributing to higher concentrations of PAH's in winter include:

- meteorological factors (like increased atmospheric stability in winter)
- higher overall emissions in winter from wood and coal burnings
- lower removal of PAH's from the atmosphere in winter due to reduced precipitation, degradation by photo-oxidation and reaction with hydroxyl radicals [67].

Since ambient air quality measurements for PAH's were conducted during summer (November-December 2005), it is therefore recommended to extend the measurement campaign to winter to account for the higher winter concentrations of particulate PAH's.

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