ENVIRONMENTAL XENOBIOTICS

PAHs IN SOIL (HEAVY METALS), INDOOR AIR AND WATER ENVIRONMENT, CASE STUDIES OF GHANA AND DENMARK

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Abstract

The thesis looked at the impact of some xenobiotic organic compounds on the urban environmental quality with special emphasis on polycyclic aromatic hydrocarbons (PAHs) in two case studies (Ghana and Denmark). The PhD program, therefore, naturally falls into three parallel pathways which considered the levels, distribution, source and the risk assessment of PAHs in (1) soil (2) particulate matter of indoor and (3) surface water body environments.

1) The fate of xenobiotic organic compounds (XOC) and other anthropogenic chemicals in the soil environment is an important domain of soil biochemistry. Research is desperately needed to determine the biochemical reactions in soil that transforms these XOCs to their mineral components. Information about their biodegradability, metabolic pathways, conjugation and de-conjugation, sorption, transport in the environment, and persistence of these xenobiotic chemicals are needed to understand their fate and impacts and to help in the formulation of policies to protect humans and the ecosystems from their effects. A soil survey was performed to determine the levels, distributions and sources of 6 polycyclic aromatic hydrocarbons (PAHs) in 9 selected soil environments in Esbjerg, Denmark. The conclusion was that there were elevated levels of the individual as well as the total PAHs in the soil samples and also, all 6 PAHs were present in all the soil samples. The average sum of the 6 PAHs in all soil samples was 2.5 mg.kg^{-1}, with a range from 0.24 to 7.6 mg kg^{-1} (dw). The total mean PAH concentration obtained was 1.67 times higher than the total 2002 limit set by the Danish Environmental Protection Agency (DEPA) whiles the mean benzo(a)pyrene (BaP) concentration (0.6 mg kg-^{1}) was also 6 times the Soil Quality Criteria (Human Health) (0.1 mg kg-^{1}) by DEPA and 2 times the Maximum Permissible Concentrations (0.26 mg kg-^{1}) by the Netherlands for BaP. However, with the new DEPA limit set since 2005, all the levels obtained (both BaP and total PAHs) in the study are within the acceptable limit in Denmark. This work is reported in two papers (1 and 2).

2) The second study was focused on the quality of indoor air. A range of xenobiotic organic compounds coming from the air act directly on the site of first contact through their cytotoxic property. For many of them, the margin of acceptable safety limit is very low or even non-existent. Polycyclic aromatic hydrocarbon compounds are a group of toxic compounds arising from various indoor combustion processes, which

might induce lung carcinoma, although the quantitative contribution is difficult to assess due to the confounding factor of smoking. A major intake of xenobiotics is coming from the indoor air. In conclusion, there were elevated levels of the individual as well as the total PAHs in the particulate matter (PM) kitchen samples and also, all 6 PAHs were present in all the collected samples. The total ∑6 PAH concentrations in indoor particulate matter (PM) ranged from 0.94 to 8.2 mg kg^{-1} d.w, with an average of 3.4 mg kg^{-1} d.w. The benzo(a)pyrene (BaP) levels in the various kitchens were also from below detection to 0.58 mg kg^{-1} d.w with an average value of 0.19 mg kg^{-1} d.w. The diagnostic ratios and the correlation analysis identified pyrogenic (oil-fumes, grilling and smoking) as the main source of indoor PAHs with some amount from petrogenic sources as well. It is worth noting that the samples used in the sturdy had formed for quit over six months period and might not necessary reflect exposure levels but only gives an indication that there is some deposition of PM-PAHs in the kitchen indoor environment which needs to be looked at. This work is reported in two papers (3 and 4).

3) The third study was also focused on xenobiotics in the water environment. Water supply, wastewater treatment systems and urban drainage were originally designed to solve just conventional problems such as supply of potable water, flood prevention and sanitation. The main problem within the conventional urban water cycle approaches is the absence of designs to deal with the emerging xenobiotics. Technologies are therefore needed to prevent xenobiotics from being discharged into surface waters where they may give rise to impacts on the chemical water quality and ecological status of receiving waters. Again, there were elevated levels of some individual as well as the total PAHs in the water samples and also, all 6 PAHs were generally not present in all the water samples. The total of the 6 PAHs in the water bodies ranged from 26.8 to 105.5 μg $L\text{-}^{1}$ with an average of 68.4 μg $L\text{-}^{1}$ whiles the mean benzo(a)pyrene (BaP) concentration is 2.6 μg $L\text{-}^{1}$. Most of the water bodies analysed was lakes which do not flow all year round. The only river (Spangbjerg møllebæk) sampled had most of the PAHs below the detection limit of the instrument.

This shows that there is some PAH deposition into the water bodies. This work is reported in two papers (5 and 6).

4) There is a fourth paper in preparation which also discusses the levels of mercury, lead, nickel and arsenic in some top soil samples. Also, it looked at the levels of PAHs in Ferry fuel oil and some filters put in the Ferry exhaust. The result showed that the heavy metals were within the acceptable limit of DEPA. Also, the spent Ferry fuel oil and the exhaust filters had all the 6 PAHs analysed present in them. This work is reported in the appendix as Supplementary experiment.

Xenobiotics (PAHs) levels in soil, air and water bodies are hitherto a scarcely explored problem in most part of the world. As a result, more studies are ongoing to strengthen this database and investigate the range and profile of carcinogenic PAHs content of the studied environments.

After the introductory chapters, six papers follow:

1) Essumang, D. K. (60%), Kowalski, K (20%) and Sogaard, E. G (20%) (2010) Levels, Distribution and Source Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in topsoils and Roadside soils in Esbjerg, Denmark .
Bull. Environ. Contam. Toxicol. (Accepted)

2) Essumang, D. K. (70%), Dodoo D. K. (5%), Obiri, S. (5%) Oduro A. K (20%) (2006) Analysis of Polycyclic Aromatic Hydrocarbons in Vehicular Fallout in Kumasi Metropolis of Ghana, Jour. Environ. Mon. Assess **2006** 121 (**1-3**) 401 408

3) Essumang, D. K. (70%), Stepien, J (10%) and Sogaard, E. G. (20%) (2010) Distribution, Levels, and Source Assessment of Polycyclic Aromatic Hydrocarbons (PAHS) in the particulate matter (PM) of some indoor environment in Esbjerg, Denmark (***Submitted to Environ Monit Assess***)

4) Essumang, D. K. (50%), Dodoo, D. K (30%). and Hadzi, G (20%) (2010) Distribution, levels, and risk assessment of polycyclic aromatic hydrocarbons in the soot of some kitchens in the Cape Coast Metropolis of Ghana, Toxicological & Environmental Chemistry, 92: 9, 1633 — 1647

5) Essumang, D. K. (60%), Ankrah, D. A (20%) and Sogaard, E. G (20%) (2010) Levels and Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in some water bodies in Esbjerg, Denmark

6) Essumang D.K. (60%), Adokoh C.K. (15%), Afriyie J (05%) and Mensah E. (20%) (2009) Source Assessment and Analysis of Polycyclic Aromatic Hydrocarbon (PAH's) In the Oblogo Waste Disposal Sites and Some Water Bodies in and around the Accra Metropolis of Ghana. JWARP **(2009)** 1(**6**) 456- 468

7) Essumang, D. K. and Sogaard, E. G (2010) Levels of Hg, Al, and Ni in soil samples from Esbjerg and PAHs in Ferry fuel oils and filters from the ferry exhaust (In preparation) Supplementary experiment

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Lastly, I want to appreciate my family and all those who helped in diverse ways in the pursuit of this work.

DEDICATION

This work is dedicated to my family; Mary, Isaac, Elizabeth, Lydia and Gloria.

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INTRODUCTION

1.0 Xenobiotics

The word, xenobiotic, is a combination of two different roots, “xeno” and “biotic”. Xeno is a Greek word which means strange, unnatural, or different whiles Biotic is a word that also means life. Xenobiotic, therefore, refers to both organic and inorganic substances that mimic natural biochemicals that are essential for life, but which have characteristics about them that are strange and unnatural. Xenobiotics are often toxic to life. Also, it is believed they may not be recognized by biochemical processes in plants and microorganisms and are thus persistent in the environment. Most xenobiotics are from anthropogenic source which include many compounds that are involved in industrial, household, medical, transport and agricultural activities. The fate of industrial solvents and other industrial chemicals in the soil environment is an important domain of soil pollution[1-4].

Xenobiotics are known dangerous pollutants which include both inorganic elements like heavy metals, metalloids and man-made organic compounds such as pesticides, surfactants, industrial solvents, fragrances, flavours, and pharmaceuticals as well as endocrine disrupters. It has been estimated that over 70,000 xenobiotics may potentially be hazardous for humans and/or ecosystems. The presence of xenobiotics in surface as well as underground waters have become a problem for urban water supply as treatment systems were originally not designed to solve xenobiotics problems[5]**.** The main problem within the conventional urban water cycle approaches is the absence of proper designs to remove xenobiotics[1-4].

1.1 Impact of xenobiotics in water

Sewage treatment plants (STPs) are the usual receptors of xenobiotic compounds that have to be co-treated with municipal wastewaters before being discharged to water bodies. The presence of trace metals, metalloids and synthetic organic chemicals, such as surfactants, polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides, pharmaceuticals and their primary degradation products in the influents of STPs may inhibit irreversibly sensitive biological processes, such as nitrification. It is known that the first step of nitrification, i.e., the oxidation of ammonium to nitrite (nitrification), is particularly sensitive to the presence of certain chemicals. Inhibition of this step under uncontrolled conditions may completely inhibit biological nitrogen production[5].

It is important for researchers to find innovative approaches to prevent xenobiotics from being discharged into surface and underground waters where they may affect the water quality and ecological status of receiving waters. This problem has already been recognized by the EU-Water Framework Directive and efforts are being made to address them[6].

Literature has stated that, out of the billions of poisonous chemicals in the environment, PAHs accumulates and with time poses an imminent threat to public health, mostly water pollution. Also, the PAHs get adsorbed onto fish skins, which can pose serious health problems to man since it is a source of food[7-8].

1.2 Impact of xenobiotics in soil

Research has stated that, the fate of xenobiotics in soil includes (i) complete mineralization or (ii) stabilization of the parent compound, or some metabolites of the compound in soil. It has also been recognised that, if the xenobiotics are toxic and the rate of degradation is very slow, adverse effects on human and on ecological health are possible. Therefore it is desirable to maintain xenobiotic concentrations in soil as low a level as possible. Because of these concerns, considerable research effort has been spent in trying to understand the metabolic degradation pathways of xenobiotics in soil[1-4].

Some researchers have stated that, the persistence of xenobiotics (heavy metals and pesticides) in soil causes different types of problems. They said, if xenobiotics remains in soil for a long period of time, this, may (i) be assimilated by plants and accumulate in the edible portions, (ii) be transported with eroding soil particles or with surface and subsurface waters to locations where its presence may cause harm or (iii) it may accumulate in the animal food chain and change the ecological balance of nature[1-4].

1.3 Impact of xenobiotics in air

Polycyclic aromatic hydrocarbons (PAHs) are known to be a group of dangerous xenobiotics that man introduces into the environment in large quantities daily with little or no awareness. These are a suit of ubiquitous organic compounds released into the environment as gas particles during incomplete combustion of organic material. A number of sources have been identified with PAHs which include: mobile sources such as cars, buses, trucks, ships, and aircrafts; industrial sources such as power generation, steelworks, coke ovens, aluminium production, and cement kilns and oil refineries. Domestic sources include combustion for heating and cooking especially solid fuel using coal and wood. Fires and smoke resulting from burning of vegetation in agricultural process, bushfires, grilling of food, or tobacco smoke[9] result in the release of large amounts of PAHs into the environment.

Substituted PAHs, mainly in the form of alkyl-substituted compounds, for example methyl, propyl and butyl derivative PAHs are known to be produced biologically (e.g. naphthalene, phenanthrene, and perylene) [10-14]. It has been reported that a number of PAHs are carcinogenic and pose a lot problems to human health[15].

1.4 What to do with xenobiotics

The problem with xenobiotics is that, new ones keep adding to the list from anthropogenic activities with very little or sometimes no information about their activities in the environment. The commonest offender of air pollution has been emissions from automobiles and cigarette smoking. In an attempt to find solution to the automobile emissions problem, catalytic convertor was developed for that purpose; however, they have also come with their problems. One of such is the deposition into the environment of platinum, palladium and rhodium referred to as Platinum Group Metals (PGMs) from catalytic convertors. The increasing use of catalytic converters based on platinum-group metals (PGM) has raised much concern as recent investigations have shown that the accumulation of PGM in roadside dust, airborne dust, soil, water bodies, grass, and in the food chain has increased dramatically [16-20].

Although sources such as dentistry, Pt-drugs (e.g. Pt-(II) and -(IV) pyrophosphato complexes, Carboplatin and Cisplatin), mining etc. could contribute PGM to the environment, those sources are minimal compared to automobile emissions [21]. The elevated PGM levels in the environment have been largely linked to the introduction of automobile catalysts [21] since it occurs naturally at very low concentrations [22]. Although the health implications of PGM ingestion have not been exhaustively studied, its continuous ingestion by people is a cause for concern.

1.5 Effects of xenobiotics on human health

There are several known diseases which result from the exposure to xenobiotics, however, a few of the effects on human health as reported in literature (other studies) are presented below.

It is known that, Primary Biliary Cirrhosis (PBC) is an autoimmune chronic cholestatic liver disease of unknown etiology predominantly affecting post-menopausal women. Serum anti-mitochondrial antibodies (AMA) are highly specific and detected in 95% of patients. The major AMA autoantigen is the E2 subunit of the pyruvate dehydrogenase complex (PDC-E2), which is also recognized by autoreactive CD4 and CD8 T cells. The disease manifests an incomplete concordance in monozygotic twins [23] which, along with a geoepidemiology pattern [24], suggests a role for environmental factors in its induction.

It has been suggested that, prenatal factors seem to play an important role in determining susceptibility to atopy and asthma. Maternal exposure to environmental xenobiotics during pregnancy represents potential exposure of the foetus via placental transfer. Environmental xenobiotics may adversely affect intrauterine life quality and development of foetal immune system [25 – 26].

Contamination of human placenta is also said to represents a unique biomarker of environmental exposure of women (and a good proxy measure for the foetal exposure). *In utero,* exposure to low levels of environmental xenobiotics may result in functional changes in tissues leading to increased susceptibility to disease later in life, including allergies [27].

Some xenobiotics are known for their carcinogenic, mutagenic (gene mutation causing agent) and teratogenic (chemicals that affect the normal development of foetus) properties [28]. PAHs have also been reported to disrupt endocrine systems in humans [29]. Also, a report by Gray (2008)[30] links the recent increases in breast cancers to exposure of women to environmental xenobiotics, hence, their presence/distribution/source in the environment and potential human health risks has become the focus of much attention in recent times.

1.6 Sources of xenobiotics

There are several sources of xenobiotics[5] some known and others unknown. However, majority of them are from anthropogenic sources of human activity. For simplicity the sources of xenobiotics are going to be grouped into twelve broad groups which indeed might not cover all. The sources include:

1. Energy generation resulting from burning of fuels and also leaks of transformer oils from electrical installations
2. Pharmaceuticals and hospital effluents
3. Electronic waste
4. Industry (Textile, Agro-chemical, paints, etc.)
5. Mining of precious minerals

6. Oil and gas production and processing
7. Agricultural practices
8. Natural emissions
9. Radioactive materials
10. Cigarette smoking
11. Transportation
12. Others

1.7 Transportation

This section will just highlight on some of the emission problems of automobiles. It is known that emissions from vehicles contain a variety of toxic chemicals such as platinum, palladium and rhodium from catalytic converters, lead from vehicles that run on leaded fuels, nickel from vehicles that also run on diesel, cadmium and zinc from vehicular tyres and copper from brakes linings and electrical wires. In addition to the above toxic chemicals from vehicular fallouts is that of persistent organic pollutant (POP), a common example being polycyclic aromatic hydrocarbons (PAHs). Most PAHs in the environment are from vehicular transport due to the incomplete burning of carbon – containing materials like oil, wood, garbage, gasoline, liquefied petroleum gasses and crude or coal [31].

Automotive catalytic converters consist basically of a monolithic honeycomb support made of cordierite (a phase of $2MgO$- $2Al_2O_3$ - $5SiO_2$) treated with an Al_2O_3 wash coat, which in turn contains rare earth oxides of between 0.10 and 0.15% (w/w) platinum (Pt), palladium (Pd) and rhodium (Rh). On the basis of documented evidence produced to date, it is generally accepted that the thermal and mechanical conditions under which such devices work, including abrasion effects and hot-temperature chemical reactions with oil fumes, can cause a significant release of the PGMs to the environment and eventually affect human health [32-33].

Platinum is of particular concern as it has a known mutagenic and toxic effect, even at exceedingly low concentrations, in urban air (affecting human health) and urban water (affecting ecosystem health) [34]. However, this situation raises fears of possible deposition of PGMs in our environment (air, water bodies and soil along the roadways). This deposition will lead to increased concentrations of PGMs in the environment, raising concerns about the environmental impact and toxicity effect of these elements [34].

Barbante et al. (2001)[35] recently reported an increase in PGMs in snow samples from Greenland. Although the amounts measured were low (ng/kg range), concentrations were found to be 40 to 120 times higher for snow dated in the 1990s compared to ice samples dated 7,000 years back [35].

1.8 Main Objective

In order to assess and understand the role of xenobiotics, information is needed with respect to their sources, flow paths, fate (transport, treatment, natural attenuation) and impact on humans, livestock and the environment. Furthermore, it is necessary to have suitable tools like chemical analytical methods or eco-toxicological test methods for collecting the information that is needed in assessing the potential risk.

The aim of this study is to understand the impact of xenobiotics on urban environmental quality with special emphasis on some trace metals and polycyclic aromatic hydrocarbons (PAHs). Levels, distribution and possibly, tracing their sources in order to adopt proper measures to minimise its impact on the environment.

1.8.1 Specific Objectives

The specific objectives will include measuring the PAH and trace metal (metals only in soil) levels, distribution and source/risk assessment of;

- Soils
- Indoor particulate matter
- Water bodies

The result will be compared to international and local/national limits in order to ascertain the health of the studied environments.

1.9 Research methodology

To achieve very good and credible result, standard analytical methods will be followed and certain analytical tools like; Atomic absorption spectrometry (AAS), Gas chromatography/Mass spectrometry (GC/MS/MS), and others would be used.

The research will be in three parts;

(i) Collection of top soil (0 – 5cm) samples for the analysis of trace metals (Hg, Pb, Al and Ni) and polycyclic aromatic hydrocarbons (PAHs)

(ii) Collection of indoor air samples from various households and the exhaust of some ferries for the analysis of PAHs

(iii) Collection of surface water and used ferry oil samples also for the analysis PAHs

(iv) The work will also try to establish an air quality monitoring station at Esbjerg to allow for continuous monitoring in order to investigate the range and profile of xenobiotics (carcinogenic PAHs) content of the harbour environments.

1.10 Statistical analysis

The result would be subjected to statistical analysis.

In order to know the pollution status of different areas of the environment, PAH Isomer Pair Ratios as Diagnostic Source Indicators, source characterization and correlation matrices for the data would also be determined using SPSS software and Excel. According to Tomlinson et al. (1980)[36], indices enable the quality of the environment to be easily understood by non-specialists.

ENVIRONMENTAL XENOBIOTICS

2.0 Xenobiotics: Trace Metals

The presence of trace metals such as Hg, Pb and Ni in the environment has been a source of worry to environmentalists, government agencies and health practitioners. This is mainly due to their health implications since they are non-essential metals [37]. Some trace metals have been classified among the most dangerous groups of anthropogenic environmental pollutants due to their toxicity and persistence in the environment [38-39]. At the biochemical level, it is believed that, the toxic effects caused by excess concentration of these metals include competition for sites with essential metabolites, replacements of essential ions (in co-enzymes), reactions with –SH groups, damage to cell membranes and reactions with the phosphate groups of adenosine diphosphate and adenosine triphosphate [40].

Research has also shown that, trace metals become more concentrated as animals feed on plants and are consumed in turn by other animals. When they reach high levels in the body, heavy metals can become poisonous, or can result in long-term health problems similar to those caused by xenobiotic organic compounds. For example, cadmium in fertilizer derived from sewage sludge can be up-taken by crops and if these crops are eaten by humans in sufficient amounts; the metal can cause diarrhoea and, over time, liver and kidney damage. Lead can get into soil from several sources including vehicular drop outs; children exposed to lead can suffer mental retardation [41].

2.1 Xenobiotics: Polycyclic Aromatic Hydrocarbons (PAHs)

The term, polycyclic aromatic hydrocarbons' (PAHs) commonly refers to a large class of organic compounds containing two or more fused aromatic rings made up of only carbon and hydrogen atoms. The general characteristics common to this class of compounds are said to be high melting- and boiling - points, low vapour pressure, and very low water solubility. PAHs are known to be soluble in many organic solvents and are highly lipophilic[42]. Hundreds of individual PAHs are known to be formed and released during incomplete combustion or pyrolysis of organic matter from industrial processes and other human activities. They are said to be formed whenever wood, coal or oil is burnt and also through natural processes, such as carbonisation, forest fire, prairie fires, volcanic activities and bacterial decay of organic materials (lignins) [43-45].

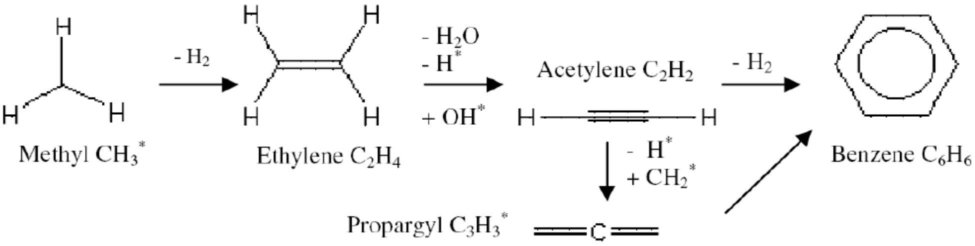
In other words, polycyclic aromatic hydrocarbons (PAHs) is said to form a group of chemical compounds that are ubiquitous in the environment [46]. They are also known for their characteristic properties, such as toxicity and carcinogenity, environmental persistence and tendency for bioaccumulation [46-50]. Their release into the environment is connected with energy and heat production, local heating facilities, vehicle exhausts, refuse burning, coke ovens, and others [43-45].

Polycyclic aromatic hydrocarbons comprise the largest class of chemical compounds, known to be genotoxic agents [43]. Owing to their mode of formation, PAHs are widely distributed in the environment and therefore enter into the food chain, via air, water and soil [51-55].

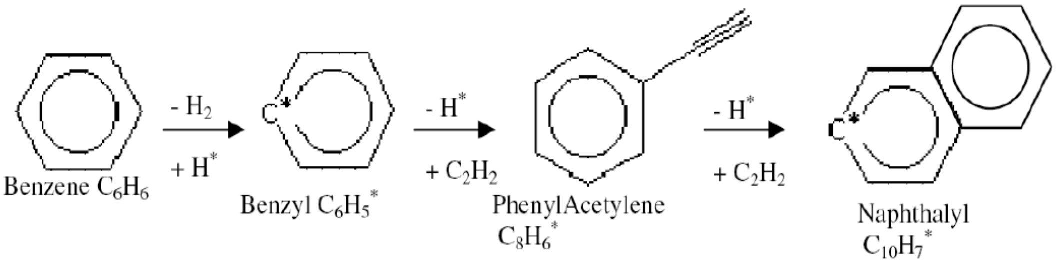
2.2 Formation of PAH

Research has shown that the major chemicals in wood smoke are phenolic and carbonylic compounds, acids, PAH and nitrogen oxides and their reaction products [56]. It has been proposed that PAHs are formed in (wood) smoke by two main routes: either by HACA (hydrogen abstraction/acetylene addition) or by thermal degradation of lignin in the wood. The mechanism as stated in Codex, (2008)[57] proposes that, during pyrolysis, thermal degradation breaks down furan and pyran heterocycles in lignin, which produces a large diversity of volatile (organic) compounds while more stable aromatic cores only lose some side groups.

The smallest pyrolysis product which is involved in soot formation is the methyl radical. A collision of two of these radicals will form ethylene. Next in the soot forming chain are acetylene and a propargyl radical which finally will form benzene [58-59]



Having the first aromatic ring is the rate determining step for further soot formation. Benzene radicals will incept acetylene. This hydrogen abstracted C_2 addition (HACA) mechanism will create an array of polycyclic aromatic hydrocarbons (PAH) [58-59]



This explains why the use of pine wood, with their higher lignin content has been found to have higher concentration of carcinogenic PAHs [60]. Jãkabsone and Bartkevics, (2006)[61] compared the emission rate of benzo(a)pyrene from some wood types. The result indicated that, spruce, hazel-tree, plum-tree and aspen (soft woods) had higher benzo(a)pyrene levels whereas apple-tree, alder and maple (hard woods) had the lowest concentration [61]. This therefore suggests that softwood species resulted in increased levels of benzo[*a*]pyrene compared to the use of hard wood and charcoal[62]. However, this soft – hard wood benzo(a)pyrene emissions has not been totally agreed upon based on other studies [63]. Burning of coconut husk is known to produce more PAH than using coconut shell due to the higher lignin content of the husk [64].

2.3 Distribution of PAHs in the environment

Both indoor and outdoor air quality has attracted much attention in recent times due to certain concerns in relation to public health. Unknowingly, man’s actions keep adding new and old chemicals into the environment every moment and this has made human exposure to polluted air to continue to increase (Directive 2004/107/EC, 2005).

Composition of particulate matter (PM) irrespective of the source is known to include many organic and inorganic matter, nitrogen and sulphur compounds, several heavy metals, radionuclides and polycyclic aromatic hydrocarbons (PAHs) [65-67].

PAHs are regarded as priority pollutants by the U.S. Environmental Protection Agency, since some of them are classified as carcinogenic and mutagenic [15, 68-69]. The largest PAH sources to the atmosphere include emissions from automobiles (traffic emissions [70-72], industrial processes and wood burning.

After being emitted into the atmosphere, they are said to be, redistributed between the gas and particle phases, and subsequently deposited to the terrestrial environment through dry or wet deposition [73]. Before being deposited, they can be transported over long distances. Thus, the soil gets contaminated with PAHs mainly from atmospheric depositions, directly or via vegetation, or in the case of arable soil with biowaste used as fertilizers [47].

PAHs enter surface waters mainly from atmospheric fallout, urban run-off, municipal effluents, oil spillage or leakage and seepages from the soil. After entering the aquatic environment, their behaviour and fate depends on their physicochemical properties.[74-75]. It is known that, volatilization, dissolution, adsorption onto suspended solids and subsequent sedimentation, biotic and abiotic degradation, uptake by aquatic organisms and accumulation are all major processes to which PAHs in water are subjected. Due to their low aqueous solubilities and hydrophobic nature (log K_{ow} ~3–8), the concentrations of dissolved PAHs in water are very low. Otherwise, PAHs associate easily with particulate matter and are finally deposited in the sediment [74-75].

2.4 Health Implications of PAHs in the Environment

On the basis of epidemiological evidence, it has been suggested that several factors associated with an increased risk of cancer (Exposure to certain chemicals, pesticides, and metals can increase an individual's risk for cancer. Carcinogens in this category include nickel, cadmium, vinyl chloride, benzene and tobacco smoke (second hand smoke)) are also associated with an increased risk of atherosclerosis and this indicates that somatic mutation is involved in the formation of the atherosclerotic plaque[76]. PAHs, including dibenz[*a*,*h*]anthracene, dibenz[*a*,*c*]anthracene, 7,12 dimethylbenz[*a*]anthracene and BaP, are known to act as initiators and/or accelerators in atherosclerotic plaque formation in chickens, pigeons and Ah-responsive mice[77-78].

The carcinogenic nature of some PAHs has warranted their inclusion in environmental control legislation. The World Health Organization has recommended the maximum permissible concentration of six representative PAHs (fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*g*,*h*,*i*]perylene and indeno[1,2,3- *c*,*d*]pyrene) not to collectively exceed 200 ng /L in drinking waters[1]. Health Canada and the Ontario Ministry of the Environment (MOE) have established a maximum acceptable concentration (MAC) of 10 ng/L for benzo[*a*]pyrene in drinking waters [74-79]. Ontario Provincial Water Quality Objectives (PWQOs), designed to protect all forms of aquatic life, are more stringent and require individual PAHs not to exceed parts per quadrillion (ppq) (pg/ L) concentrations. PWQOs for anthracene, benzo[*k*]fluoranthene and chrysene are 0.8, 0.2 and 0.1 ng/ L, respectively[75].

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental carcinogens and are said to be metabolized by a variety of xenobiotic-metabolizing enzymes such as cytochrome P450 (P450 or CYP), epoxide hydrolase, glutathione transferase, UDP-glucuronosyltransferase, sulfotransferase, NAD(P)H quinone oxidoreductase 1, and aldo-keto reductase. Studies have shown that, these enzymes mainly participate in the conversion of PAHs to more polar and water-soluble metabolites, and the resultant metabolites are readily excreted from the body. However, during the course of metabolism, a variety of unstable and reactive intermediates of PAHs are said to be formed, and these metabolites attack DNA, causing cell toxicity and transformation. It has been suggested that, P450s and epoxide hydrolase are able to convert PAHs to proximate carcinogenic metabolites, PAH-diols, and these products are further metabolized by P450s to ultimate carcinogenic metabolites, PAH diol epoxides, or by aldo-keto reductase to reactive PAH *o*-quinones [80].

Shimada, (2006)[80] reported of the activation of PAHs by P450 and peroxidases to reactive radical cations that bind covalently to DNA. The report also stated that, oxygenated and reactive metabolites of PAHs are usually converted to more polar and detoxified products by phase II enzymes. Inter-individual differences was seen to exist in levels of expression and catalytic activities of a variety of enzymes that activate and/or detoxify PAHs in various organs of humans and these phenomena are thought to be critical in understanding the basis of individual differences in response to PAHs [80].

Breast cancer is the major cause of cancer death in women worldwide. Williams and Phillips, (2000)[81] reported that, high penetrance genes accounted for only 5% of cases, whereas polymorphic low penetrance genes acting in concert with lifestyle/environmental risk factors are likely to account for a much higher proportion. Genotoxic compounds which are said to implicate human breast carcinogenesis include endogenous compounds, estrogens, and dietary or environmental xenobiotics–heterocyclic amines, aromatic amines, polycyclic aromatic hydrocarbons, and nitro-polycyclic aromatic hydrocarbons [81].

Williams and Phillips, (2000)[81] in their review showed evidence of the role of mammary-expressed enzymes that metabolically activate and/or detoxify potential genotoxic breast carcinogens: cytochrome P-450s, catechol-*O*-methyltransferase, epoxide hydrolase, peroxidases, glutathione *S*-transferases, *N*-acetyltransferases, sulfotransferases, and other enzymes catalyzing conjugation reactions. This information is particularly relevant in the light of evidence for the presence of genotoxic agents that require metabolic activation in mammary lipid, in nipple aspirates and in breast milk, and for the presence of DNA adducts in human mammary epithelial cells (from which most breast carcinomas originate). The evidence for the role of genotoxic carcinogens in the etiology of breast cancer is compelling, but mammary-specific enzyme expression should be taken into account when considering the contribution of polymorphisms to risk [81].

It is a known fact that, maternal smoking during pregnancy has been associated with a variety of adverse neonatal outcomes including altered reproductive performance. Jurisicova et al., (2007)[82] in their study provided molecular evidence for a pathway involved in the elimination of the female germline due to prepregnancy and/or lactational exposure to polycyclic aromatic hydrocarbons (PAHs), environmental toxicants found in cigarette smoke. They also showed that ovaries of offspring born to mice exposed to PAHs contained only a third of the ovarian follicle pool compared with offspring of unexposed female mice. The report indicated that, activation of the cell death pathway in immature follicles of exposed females was mediated by the aryl hydrocarbon receptor (Ahr), as ovarian reserve was fully rescued by maternal cotreatment with the Ahr antagonist, resveratrol, or by inactivation of the *Ahr* gene. Furthermore, in response to PAHs, Ahr-mediated activation of the harakiri, BCL2 interacting protein (contains only BH3 domain), was necessary for execution of cell death. It stated that, this pathway appeared to be conserved between mouse and human, as xenotransplanted human ovarian cortex exposed to PAHs responded by activation of the identical cell death cascade. Their data indicated that maternal exposure to PAHs prior to pregnancy and/or during lactation compromises ovarian reserve of female offspring, raising the concern about the trans-generational impact of maternal smoking on ovarian function in the human [82].

PAHs IN THE SOIL ENVIRONMENT

3.0 PAHs in the soil environment

In recent years man's activities have increased PAH levels in the upper soil layers in most cities. For instance, coal tar has been used for wood preservation and coal is being used to generate energy in many cities. Large amounts of pyrogenic PAHs have been released to the air by combustion of wood, coal, and petroleum used for heating, and PAH-containing particles have been spread in most city environments. It has been reported that emission of PAHs from domestic wood burning is in the range 4 to 380 mg kg^{-1} (median 22 mg kg^{-1}, Σ19PAHs) depending on the combustion conditions [83]. Since the advent of motoring, a considerable amount of petrogenic PAHs has been emitted by diesel, gasoline and liquefied petroleum gas engines. Rogge et al. (1993a)[84] puts the emission PAHs in fine particles from automobiles with no catalyst (gasoline, Σ32PAHs) at 1,406 μg km^{-1}, whereas automobiles with catalytic converters (gasoline, Σ32PAHs) emit only 53 μg km^{-1} [84].

Soil contamination by PAHs (xenobiotics) is considered by many researchers as a good indicator of the level of environmental pollution from anthropogenic sources [73, 85]. It is known to provide information on regional pollution sources, the long-range transport of PAHs, the rates of pollutant retention and their ultimate destination [86-87].

In most studies on the contamination of soils with PAHs, homogenized bulk soil samples are used. However, it has been shown that PAHs may accumulate preferentially on the surfaces of soil aggregates and preferential flow paths [88-91]. As the biological activity (root growth and microbial activity) is higher in the aggregate exterior than in bulk soil[92-93] conventional analyses may underestimate the ecological risk of PAHs in soils. It has been hypothesized that the gradients of PAH concentrations in aggregates are caused by higher inputs of PAHs from the atmosphere or above-lying soil horizons, mainly transported along preferential flow paths in contact with aggregate surfaces, compared with losses by leaching, volatilization, and degradation [88].

Many studies of environmental degradation of PAHs state in their introductions that PAHs are compounds of ubiquitous distribution in the environment. However, most studies then go on to investigate microbial PAH degradation of “hotspot” contaminations like gasworks soil or oil-polluted soil. These hot spots are limited in area, have high PAH concentrations, and the PAHs most often originate from a single, well-defined point source [94].

Diffuse PAH pollution of surface soil, in contrast, is characterized by large area extents, low PAH concentrations, and the lack of identifiable point sources. Diffuse PAH pollution may be equally important considering the large areas and the large volumes of polluted soil [94].

According to Simonich and Hites’ (1994a) [95], model over 50 % of PAHs emitted to the atmosphere from local sources are deposited to soils either through direct deposition or from plant litter (those deposited on leaves) (Figure 1). Soils are major sinks of PAHs and on average; concentrations of these hydrocarbons are said to be 10-100 times higher in soils than in vegetation [96-97]. Thus, substantial amounts of PAHs could be available for uptake by root systems which eventually enter the food chain to affect man.

Fig. 1: A picture showing the deposition of PAH containing particulate matter on the soil

3.1 PAH exposure from the soil environment

There have been some studies suggesting that PAHs are up-taken by plants and their subsequent accumulation and translocation in them even though other studies are not in full agreement [98]. This therefore makes PAHs available in the food. Exposure of these chemicals through ingestion has been noted to be a major route of exposure as most cereals have been noted to have elevated PAH levels [99].

Also children playing on the ground get exposed to PAHs if present in the soil as it is a major sink for most of these air-borne chemicals. Their presence in the soil also threatens ground water as some studies has identified elevated PAH levels in some groundwater as certain PAHs move through soil to contaminate underground water.

With this, it is important that every effort is made at both the individual and governmental levels to minimise the emissions of such xenobiotic organic compounds onto the soil environment. The studies of PAHs on the soil environment are presented in papers 1 and 2 that follows.

Fig. 2: Picture showing soil pollution scenario of PAH containing chemicals

PAHs IN THE AIR ENVIRONMENT

4.0 PAHs in the indoor environment

Indoor air pollution has gained public attention during the last decade. This is so because people spend more of their time in the indoor environments (homes, schools, offices and restaurants). Cooking, heating and tobacco smoking are some of the factors that affect indoor air quality. These activities release a great deal of PAHs, which pollute the indoor environment. Cigarette smoking (combustion of tobacco) generates inhalable particulates matter that is strongly associated with toxic compounds such as PAHs [100], especially the higher molecular weights ones, which are also known to be the most carcinogenic [15, 69, 101]. These sources are considered the most important indoor PAH source [100, 102-103]. However, secondary smoking has also become an important health issue in countries where adult smoking prevalence is over 50%. WHO, (2000) [102] estimated that over 50% of homes are occupied by at least one smoker [104], resulting in high levels of environmental tobacco smoke exposure, that increases the risk factor of developing asthma [104].

Apart from cooking, heating and smoking, indoor air quality is also influenced by outdoor air. Studies have shown that, the presence of potentially carcinogenic PAHs (4-6 rings) in indoor air may have come from outdoor air originated mainly by vehicular emissions [105-106]. The movement of pollutants from outdoor air to indoor air is influenced by certain factors such as geographic location, level of pollutants in outdoor air, type of residence, type of ventilation and the volume of vehicular movement.

There has been a special interest in analysing the exposure to PAHs in indoor environments and evaluating the influence of the main indoor emission sources. Several studies have identified a linkage between the quality of indoor air and the quality of human health. Liu *et al*. (2001)[107] indicated that PAH concentrations in indoor air can be higher than in outdoor air [107].

Fig. 3: Air Pollution picture showing smoke causing pollution from a food shop

4.1 Occurrence in air

Over 500 PAHs and their related compounds have been detected in the ambient air, but most measurements have been made on benzo(a)pyrene (BaP) as the reference carcinogenic indicator [108]. The natural background level of BaP may be almost zero in places where there is no anthropogenic activities. In most developed countries BaP concentrations have decreased substantially over the past 30 years [109]. This is as a result of the increased use of catalytic converters in motor vehicles, a reduction in the use of dirty fossil fuels (coal), increased use of oil and natural gas for energy, and improved combustion technologies [109]. In 1990, a study in Germany looked at three different emissions scenarios and found out that BaP concentrations of areas not affected by emission sources were below 1 ng/m^3, those close to traffic were from 1.77–3.15 ng/m^3, and those stations affected by both traffic and additional industrial emission sources had values of 2.88–4.19 ng/m^3. The annual (1989-1990) average concentration of BaP close to traffic in the Rhine-Ruhr area was reported to be between 3–6 ng/m^3 [110]**.** In Copenhagen, Denmark, the mean BaP levels in ambient air (January to March 1992) at a station in a busy street was found to be 4.4 ng/m^3 [111]. The relationship between the amount of BaP and some other PAHs is generally termed the "PAH profile".

4.2 Occurrence of PAHs in Space

Polycyclic aromatic hydrocarbons (PAHs) have become very widespread beyond one’s imagination as it has been detected in space by an astrochemistry laboratory. “we are interested in PAHs (and other related molecules) because they are very common in space and as a result they can act as probes of conditions in distant regions” as stated by an astrochemist [112]. They went on to say that, the light from the glow of PAHs (they emit light when excited either by heat or radiation resulting in fluorescence activities) has been detected coming from hot regions of space where stars are born, and around dying stars, and even from other galaxies as well. For the astrochemist the presence of PAH in space could be used in their search for life in the Solar System, because of its linkage to anthropogenic activities (because on earth, these molecules are used as biomarkers) [112]**.**

PAHs levels of the air environment (indoor and outdoor) may be considered a serious public health problem, because all people are subject to the conditions of indoor and outdoor air, either by direct exposure or through the natural ventilation in indoor spaces. This study looked at the quality of indoor air of some kitchens in Ghana and Denmark. The report is presented in papers 3 and 4 that follows.

Fig. 4: Air Pollution picture showing smoke causing pollution from open burning

PAHs IN THE WATER ENVIRONMENT

5.0 PAHs in the water environment

Xenobiotic organic compounds (XOC) are of rising concern in the urban water cycle. The major reason is that water supply, urban drainage and wastewater treatment systems in the 20th century were originally designed to solve conventional problems such as for the supply of potable water, prevention of floods and sanitation. Pollutants of concern at the time were focused on the conventional parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), nitrate (NO_3^-), phosphate (PO_4^{2-}) micro-organisms and some metals like iron). There is now the need to understand, in full, the manner, the sources, flow paths, fate (transport, treatment, natural attenuation) and impact of xenobiotics on both humans and environment in this technical system **[113]**.

Many nations and blocks (EU, US) have seen the need to be ahead of time. It is against this backdrop that some EU-countries agreed recently to participate in the COST project to mitigate the possible effect of xenobiotics on human health. The countries are Austria, Belgium, Czech Republic, Denmark, Finland, France, Italy, Latvia, Luxembourg, Netherlands, Norway, Portugal, Romania, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom**[5]**.

The EU-Water Framework Directive has noted that current wastewater treatment technologies only takes care of conventional parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), nitrate, phosphate and micro-organisms. However, chemical pollution in rainfall-runoff and wastewater resulting from atmospheric washout, erosion of building materials, traffic emissions, pesticides application, industrial production, use of household chemicals, personal care products and pharmaceuticals enters the urban water system without any proper treatment.

The integrated nature of the urban water systems and the ability of xenobiotics to spread across structural boundaries and into the environment where ecological systems and humans are exposed calls for holistic, intersectorial and multidisciplinary approach to find affordable solutions to this problem.

Information about the biodegradability, metabolic pathways, conjugation and de-conjugation, sorption, transport in the environment, and persistence of PAHs are needed to predict their fate and impacts and to help in the creation of policy to protect humans and ecosystems from their effects. Research is desperately needed to determine the degradation reactions in soil that transform these PAH compounds to their mineral components.

Fig. 5: Air Pollution picture showing smoke causing pollution from open burning

5.1 Distribution of PAHs in water

Whenever, PAHs enters the water environment, they distribute themselves among various compartments including water, suspended particles, colloidal matter and sediment solids. It has been shown that PAHs associate themselves strongly with colloidal matter or dissolved organic matter (DOM) in aquatic environment, enhancing their apparent solubility but making them less available to the sediment phases [79]. Sediment porewater has been shown to play an important role in PAH speciation. In water environment, studies have shown that only the freely dissolved fractions of PAHs are available for bio-uptake (fish, shell fish and aquatic plants) [74]. Thus, the existence of DOM in the water environment can greatly influence the bioavailability and distribution of PAHs in water[114]

Land based activities and run offs input of PAHs into the marine environment has increased in recent times. Most estuaries have had heavy loads of PAHs. The estuaries serve as a breeding ground for several fish species and as such the presence of PAHs there allows for bioaccumulation of these XOC by the developing fish. It has been suggested that most of the PAHs entering the aquatic environment get localised into rivers, estuaries, sediments and coastal marine water [115]. Jaffe, (1993)[116] observed that after being discharged into the environment; these hydrophobic pollutants are mixed and diluted by turbulence and since they are less sensitive to photo oxidation in water than in air, they are more persistent in the aquatic environment. PAHs in water quickly get absorbed onto particulate matter and get deposited in the bottom sediment. This means that higher concentrations of PAHs are generally found in the sediments and lowest in the water column as reported by Jaffe (1993)[116].

Sediments can therefore serve as a long-term sink for water borne petrogenic polycyclic aromatic hydrocarbons. Petroleum inputs to the aquatic environment will remain in the sediment for a period for several years in quite significant level [117].

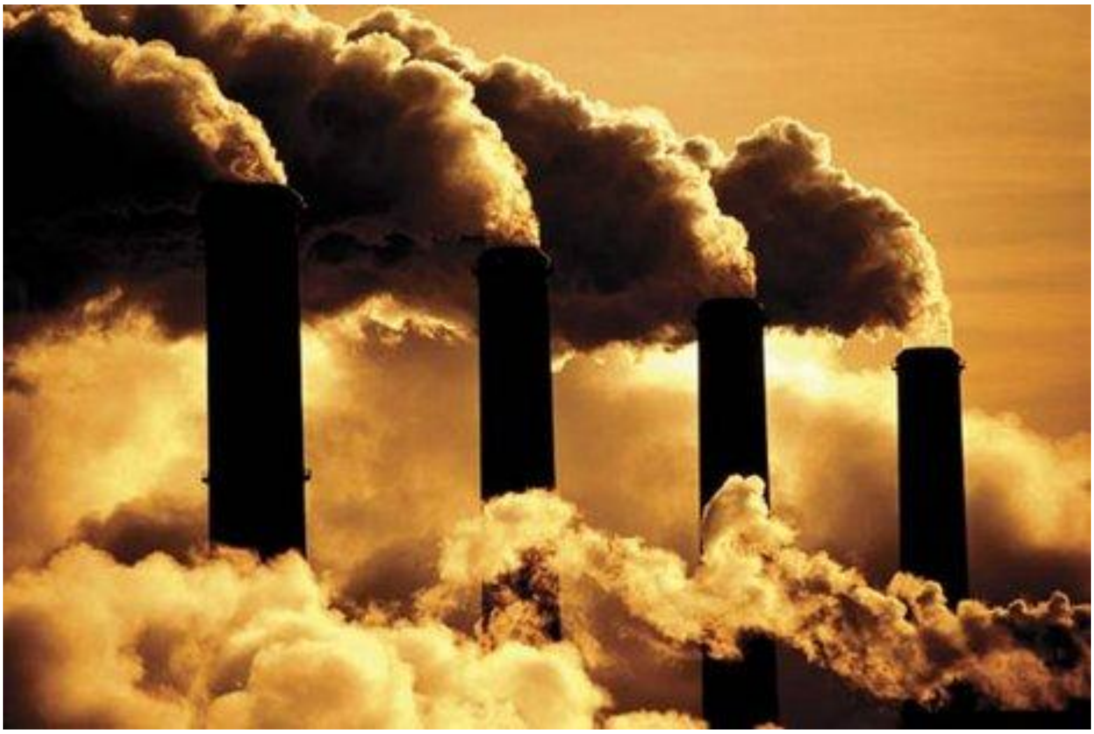


Fig. 6: Air Pollution picture showing industrial air pollution

5.2 PAHs in drinking water

PAHs have been found in some drinking water supplies in the United States. Background levels of PAHs in drinking water range from 4 to 24 ng/L[118]. Distribution and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in drinking water resources were studied for the first time by Ying-Ge et al. (2008) [119] in the Henan Province, China. Water samples collected from four river systems and their tributaries, as well as groundwater resources, were analysed and the total concentrations of the 16 priority PAHs in water samples ranged from 15 to 844 ng/L with a mean value of 178 ±210 ng/L (n= 68). Anyakora and Coker (2009)[120] in a study, sampled water from several hand-dug wells in the Niger Delta region of Nigeria, where, there is extensive crude oil production activities. These water samples were analysed for the presence of 16 US EPA priority PAHs and the sum of their concentrations ranged from 1.92 μg/L to 40.47 μg/L. These concentrations are above the WHO recommended maximum for safe drinking water [120].

GENERAL DISCUSSION

6.0 General Discussion

The report of most of the study is given in the 6 papers that follow, however this section will present an overview of all of them. Generally, there were elevated levels of the polycyclic aromatic hydrocarbons (PAHs) analysed in all the matrixes of the environment. The mean total PAHs analysed in the soil, indoor air and water bodies in Esbjerg city were from, 0.24 mg kg^{-1} to 7.6 mg kg^{-1} d.w, 0.94 to 8.2 mg kg^{-1} d.w and 26.8 µg L^{-1} to 105.5 µg L^{-1} respectively, and their mean total PAHs concentration were also, 2.5 mg kg^{-1} d.w, 3.4 mg kg^{-1} d.w, and 68.4 µg L^{-1} for the ∑6 PAHs respectively.

The mean benzo(a)pyrene (BaP) concentrations for the various matrices in Esbjerg were 0.6 mg kg-^{1}, 0.191 mg/kg and 2.6 µgL-^{1} for soil, indoor air and water respectively. This shows that there are some levels of PAH deposition on the Esbjerg environment which needs attention. Influences from most PAH sources (Energy generation, combustion, industries and transport) are evident. To control PAH emissions, it would be good if public transportation is encouraged.

6.1 Distribution of PAHs in the soil, indoor particulate matter and water bodies

The results show that fluorene and fluoranthene were generally higher than the other PAHs for all the samples analysed. However, except for the water samples, all the 6 PAHs analysed were well distributed in the soil and the indoor air samples.

6.2 PAH diagnostic ratio analysis

In all, the PAH sources could be categorized into three main groups as stated by the Jones Environmental Forensics (2008)[121] PAH diagnostic can be summarised into three distinct groups:

- **Phytogenic** – hydrocarbon compounds derived from plants (phyto = plant)
- **Petrogenic** – hydrocarbon compounds associated with petroleum (petro= petroleum)
- **Pyrogenic** – hydrocarbon compounds associated with the combustion of petroleum, wood, coal etc including creosote, coal tar (pyro = fire/burn)

It is important to note that PAHs from petrogenic sources are usually not persistent and do not accumulate in sediments. By plotting ratios of various PAHs including anthracene / anthracene+phenanthrene; fluoranthene / fluoranthene+pyrene; benzo(a)anthracene / chrysene and fluoranthene / pyrene it is possible to distinguish between combustion and petroleum sources, but caution is always required when reviewing these ratios in isolation, and further analysis including biomarkers is often required. Phytogenic PAHs usually result from peats, lignin, pine and other woody materials

As a result, diagnostic ratios of selected PAH compounds are generally considered to be a good indicator of their sources and the mechanism of transport in the environment. Fluoranthene to fluoranthene (mass 202) plus pyrene (202) (FTH/FTHl+Py) ratio of 0.50 is usually defined as the petroleum/combustion transition point [122], but in practice this boundary appears to be less definitive than 0.10 for Anthracene/178. However, vehicle and crude oil combustion particulates are more uniform with ratios between (0.41–0.49) and closer to the 0.50 boundary than diesel exhaust (particulate plus vapour 0.20–0.58), suggesting that unburned diesel depresses the fluoranthene. Overall, however, the petroleum boundary ratio appears closer to 0.40 than 0.50 for FTH/FTH+Py and ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion, whereas ratios>0.50 are characteristic of grass, wood or coal combustion.

Combustion-derived PAHs (pyrogenic) usually contains the high molecular weight PAHs (HMW-PAHs) which are abundantly generated at high temperature >700^{o}C (lower molecular weight PAHs get into the vapour phase), while the petroleum-derived residues (petrogenic) occurs at a relatively lower temperature >300^{o}C and contains relatively high abundances of low molecular weight PAHs (LMW-PAHs)[123]. The temperatures generated by cars are usually less than 700^{o}C and as such lower molecular weight PAHs are produced. Then, the ratio of LMW/HMW could be an index used to apportion the anthropogenic sources of PAHs. For example, a value of Indeno[1,2,3-c,d]pyrene to indeno[1,2,3-c,d]pyrene plus benzo(ghi)perylene [Ind/(Ind+BghiP)] > 0.5 indicates grass/coal/wood combustion sources (formed by the help of cellulose and lignins). Values of FTH/(FTH+Pyr) > 0.4 indicates pyrogenic sources, and we can distinguish between the values 0.4-0.5 for fuel combustion and > 0.5 for grass/coal/wood combustion sources. The ratio of (LMW/HMW) BaP(252)/BghiP(276) as stated above can also be used as an indicator for the determination of traffic and non-traffic sources, when the value (> 0.6) is characteristic of traffic sources [87, 124]. This means that the higher the ratio (LMW/HMW) BaP(252)/BghiP(276) (> 0.6), more lower molecular weight PAHs are present whiles lower ratio (< 0.6), high molecular weight PAHs are also present.

The summary of the results of the diagnostic ratios obtained for soil, indoor air and water samples collected in Esbjerg shows a strong indication of mixed petroleum and combustion sources of PAHs (mixed biomass, tobacco, coal, diesel and petrol burning). Variations in additional input sources (e.g., high or medium temperature combustion processes, different fossil materials) may also account for the differences in the composition pattern of PAHs between sampling sites [125-128].

6.3 Correlation Analysis

In order to investigate the relationship between the various sampling points, correlation analysis of the PAHs data was conducted using Pearson's method. The result presented show that most of the sampling points were strongly positively related ($r > 0.7$, $p < 0.05$) to each other with regards to the monitored PAHs. This result may suggest that all the sampling sites are almost equally affected by these pollutants from their source(s) or the pollutants to these sites may come from the common sources. This may mean that all the sampling points receive their PAHs from pyrogenic as well as petrogenic depositions [129].

CONCLUSION AND RECOMMENDATION

7.0 Conclusion

The proposed air quality monitoring station is on course. The Moudi and Sootie equipment have been fixed and currently running in the laboratory. A temporal place at the Esbjerg harbour where this equipment have been stationed and the monitoring program is on-going.

The trace metal measurement also showed the presence of lead (Pb), aluminium (Al) and nickel (Ni) with mercury (Hg) levels below the detection limit of the ICP-OES instrument used. The trace metal levels were within acceptable limit and do not seems to pose any immediate health problem.

However, most of the concentrations of the PAHs measured were above acceptable limits in soil, indoor air and water bodies. The results obtained from these studies clearly demonstrate anthropogenic influences of most PAH sources (combustion, industrial, energy and transport) are evident. Most of these PAHs have been classified as carcinogenic and therefore their presence in the environment ought to be minimized to reduce possible cancer risks resulting from their exposure. With the advent of automobile catalytic convertors, the levels of lead (stoppage of the use of leaded fuel), NOx and carbon monoxide have fallen drastically, yet PAHs still remains a problem. Also, most sea going vessels are not fitted with catalytic convertors and as such releases large amount of PAHs and trace metals into the environment. Filters (from Ferry exhaust) and spent Ferry fuel oil analysed gave elevated levels of PAHs. This calls for the need for the development of marine vessel catalyst to reduce PAH emissions.

The diagnostic ratios gave distinct mixed unburned petroleum and combustion situations at most of the studied environments. There was also an observed wood and coal burning situations as well. The correlation analysis identified mixed petrogenic and pyrogenic sources as the main contributors of PAHs on the studied environments.

Carcinogenic PAHs pollution in the studied environments owing to combustion, vehicular, thermal, industry in soil, water, outdoor and indoor air is hitherto a scarcely explored problem. More studies are ongoing to strengthen this database and investigate the range and profile of carcinogenic PAHs content in the studied environments.

The bad news with xenobiotics is that, they are everywhere: in the air you are breathing, the water you are drinking, the food you are eating, the clothes you wear, things you hold and touch - even implanted into your body and therefore one cannot avoid its exposure [130].

7.1 Recommendations

From the results of the studies it is recommended that:

- Further studies should be done to identify the various sources of xenobiotic pollution on the environment.
- The levels of PAHs in groundwater should be determined
- The contribution of PAHs from scooters should be analysed
- People should be encouraged to take public transport

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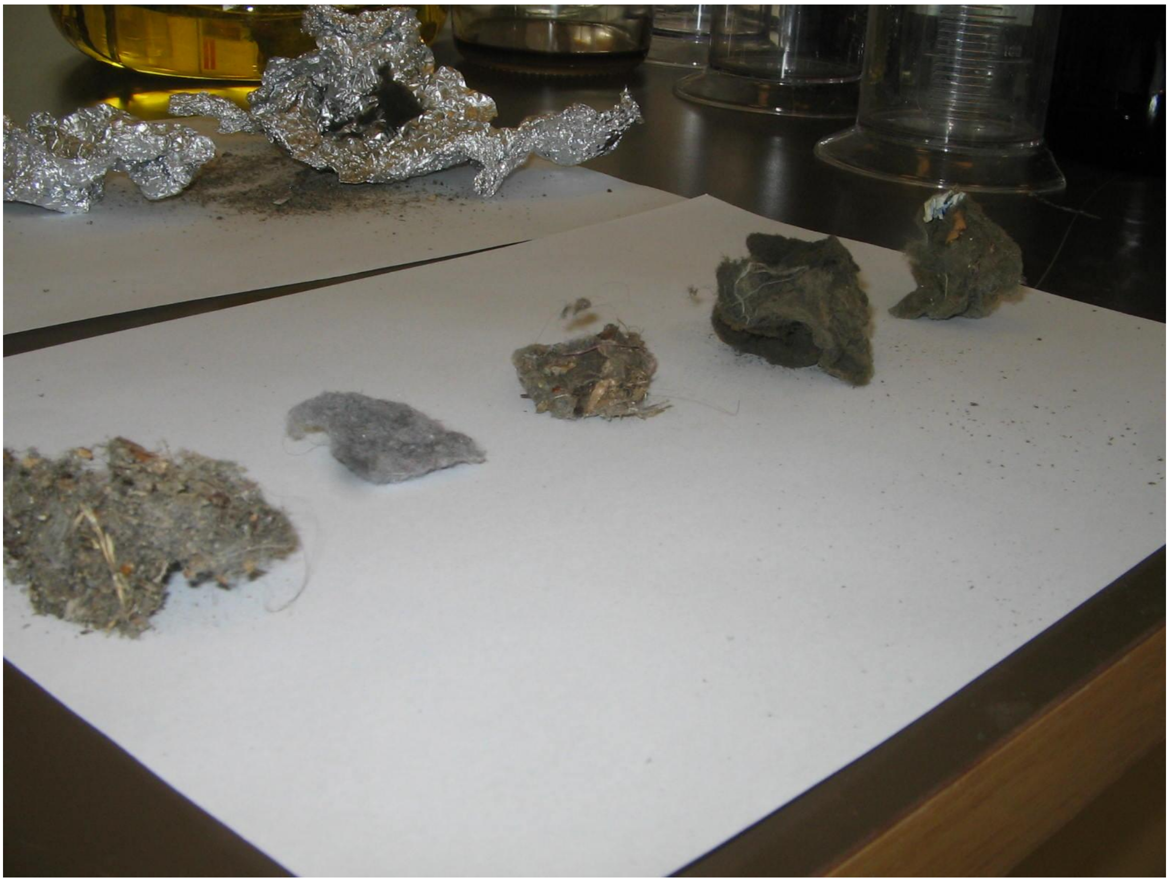

Spider Webb samples

Suppliment 1

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Levels, Distribution and Source Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in Topsoils and Roadside Soils in Esbjerg, Denmark

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Abstract A soil survey was performed to determine the levels, distributions and sources of 6 polycyclic aromatic hydrocarbons (PAHs) in 9 selected soil environments in Esbjerg, Denmark. In all, 24 soil samples were collected and the PAHs present were extracted with dichloromethane and analysed using GC/MS/MS with ion trap detector (TCD). There were elevated levels of the individual as well as the total PAHs in the soil samples and also, all 6 PAHs were present in all the soil samples. The most abundant components were fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene. The average sum of the 6 PAHs in all soil samples was 2.5 mg.kg^{-1}, with range from 0.24 to 7.6 mg kg^{-1}. The total mean PAH concentration obtained was 1.67 times higher than the total limit set by the Danish Environmental Protection Agency (DEPA) whiles the mean benzo(a)pyrene (BaP) concentration (0.6 mg kg^{-1}) also 6 times the Soil Quality Criteria (Human Health) (0.1 mg kg^{-1}) by DEPA and 2 times the Maximum Permissible Concentrations (0.26 mg kg^{-1}) by the Netherlands for BaP. This shows that there are elevated levels of PAH deposition on the Esbjerg soil environment which needs an urgent attention. The diagnostic ratios and the correlation analysis identified mixed petrogenic and pyrogenic sources as the main contributors of PAHs on the Esbjerg environment.

Keywords Source characterization · Polycyclic aromatic hydrocarbons · Top soils · Road dust

Polycyclic aromatic hydrocarbons (PAHs) are a group of dangerous xenobiotic compounds that man introduces into the environment in large quantities daily with little or no awareness. These are a suit of organic compounds released into the environment as gas particles during incomplete combustion of organic material. PAHs have a number of sources including: mobile sources such as cars, buses, trucks, ships, and aircrafts; industrial sources such as power generation, steelworks, coke ovens, aluminium production, and cement kilns and oil refining (Biswas et al. 2003). Domestic sources include combustion for heating and cooking especially solid fuel using coal and wood. Fires and smokes resulting from burning of vegetation in agricultural process, bushfires, grilling of food, or tobacco smoke (Arias-Estévez et al. 2007) results in the releases of large amount of PAHs into the environment.

Polycyclic aromatic hydrocarbons (PAHs) occur ubiquitously in the environment (Liu et al. 2005) and can be found in sediments, soils and water either in solution or adsorbed on particulate material. Most PAHs in the environment are from incomplete burning of carbon—containing materials like oil, wood, garbage or coal. Even though PAHs are associated with combustion processes, it has also been suggested that biological sources may be more important than previously assumed. There is some evidence that at least some PAHs are produced biologically.

Thus, the soil is contaminated with PAHs mainly from atmospheric depositions, directly or via vegetation, or in the case of arable soil with biowaste used as fertilizers (Maliszewska-Kordybach et al. 2008). Soil contamination by PAHs is considered to be a good indicator of the level of environmental pollution by human activities (Chung et al. 2007). It can provide information on regional pollution sources, the long-range transport of PAHs, the rates of pollutant retention and their ultimate destination (Nam et al. 2008; Yin et al. 2008).

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Health effects resulting from PAH exposure have been discussed extensively in recent times (Shen et al. 2008). This include growth retardation, low birth weight, small head circumference, low IQ, damaged DNA in unborn children and the disruption of endocrine systems, such as estrogens, thyroid and steroids. Skin changes (thickening, darkening, and pimples) and reproductive related effects such as early menopause due to destruction of ovum have also been identified with PAHs. PAHs are dangerous, thus, increases risk of cancer (breast cancer) and creates advance glycogen end product which leads to an increased risk of coronary heart disease and diabetes (Anyakora et al. 2004; Gray 2008). PAHs from soil and water are very dangerous to human health because plant root uptake, bioconcentrate and translocate them (Liu and Korenaga 2001).

In 2002, air quality was measured in four Danish cities and at two background sites. Nitrogen dioxide (NO_2) and PM $_{10}$ were at several stations found in concentrations above the new EU limit values, which member States would have to comply within 2005 and 2010. Esbjerg a Danish harbour city in southwest Denmark has not had its air quality measured over the period under review. Esbjerg with a population of 71,025 (2009) is the fifth largest city in Denmark. Its municipality has a population of 114.806 (Esbjerg Kommune: Population in Esbjerg 2nd quarter 2009). Esbjerg derives most of its energy from coal-run power plant and incineration facility which are all possible sources of PAHs in the environment (Biswas et al. 2003).

Although private car ownership in Esbjerg is low by OECD standards (35 vehicles per 100 persons), the number of diesel-powered cars increased in the last decade, resulting in high PM pollution in closure to traffic roads. From 1985 to 2004, usage of diesel fuel in the transport sector increased by 32%. Estimates show that the concentration of PM 2.5 can be reduced by 20% by installing filters on all diesel-power/heavy vehicles in Denmark even very old ones and by introducing more low emissions zones in the cities (Ministry of Traffic 2003). It would be very helpful to also improve education about eco- driving.

A study by Stepien et al. (2010) concluded that the average measured concentrations of PM 10 in 8 sites out of 13 of Esbjerg were above 20 $\mu g/m^3$. The particulate matter levels from the study were quite high compared to the annual national averages in Denmark. The reason for such a high PM pollution in the city of Esbjerg has been investigated and three possible main PM sources were identified; vehicular traffic, industrial activities and the activities at the harbour (Stepien et al. 2010).

The present study looked at the levels, distribution and characterized the possible sources of the 6 carcinogenic/mutagenic polycyclic aromatic hydrocarbon depositions on the soils of the Esbjerg environment.

Materials and Methods

Top soils (at the depth of 0–5 cm) used in this study were collected from 9 main different functional sections in the Esbjerg area. These sampling areas could be categorized into industrial, non—industrial and roadside. Road dust soil samples were also collected for comparison. In total 24 soil samples were collected, and each sample consisted of 3–4 sub-samples collected randomly from the surrounding of each site and bulked together to form one composite sample. Among the 24 soil samples, 6 were from roadsides (Station, Beach Area), 9 were from an incineration facility and a power plant (Incineration, 100 m off Incineration Plant, Power Plant), 3 were from industrial areas (Industrial Area), 3 were from waste water treatment facility (WWTA) and 3 road dust soils. All the samples were immediately wrapped in an aluminium foil and transported to the laboratory. The composite soil samples were air dried for 4 days and sieved through 2-mm mesh after removing stones, residual roots and other unwanted materials, then sealed in an aluminium foil and kept in the refrigerator prior to analysis of PAHs.

Dichloromethane, acetone, acetonitrile, isooctane and cyclohexane solvents were of chromatographic grade and purchased from Sigma–Aldrich, Germany. The stock reference standard of 6 PAHs (not a mixture) from Sigma–Aldrich, Germany includes fluorene, fluoranthene, benzo (k) fluoranthene, benzo (b) fluoranthene, benzo (a) pyrene, and benzo (ghi) perylene at 98% purity.

Soil samples (about 10 g dry weight) were weighed precisely and were then covered with 50 mL dichloromethane (DCM) and sonicated for 24 h at room temperature (Jorgensen 1999; Guerin 1999). The particle/liquid suspension and additional DCM used to rinse the jar were then filtered using a 0.2-μm pore size PTFE filter. The solvents were removed by rotary evaporation after adding 5 mL of isooctane and 3 mL internal standard Methylheptadecanoic acid (IS MHD). This was further concentrated (at 55°C) to approximately 2 mL prior to clean-up. The samples were cleaned up using solid phase extraction (SPE) columns (Isolute SPE column USA: Isolute PAH 1.5 g/6 mL Part # 927-0150-C). Dichloromethane was used to elute the PAH fractions from the SPE (Cui et al. 2002) and finally evaporated to dryness under a gentle stream of pure nitrogen, then dissolved to 3 mL with cyclohexane for analysis of the PAHs. The final concentrated extracts from the soil samples were analyzed using Varian 8200 Cx Auto Sampler and Varian 3800 GC coupled with Varian Saturn 2000 GC/MS/MS with ion trap detector (TCD).

The analytical precision and recovery was checked by the analysis of variance for each triplicate of soil samples and PAH results were not significantly different at the 95%

confidence level. There was a 98% recovery of each triplicate analysis of the internal standard Methylheptadecanoic acid (IS MHD). The internal standard was also run along with the samples to ensure accurate readings. The Limits of Detection (LOD) is as follows: [fluorene, benzo (k) fluoranthene, benzo (b) fluoranthene, benzo(a)pyrene and benzo(ghi)perylene] = 0.001 mg kg^{-1} and [fluoranthene] = 0.005 mg kg^{-1}.

Results and Discussion

The total PAHs in topsoil of Esbjerg city were from 0.24 mg kg^{-1} to 7.6 mg kg^{-1} (dry weight) (Table 1), and the mean concentration of total PAHs was 2.5 mg kg^{-1} for the 6 PAHs. The total mean concentration obtained is 1.67 times higher than the total limit set by the Danish Environmental Protection Agency (DEPA) (1.5 mg kg^{-1}) (CCME (Canadian Council of Ministers of the Environment) 2008). High molecular weight PAHs with 4–6-rings had elevated levels of the total soil PAHs in topsoil of Esbjerg city.

The mean benzo (a) pyrene (BaP) concentration in Esbjerg soil is 0.6 mg kg^{-1} and this value is 6 times the Soil Quality Criteria (2002) (Human Health) (0.1 mg kg^{-1}) set by DEPA (2002) and 2 times that of the Maximum Permissible Concentrations (0.26 mg kg^{-1}) set by the Netherlands for BaP (CCME (Canadian Council of Ministers of the Environment) 2008). This shows that there are elevated levels of PAH deposition on the Esbjerg soil environment which needs an urgent attention.

The highest concentrations of the 6 selected PAHs were identified in soils which were very close to heavily traffic roads and near an incineration facility. Influences from most PAH sources (industrial and transport) are evident. The PAH atmospheric dispersion is greater in areas with heavy vehicular activity, and a high level of PAH deposition occurred at roadside soils.

All the 6 PAHs analysed (fluorene, fluoranthene, benzo (k) fluoranthene, benzo (b) fluoranthene, benzo(a)pyrene and benzo(ghi)perylene) were present in all the top soil samples (Table 1). However, fluoranthene was generally higher than the other PAHs at almost all the nine (9) sites. A similar study conducted in Great Britain (Barnabas et al. 1995) stated that fluoranthene usually has the highest concentrations in topsoil. In fact, total PAH concentration in main roadsides soils recorded 7.6 mg kg^{-1} with benzo (a) pyrene concentration of 2.2 mg kg^{-1} which is about 30%. The benzo(a)pyrene levels are high and there is the potential for exposure to high levels of carcinogenic PAHs for road users and those living in those areas (Essumang et al. 2006). In Esbjerg, most of the residential areas are very close to major roads thereby putting many people at the risk of PAH exposure. The high levels of benzo(a)pyrene in the soils is an indication of both pyrogenic and petrogenic sources of PAH pollution on the environment. This is quite worrying as BaP is a known carcinogen (Denissenko et al. 1996).

Polycyclic Aromatic Hydrocarbons (PAH) ratios of selected compounds are generally considered to be a good indicator of the pollution sources and of the mechanism of PAH transport into the soil. The ratios Ind/(Ind + BghiP) and Flt/(Flt + Pyr) are often used to distinguish between pyrogenic and petrogenic sources. Combustion-derived PAHs (pyrogenic) usually contains the high molecular weight PAHs (HMW-PAHs) which are abundantly generated at high temperature, while the petroleum-derived residues (petrogenic) contain relatively high abundances of Low molecular weight PAHs (LMW-PAHs) (Mai et al. 2003). Then, the ratio of LMW/HMW could be an index used to apportion the anthropogenic sources of PAHs.

Table 1 Mean concentration of PAHs in the soils of the Esbjerg environment (n = 3) in mg/kg

PAHs	Fluorene	Fluoranthene	Benzo (k) fluoranthene	Benzo (b) fluoranthene	Benzo(a) pyrene	Benzo(ghi) perylene	$\sum$6 PAHs (Total)
Station	0.02	1.3	0.85	0.32	0.54	0.29	3.31
Industrial area	0.01	0.43	0.04	0.04	0.03	0.02	0.57
Incineration	0.01	0.36	0.03	0.04	0.06	0.03	0.53
Power plant	0.03	0.11	0.02	0.02	0.04	0.02	0.24
100 m off incinerat Plant	0.04	0.91	1.0	1.6	1.7	1.4	6.70
Beach area	0.02	0.80	0.75	0.27	0.37	0.28	2.50
WWTA	0.02	0.21	0.08	0.05	0.05	0.05	0.47
Harbour	0.05	0.48	0.08	0.09	0.02	0.06	0.78
Road dust	0.05	2.0	1.65	0.62	2.2	1.1	7.6
Averages	0.03	0.73	0.50	0.34	0.55	0.36	2.5
Std. Dev.	0.015	0.605	0.588	0.526	0.812	0.511	2.820
Variance	0.00002	0.366	0.345	0.277	0.660	0.261	7.954

A value of Ind/(Ind + BghiP) >0.5 indicates grass/coal/wood combustion sources. Values of Flt/(Flt + Pyr) >0.4 indicates pyrogenic sources, and we can distinguish between the values 0.4 and 0.5 for fuel combustion and >0.5 for grass/coal/wood combustion sources.

The ratio of (LMW/HMW) BaP(252)/BghiP(276) as stated above can also be used as an indicator for the determination of traffic and non-traffic sources, when the value >0.6 is characteristic of traffic sources (Maliszewska-Kordybach et al. 2008; Yin et al. 2008). The values of Ant/(Ant + Phe) <0.1 and Baa/(Baa + Chry) <0.2 correspond to petrogenic sources; values >0.1 and >0.35, respectively, indicate pyrogenic sources. The values of the ratio Baa/(Baa + Chry) between 0.20 and 0.35 indicate mixed petrogenic and pyrogenic sources (Pies et al. 2008; Zhang et al. 2006).

The ratios in this study demonstrated mixed petroleum and combustion source with values ranging from 0.014 to 2.623. Most of the BaP/BghiP ratios were between 0.96 and 2.071 (>0.6) indicating traffic sources of PAHs (Maliszewska-Kordybach et al. 2008; Yin et al. 2008; Plachá et al. 2009). The station sites shows petrogenic source with mixed unburned petroleum source (<0.1 and <0.4) and with values >0.35 demonstrating predominance of combustion source. Almost all the results showed similar trends with those close to highway (100 m of Incineration Plant, Beach Area and Harbour) demonstrating distinct mixed unburned petroleum and combustion situations (Yunker et al. 2002; Zhu and Wang 2004). There is also wood burning and coal burning situations observed with values ranging from 1.2 to 5.0 for B(k)F/B(ghi)P and BaP/BghiP ratios for all the sites except for WWAT (Maher and Aislabie 1992). The diagnostic ratios are presented in Table 2.

There were similar variation patterns for the PAHs especially for fluoranthene and benzo(ghi)perylene at all the sites which may indicate a common emission sources. These two are among other five PAHs which are considered vehicular markers (García-Alonso et al. 2003) meaning that there is enormous contribution from vehicular emissions.

To assess PAH associations and their possible origins, correlation analyses were conducted among the concentration of the individual PAHs in the soil samples. It is known that where two compounds have a common source, there is more likely to be a correlation between their concentrations (Gilbert et al. 2006). Strong positive significant correlation was observed between individual PAH benzo(ghi)perylene and benzo(b)fluoranthene showing the highest PAH interrelationship with correlation coefficient of 0.983 followed by benzo(b)fluoranthene/benzo(k)fluoranthene (0.967),benzo(b) fluoranthene/benzo(ghi)perylene (0.950) with benzo(b) fluoranthene/fluoranthene, benzo(ghi)perylene/fluoranthene, benzo(k)fluoranthene/fluoranthene correlated at 0.900 and 0.883 respectively significant at 0.01 levels. The least significant correlation at 0.05 significant level was between benzo(k)fluoranthene and benzo(a)pyrene (0.800) (Table 3). The following pairs also interrelated strongly at the significant level of 0.05: benzo(ghi)perylene/benzo(a)pyrene (0.783), benzo(a)pyrene/benzo(b)fluoranthene (0.733) and benzo(ghi)perylene/fluoranthene (0.717).

The results reveal that these compounds, to a lesser extent fluoranthene, were possibly derived from a common anthropogenic origin. No significant correlation was identified between fluorene and any of the other PAHs compounds measured which indicates heterogeneous source of these PAHs.

Interrelationships among sampling sites were also analysed by Spearman's correlation method and the result is reported in Table 4. Strong positive correlation was identified between WWTA and station which was the highest followed by WWTA and industrial area with correlation coefficient of 0.943 and 0.928 respectively at 0.01 significant level. Other strong positive significant correlation

Table 2 Sample sites/PAH Ratios

Sample site/PAHs ratios	F/F + FTH	FTH/FTH + BkF	B(k)F/B(ghi)P	BaP/BghiP	BkF/BkF + BbF	BbF/BbF + BaP
Station	0.014	0.606	1.285	1.891	0.729	0.369
Industrial area	0.023	0.919	1.727	1.409	0.5	0.551
Incineration	0.037	0.917	1.179	2.071	1	0.376
Power Plant	0.213	0.828	1.211	2.052	0.511	0.361
100 m of incineration plant	0.046	0.476	0.735	1.259	0.378	0.489
Beach area	0.027	0.516	2.623	1.296	0.733	0.425
WWTA	0.101	0.717	1.68	0.96	0.609	0.529
Harbour	0.091	0.855	1.266	0.375	0.485	0.782
Road dust	0.023	0.548	1.498	1.961	0.725	0.224

Fluorene (F), Fluoranthene (FTH), Benzo(b, k) Fluoranthene [B(b)F], Benzo (k) Fluoranthene [B(k)F],Benzo(a)pyrene (BaP), benzo(ghi)perylene [B(ghi)P]

Table 3 Correlation of the PAHs

	Fluorene	Fluoranthene	Benzo (k) fluoranthene	Benzo(b) fluoranthene	Benzo(a)pyrene	Benzo(ghi) perylene
Fluorene	1					
Fluoranthene	0.25	1				
Benzo (k) Fluoranthene	0.367	0.883**	1			
Benzo (b) Fluoranthene	0.417	0.900**	0.967**	1		
Benzo(a)pyrene	0.117	0.717*	0.800**	0.733*	1	
Benzo(ghi)perylene	0.433	0.883**	0.950**	0.983**	0.783*	1

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Table 4 Correlation of PAHs with the sampling sites

	Station	Industrial area	Incineration	Power plant	100 m off incineration Plant	Beach area	WVWA	Harbour	Road dust
Station									
Industrial area	0.899*	1							
Incineration	0.829*	0.812*	1						
Power plant	0.543	0.348	0.6	1					
100 m off Incineration plant	0.086	0.087	0.371	−0.257	1				
Beach area	0.943**	0.754	0.714	0.486	0.029	1			
WWTA	0.829*	0.928**	0.6	0.143	−0.086	0.771	1		
Harbour	0.543	0.812*	0.429	0.029	−0.257	0.429	0.886*	1	
Road dust	0.771	0.493	0.771	0.543	0.429	0.829*	0.371	−0.029	1

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

coefficients at 0.05 levels were as follows: industrial area/station (0.899), harbour/WWTA (0.886), Road dust/Beach area and Incineration/Station, WWTA/Station (0.829) as well as Harbour/Industrial area and Incineration/industrial area recording 0.821. This demonstrates that, the sources of PAHs in these areas are likely coming from a common source. Power plant and 100 m off-incineration plant did not show any interrelationship with any of the other sites which probably means different source of pollution to these two areas. As it has been shown by the PAH diagnostic ratios of source assessment, it could be inferred that those areas correlated may be linked to petrogenic sources of pollution.

The result obtained from this study clearly demonstrates that the influences from most PAH sources (industrial, energy and transport) are evident. The average concentration of PAHs in the soil ranged from 0.029 mg kg^{-1}, for fluorene to 0.734 mg kg^{-1} fluoranthene. Most of these PAHs have been classified as carcinogenic and therefore their presence in the environment ought to be minimized. All the 6 PAHs analysed were present in the soils at significant levels exposing people to the harmful effects of these chemicals. The diagnostic ratios gave distinct mixed unburned petroleum and combustion situations (Zhu and Wang 2004; Yunker et al. 2002). There was also an observed wood and coal burning situations with values ranging from 1.2 to 5.0 or B(k)F/B(ghi)P and BaP/BghiP ratios for most of the sites (Maher and Aislabie 1992). The correlation analysis identified mixed petrogenic and pyrogenic sources as the main contributors of PAHs on the Esbjerg environment.

Carcinogenic PAHs pollution in Esbjerg owing to vehicular, thermal, industry in both outdoor and indoor air is hitherto a scarcely explored problem. More studies are ongoing to strengthen this database and investigate the range and profile of carcinogenic PAHs content in the Esbjerg environment.

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Source Assessment and Analysis of Polycyclic Aromatic Hydrocarbon (PAH's) in the Oblogo Waste Disposal Sites and Some Water Bodies in and around the Accra Metropolis of Ghana

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Abstract

The study looked at the levels of polycyclic aromatic hydrocarbons (PAHs) in leachates from a solid waste disposal site and an effluent from an oil refinery in some water bodies around Accra. Sixteen (PAHs) were extracted simultaneously by solid phase and analysis by gas chromatograph. The results of this study generally demonstrated that there were elevated levels of PAHs in the water sample of the Densu River, Chemu, Korle and Kpeshi Lagoons. The average concentration of PAHs in the water ranged from 0.000 of many of the PAHs to 0.552µg/L, for Acenapththene to 11.399µg/L for Benzo (ghi) perylene of the Chemu Lagoon, 0.00µg/L for Benzo (a) Pyrene to 8.800µg/L for Benzo (ghi) perylene (Korle Lagoon) and 0.052µg/L for Pyrene to 4.703ug/L for Acenaphthylene of the Kpeshi Lagoon and 0.00µg/L for pyrene to Acenaphthylene 2.926µg/L of the Weija Dam. Concentrations ranging from below detection level to 14.587µg/L were also recorded at the Oblogo solid waste dump and it's environ. The Weija dam supply over two million gallons of portable water daily to the people of Accra and the levels of the PAH determined is worrying, as a result, the Oblogoh disposal site ought to be re-located to avert any possible epidemic.

Keywords: Accra Metropolitan Assembly (AMA), Oblogo Dumping Site, Weija Dam, Densu River, PAHs, Chemu Lagoon, Korle Lagoon, Kpeshi Lagoon

1. Introduction

The disposal of wastes by land filling or land spreading is the ultimate fate of all solid wastes, whether they are residential wastes collected and transported directly to a landfill site, residual materials from materials recovery facilities (MRFs), residue from the combustion of solid waste, compost or other substances from various solid waste processing facilities. Disposing of solid waste in open dumps and burning of such solid waste, is the most common solid waste disposal method in Ghana. Open dump and burning of their content which is a health hazard, is not an acceptable method of solid waste disposal and must henceforth, be discouraged. For example, vinyl chloride and polythene form greater proportion of the solid waste in terms of volume as a result of the packaging industry [1]. Solid waste includes domestic refuse and discarded solid materials such as those from commercial, industrial and agricultural operations. They contain increasing amount of paper, cardboards, plastics, glass, packing materials and toxic substances. Combustion of these wastes completely and incompletely results in the production of toxic and corrosive chemicals such as PAH's, PCB's and hydrogen chloride just to mention a few [1].

Leachates from solid waste disposal sites which are chemicals removed from the waste as a result of water passing through is one of the major soil and water pollutants. These leachates are released into water bodies which tend to pollute them and needs to be monitored. A comprehensive waste management program must combine a variety of social, transportation, and treatment technologies. Components, in order of desirability, include prevention of wastes at the source; reuse, recycling, or composting; energy recovery; and putting in a landfill only those materials not amenable to other strategies [2].

The plan should consider impacts on air quality, water quality, traffic, noise, odor, socioeconomic effects, and community acceptance [3]. A modern sanitary landfill is not a dump; it is an engineered facility used for disposing of solid wastes on land without creating nuisances or hazards to public health or safety, such as the breeding of rats and insects and the contamination of ground water [4]. This is not the case in Ghana as open dumping and burning of solid waste is the only way of treating waste in Ghana.

Solid waste comes from various sources. Other forms of waste that can vary by location include agricultural waste, mining waste, and hazardous waste. Waste streams differ in the following attributes: physical (e.g., compatibility, density); combustion (temperature, residual ash percentage, heat content in BTUs); chemical composition, percentage of nitrogen, carbon, oxygen, chlorine; and concentrations of toxic polycyclic aromatic hydrocarbons (PAHs) and metals; potential for recycling various components; and ease of separation [3].

Polycyclic aromatic hydrocarbons (PAHs) are another group of dangerous compounds which man introduces into the environment in large quantities with little or no awareness. These are a suit of organic compounds release into the environment as gas particles during incomplete combustion of organic material. PAHs have a number of sources including: Mobil sources such as cars, buses, trucks, ships, and aircrafts; industrial sources such as power generation, steelworks, and coke ovens, aluminum production, and cement kilns, oil refining as well as waste from incineration. Domestic sources include combustion for heating and cooking especially solid fuel using coal and wood. Fires and smoke resulting from burning of vegetation in agricultural process, bushfires, grilling of food, or tobacco smoke [5].

These compounds (PAHs) are also cumulative and may cause a whole lot of health related complications ranging from mutations in lower animals to cancerous cells in humans [5,6]. Other environmental factors affect the distribution of PAHs. For example it has been proved by Shahunthala 2006 that increases in salinity decreases the exposure of PAHs and also dispersant effectiveness decreased only at the highest salinity. Hence, risks to fish of PAH from dispersed oil will be greatest in coastal waters where salinities are low [7].

The smallest member of the PAH group is naphthalene, a two-ring compound, which is gaseous at room temperature. PAHs are usually found as a mixture containing two or more of these compounds, such as soot. PAHs are highly potent carcinogens that can produce tumors in some organisms at even single doses; but other non-cancer-causing effects are not well understood [8]. PAHs can occur naturally or can be man-made. Manufactured PAHs usually exist as colorless, white, or pale yellow-green solids. PAHs are commonly found in coal tar, crude oil, creosote, and roofing tar. Some are used in medicines or to make dyes, plastics, and pesticides [9]. Man made sources such as automobile exhausts and coal burning contribute far more PAHs to the environment than natural sources.

PAHs are dangerous, thus, increases risk of cancer and creates advance glycogen end product which leads to an increased risk of coronary heart disease and diabetes [10]. Laboratory and field evidence indicates that PAHs induce neoplastic and genotoxic effects in aquatic biota. Data from mammals indicate that these animals may be susceptible to such effects, but no studies were identified documenting such effects in wild mammals. PAHs known for their carcinogenic, mutagenic (gene mutation causing agent) and teratogenic (chemicals that affect the normal development of foetus) properties are Benzo[a] pyrene, Benzo[a]anthracene chrysene, Benzo[b] fluoranthene, Benzo [j]fluoranthene, Benzo[k] fluoranthene, Benzo [ghi] perilene, coronene, Dibenz[a,h] anthracene ($C_{20}H_{14}$), Indeno [1,2,3-cd]pyrene ($C_{22}H_{12}$) and ovalene. Mice that were fed high levels of one PAH during pregnancy had difficulty reproducing and so did their offspring. These offspring also had higher rates of birth defects and lower body weights. It is not known whether these effects occur in humans. Animal studies have also shown that PAHs can cause harmful effects on the skin, body fluids, and ability to fight disease after both short- and long- term exposure. But these effects have not been seen in human beings. Some people who have breathed or touched mixtures of PAHs and other chemicals for long periods of time have developed cancer [11].

Some PAHs have caused cancer in laboratory animals when they breathed air containing them (lung cancer), ingested them in food (stomach cancer), or had them applied to their skin (skin cancer). A research conducted by the Agency for Toxic Substances and Disease Registry [12] under the Canadian department of Health and Human services in the year 2007, ranked PAHs as the sixth most hazardous substance among a number of 275 compounds on which the research was conducted. According to the research the first six most hazardous compounds were arsenic, lead, mercury, vinyl chloride, polychlorinated biphenyls and PAHs.

Although solid waste can be properly treated before disposal, solid waste problem arise from; rapid increase of human population, aggregation of people in urban areas (rapid advance in technology and social attitudes).

Solid waste materials pose a serious threat because the leach from it remain in place for a relatively longer period of time unless removed, burned or otherwise destroyed [13]. The combustion of solid waste leads to the formation of PAHs and the main problem of this study is to analyze the concentration of PAH in the leach from solid waste disposal site since burning of solid waste is the only way of treating waste in Ghana. The leachates from this waste deposition site run into water bodies eg. Densu River flows to join Weija Dam and other lagoons in Accra Metropolitan Assembly. The Ghanaian ecosystem plays host to a number of lagoons which serve various functions. The most important of them is being the home for various species of fish. For example the tilapia which is a delicacy in most Ghanaian communities finds its haven in most of the lagoons. The Kpeshie, Korle, and the Chemu lagoons (all in the greater Accra region), the Fosu lagoon (central region) and others throughout the country until recently had been a good sources of fish (mainly tilapia). The Korle lagoon, owing to its extent of pollution, not much living things were present in it for some years, it has recently been dredged. Its scent wafts back to envelope the adjoining shanty town which is the home of hundreds of families who, because they have no sanitation facilities, have turned the shores of the lagoon into a giant latrine. Large portions of the Kpeshie lagoon and it mangrove at La an Accra suburb are being reclaimed and sold to individuals for residential and business development purposes. As a result the lagoon and it mangrove are disappearing fast. Extensive portion of the lagoon have been filled with sand, construction debris and garbage ready to be sold to prospective buyers.

In addition the Korle, Kpeshie and the Chemu lagoons are close to solid waste disposal site and are near major roads used by various kinds of motorists which emit smoke continuously into the environment. Also near the Korle lagoon is located a slaughter house which produces smoke continuously from the processing of hide using car tire. The Chemu lagoon located in Tema New town is being exposed to smoke from vehicles. It is also close to the Tema oil refinery which continuously emits smoke into the environment. Due to the above mentioned facts it is suspected that the Korle, Kpeshie, and the Chemu lagoons may have considerable amounts of PAHs dissolved in them. It is in this views that this study has been designed to determine the level and distribution of PAHs in leachates from the Oblogo solid waste disposal site, waters of the Korle, Kpeshie and the Chemu lagoons and their interrelationships with physiochemical parameters such as pH, salinity, chloride, turbidity and conductivity in the greater Accra regions of Ghana.

2. Materials and Methods

2.1. Sample Collection

Samples were collected from Oblogo solid disposal waste site, Weija dam and the down stream of River Densu (thus, the mixture of the Weija dam and leach) as well as three lagoons namely, Kpeshie, Korle and the Chemu lagoons. These samples were taken from different points on the lagoons so as to get fairly representative samples of each of the lagoons. Three samples were taken from each of the lagoons and four samples from oblogo solid waste site bringing the total number of samples taken to thirteen. Since all the three lagoons were connected directly to the sea, all the first samples taken were made closer to the sea and the other two taken from different intervals (0.5km) from the bank of the lagoons.

Clean amber glass bottles were used in the collection of the sample to prevent sunrays and it effect on any present bacteria. The amber glass bottles were washed with detergents (liquid soap) and rinsed with lot of water to remove any trace of soap, distilled water is then used to wash the bottles to remove ions present. The water samples were then collected into the bottles, covered in an ice chest with ice and transported to the laboratory for analysis.

2.2. Methodology

The research was carried out at the Centre for Scientific and Industrial Research (CSIR), Environmental Division (ED), Water Research Institute (WRI), Organic Laboratory. The parameters measured includes; conductivity, pH, salinity and Polycyclic Aromatic Hydrocarbons.

2.3. Conductivity

The conductivity was measured by mixing the sample very well and pouring into a clean cup. The conductivity meter was immersed in the water sample and the cup swirled to get the appropriate reading and recorded in microsiemens (µs). The instrument was calibrated using standard KCl (0.01M) which has a conductivity of 141µs/cm at 25°C, each reading was done three times [14].

For theoretical purpose; $K= km \times c /(1+0.0191)(T-25)$

Where, Km = measured conductivity, mS/cm at 25°C

C= cell constant, cm^{-1}, T= temperature of sample

2.4. pH

The pH was determined by using the pH meter and combination electrode for measurement, the electrode was immersed into the water sample and the cup swirled to get accurate results. The pH was recorded in pH units. Calibrate by; washing the electrode of the meter very well with distilled water, the electrode is first calibrated against a pH buffer 4 then 9 and then 7, a reference solution of known pH was measured to check the sensitivity and accuracy of the electrode.

2.5. Salinity

For salinity, chloride was determined. 50ml of the sample was used for the determination of chloride but due to high conductivity of the Oblogo leachates and diluted Oblogo leachates, 1ml of the sample was used and diluted to 50ml with distilled water. When diluted, endpoint was easy to attain. 1ml of potassium chromate was added and titrated against 0.0141M silver nitrate to obtain a pinkish yellow endpoint. The reading on the 50ml graduated burette was recorded.

To calculate for chloride; $MgCl^{-}/L = (A-B) \times M \times 3540$ ml sample

A= ml titration for sample

B= ml titration for blank

M= molarity of $AgNO_3$

To ensure accuracy of work, the $AgNO_3$ was standardized with NaCl; thus

About 10mL of standard NaCl solution was measured (pipetted) into a flask and 2 drops of potassium chromate indicator was added. This was titrated with the $AgNO_3$ solution to obtain a pinkish yellow end point.

To calculate for salinity;

$S\% = 0.03+1.805(Cl^{-} \times 1.00045)/1000$ [15].

2.6. Extraction of PAH from Water

For PAHs, 1000ml (1L) of water sample was poured into a separating funnel. 50ml of dichloromethane was added followed by 0.2ml internal standard to correct errors using micro syringe. The content of the separating funnel was shaken well for the dichloromethane to extract as much organic components as possible from the water sample. The separating funnel was left undisturbed on a retort stand for sometime, so that the mixture separates into the organic and water layer. The separating funnel was then opened to drain the water layer. The organic layer was drained through a glass funnel which was plugged with glass wool, filter paper and sodium sulphate into a Zymark tube. The sodium sulphate was used to absorb water that might be present in the organic layer.

A second extraction was carried out using 50mL of dichloromethane and the extract was added to the one in the Zymark tube. One drop of iso-octane was added to the contents in the Zymark tube and was placed into a Turbo Evaporation Unit to reduce the volume to 1ml by evaporation. The iso-octane served as a keeper to prevent evaporation of the needed components. The extract in the Zymark tube was then transferred into test tubes using pasture pipettes. The Zymark tube was washed with 2ml of dichloromethane and added to the content in the test tube. The test tube was heated in a block heater and a gentle steam of nitrogen was used to reduce the volume to 0.5ml. 1ml of cyclohexane was added and the mixture was evaporated to dryness followed by the addition of 0.5ml hexane [16-17].

2.7. Clean-Up

Most of the unwanted components were removed from the extract leaving the components of interest. This was achieved by using solid phase extraction tubes containing 500mg florisil, 3ml by volume. This solid phase was conditioned using 6ml of hexane. 0.5mL of the extract was added and eluted with 6.0mL hexane into a test tube. The PAHs in the extract was held by the florisil column. The column was eluted again using 20% dichloromethane in hexane into another test tube and this fraction contained the PAHs. The volume was reduced to 0.5ml and was transferred into sample vials for gas chromatography run [11].

2.8. Gas Chromatography

Gas chromatography (GC) is a common confirmation test. GC analysis separates all of the components in a sample and provides a representative spectral output. Before the sample was analyzed, the instrument was tuned and calibrated. Tuning was accomplished using specific concentrations of Decafluorotriphenylphosphine and p-Bromofluorobenzene to test the instruments reporting accuracy. The sample vials that contained the extracts were arranged on a plate at the injection point and the injection was done automatically by the machine.

The sample was introduced as a vapor onto the chromatographic column. On the column, the solubility of each component in the gas phase was dependent on it vapor pressure, which was in turn a function of the column temperature and the affinity between the compound and the stationary phase. To ensure proper separation, the sample must enter the column in a discreet, compact pocket. The gas chromatography instrument uses the flame ionization detector with the model 6890N to measure the different compounds as they emerge from the column. The principle behind Gas Chromatography states that the rate of migration of the solute depends upon the rate of interaction of the solute with a two phase, the mobile phase and the stationary phase as the compound travels through the supporting medium.

3. Results and Discussions

Reliability of any analytical results can be verified using certain indicators which include the method and equipment used, accuracy, precision, etc. The precision and suitability of the method to the measuring equipment used, was initially established using the certified reference material. This was done by using the reference material alone and also treated as a sample. The percentage recoveries were then calculated. The method verification and sample results are tabulated in Table 1 below.

3.1. Data Analysis

Estimation of PAHs was done by expression: Concentra-

Table 1. Summary of system suitability and percentage recovery using certified reference material.

COMPOUND NAME	AMOUNT µg/ml			AVE (µg/ml)	TRUE Value µg/ml	Rel. Error (%)	Stand. Dev.	% recovery	Rel. Stand. Dev. %
	1	2	3						
Naphthalene	14.2	14.3	14.2	14.2	15.0	-5.3	0.0577	94.67	0.4063
2- Methylnaphthalene	14.7	14.8	14.8	14.8	15.0	-1.3	0.0577	98.67	0.3899
1-Methylphthalene	14.7	14.8	14.7	14.7	15.0	-2.0	0.0577	98.00	0.3925
Biphenyl	14.8	15.2	14.8	14.9	15.0	-0.7	0.2309	99.33	1.5497
2,6-Dimethylnaphthalene	14.8	14.9	14.8	14.8	15.0	-1.3	0.0577	98.67	0.3899
Acenaphthylene	14.8	14.9	14.7	14.8	15.0	-1.3	0.1000	98.67	0.6757
Acenaphthene	14.8	14.8	14.8	14.8	15.0	-1.3	0.0000	98.67	0.0000
2,3,5-Trimethylnaphthalen	14.7	14.7	14.7	14.7	15.0	-2.0	0.0000	98.00	0.0000
Fluorene	14.7	14.9	14.8	14.8	15.0	-1.3	0.1000	98.67	0.6757
Phenanthrene	14.7	14.8	14.8	14.8	15.0	-1.3	0.0577	98.67	0.3899
Anthracene	14.8	14.9	14.9	14.9	15.0	-0.7	0.0577	99.33	0.3872
1-Methylphenanthrene	12.8*	14.7	14.7	14.7	15.0	-2.0	0.0000	98.00	0.0000
IS 3,6-DMP	10.0	10.0	10.0	10.0	10.0	0.0	0.0000	100.00	0.0000
Fluoranthene	14.8	14.8	14.8	14.8	15.0	-1.3	0.0000	98.67	0.0000
Pyrene	14.2	14.2	14.2	14.2	15.0	-5.3	0.0000	94.67	0.0000
Benzo(a)anthracene	14.5	14.5	14.4	14.5	15.0	-3.3	0.0577	96.67	0.3979
Chrysene	14.6	14.5	14.5	14.5	15.0	-3.3	0.0577	96.67	0.3979
IS BB-Biphenyl	10.0	10.0	10.0	10.0	10.0	0.0	0.0000	100.00	0.0000
Benzo(b)fluoranthene	15.3	15.0	15.3	15.2	15.0	1.3	0.1732	101.33	1.1395
Benzo(k)fluoranthene	14.1	14.0	14.1	14.1	15.0	-6.0	0.0577	94.00	0.4092
Benzo(e)pyrene	14.7	14.3	14.5	14.5	15.0	-3.3	0.2000	96.67	1.3793
Benzo(a)pyrene	14.8	14.4	14.3	14.5	15.0	-3.3	0.2646	96.67	1.8248
Perylene	14.8	14.4	14.7	14.6	15.0	-2.7	0.2082	97.33	1.4260
Indeno(1,2,3cd)pyrene	15.3	14.1	14.9	14.8	15.0	-1.3	0.6110	98.67	4.1284
Dibenz(a,h)anthracene	14.1	13.4	14.8	14.1	15.0	-6.0	0.7000	94.00	4.9645
Benzo(g,h,i)perylene	14.8	13.6	14.6	14.3	15.0	-4.7	0.6429	95.33	4.4958

* Statistically rejected data as an outlier using Q-Test.

Table 2. Summary of physico-chemical parameters (levels) of the water samples.

Name of sample	Average Conductivity (S/m)	Average (pH unit)	Average Salinity (ppm)
Leach from Oblogo solid waste site	1.333	8.43	3.5×10-3
Leach diluted with rain water	0.976	8.38	2.3×10-3
Down stream of river Densu	0.025	7.75	7.7×10-5
Weija dam	0.027	7.51	7.5×10-5
Chemu Lagoon	5.677	7.687	5.72
Korle Lagoon	40.83	7.52	26.53
Kpeshie Lagoon	40.50	7.52	26.20

Table 2 shows the detailed data of the physicochemical properties of the sampling site, the average pH was around neutral with a value ranging 7.51 to 8.43. The Chemu, korle and kpeshie lagoons recorded an average high conductivity of 5.677, 40.83 and 40.50 S/m respectively, while samples from oblogo sampling sites recorded very low conductivity range of 0.027 - 1.333 S/m. The very high value in the Lagoons is expected because the Chemu as well as the other two lagoons flow into the sea and the concentration of dissolved ions is expected to be very high which has been proved by high salinity values (5.72 – 26.53) recorded as shown in Table 3 above.

Table 3. Summary of mean concentrations of PAHs in the Oblogo dumping sites and its environ.

	Mean Concentration in μg/L±SD				
PAHs	**Leach from Oblogo solid waste disposal site**	**Leach diluted with rain water**	**Down stream of River Densu**	**Weija dam site**	**Average**
Naphthalene	2.248	2.165	2.42	2.171	2.251±
Acenaphthylene	9.878	2.495	1.318	2.926	4.154±3.87
Acenaphthene	2.624	14.587	5.091	0.051	5.588±6.342
Fluorine	2.715	0.648	13.539	0.691	4.398±6.169
Phenanthrene	0	1.199	5.188	0.141	2.531±2.286
Anthracene	5.368	2.43	6.382	0.486	3.667±2.703
Fluoranthene	1.912	2.548	1.412	1.638	1.878±0.492
Pyrene	0.029	0	0.105	0	0.045±0.054
Benzo[a] anthracene	0	0.323	3.018	0.03	1.124±1.647
Chrysene	0	0	1.295	0	1.295±0.000
Benzo[b] fluoranthene	4.921	1.26	0.88	1.156	2.054±1.918
Benzo[k] fluoranthene	0	0	0.059	0.058	0.058±7.071
Benzo[a] pyrene	0.199	0	0	0.085	0.071±0.081
Indeno [1,2,3-cd] pyrene	0.779	0	1.788	0	0.856±0.713
Dibenz[a,h] anthracene	1.731	0	0.093	0	0.608±1.158
Benzo[ghi] perylene	1.905	1.042	0.647	0.626	1.055±0.699
Total	37.906	28.699	43.235	10.058	31.633

tion = Amount (μg/ml)X Final volume of Extract (ml) / Weight taken (g)

From Table 3, the PAHs distribution in the leach from Oblogo solid waste site has been observed with Acenaphthylene recording the highest concentration of 9.878 μg/L and Pyrene with the least concentration of 0.029 μg/L. The carcinogenic PAH detected at this site were Benzo[b]fluoranthene, Benzo[a]pyrene, Indino [1,2,3-cd] perilene and Dibenz[a,h]anthracene with concentration of 4.921μg/L, 0.199 μg/L, 0.779 μg/L, 1.731 μg/L respectively (Table 3). These concentrations may resulted from the combustion of the solid waste with the presence of domestic refuse and discarded solid materials such as those from commercial, industrial and agricultural operations: they contain increasing amount of paper, cardboards, plastics, glass, packing materials and toxic substances.

The PAHs distribution in the leach diluted with rain water has been observed with Acenaphthene recording the highest concentration of 14.587μg/L and Benzo (a) anthracene with the least concentration level of 0.323 μg/L. The carcinogenic PAHs detected at this site were Benzo (a) anthracene and Benzo (b) fluoranthene with concentrations of 0.323μg/L and 1.26μg/L respectively. All the concentrations detected at this site were above the WHO's limit of 0.05μg/L [13]; this indicates high level of contamination in the leach diluted with rain water. The higher concentration of some PAHs in the diluted leach with rain water shows how the atmosphere has been polluted through anthropogenic source (automobiles, burning of biogas, industrial activities etc). PAH distribution in the downstream of river Densu has been observed with Fluorine recording the highest concentration of 13.539μg/L and Benzo[k] fluoranthene with the least concentration of 0.059μg/L. The carcinogenic PAHs detected at this site were chrysene, Benzo [a] anthracene, Benzo[b] fluoranthene and Benzo [k] fluoranthene Indino[1,2,3-cd]pyrene and Dibenz[a,h] anthracene with concentrations of 1.295μg/ L, 3.018μg/ L, 0.8 8μg/

L, 0.059μg/L and 1.788 μg/L and 0.093 μg/L respectively (Table 3).

All the concentrations detected at this site were also above the WHO's limit of 0.05μg/L [13]; this indicates high level of contamination in the downstream of river Densu. These concentrations could be due to the leach joining the downstream of river Densu. PAH distribution in the Weija dam has been observed with Acenaphthylene recording the highest concentration of 2.926μg/L and Benzo[a] anthracene with the least concentration of 0.030μg/L (Table 3). The carcinogenic PAHs detected at this site were Benzo[a] anthracene, Benzo[b] fluoranthene and Benzo[k] fluoranthene and Benzo[a]pyrene with concentrations of 0.030μg/ L, 1.156μg/ L and 0.058μg/L and 0.085μg/L respectively.

Table 4 compares the average concentration of the individual PAHs compounds in the three lagoons. In all, the Chemu lagoon recorded the highest PAHs concentration with a total of 61.712μg/L followed by the Korle lagoon and then the Kpeshie lagoon with total PAHs of 38.889ug/L and 34.09μg/L respectively. Both the Chemu and the Korle lagoons had Benzo (ghi) perylene as the compound with the highest concentration, whiles the Kpeshie lagoon on the other hand had Acenaphthylene as the compound with the highest average concentration. Samples from Oblogo damping site and it's environ recorded appreciably PAH values with 14.587μg/L of Acenaphthylene being the highest compared to the three lagoons. This could be as a result of the low salinity nature of the water which may increase dispersant effectiveness. Hence, risks to fish of PAH from other sources would be greatest in coastal waters where salinities are low and however fish from Densu River and Weija Dam may be at risk [18].

The average concentration of the PAHs in the lagoon water ranged from 0.552μg/L, for Acenapththene to 11.399ug/ L for Benzo (b) fluoranthene. Other PAHs which recorded extremely high average values in the Chemu lagoon are Acenaphthylene (9.146μg/L), Benzo (k) fluora- nthene (6.644μg/L), Benzo (b) fluoranthene (9.948μg/L). This high PAHs contamination may result from the fact that Chemu lagoon has various refuse dumping sites along the bank where continuous burning of refuse are carried out, also fish smoking homes are located near the banks. In addition smoke emitting vehicles that continuously pry the road near and across some parts of the lagoon coupled with smoke emission from the chimney of the Tema oil refinery may be the major contributing factors to the high levels of contamination in the Chemu lagoon.

The average concentration of PAHs in the water sample of the Korle lagoon ranges from 0.00ug/L for Benzo (a) pyrene to 8.800μg/L for Benzo (ghi) perylene. Apart from Benzo (a) pyrene which recorded zero micrograms per liter in the Korle lagoon. Other PAHs which recorded extremely high values in the Korle lagoon include Anthracene, Fluoranthene, Chrysene, Dibenz (a, h) anthracene and Acenaphthylene with average concentrations of 8.310μg/L, 7.796μg/L, 3.099μg/ L, 6.198μg/ L, 2.978-μg/L respectively (Table 4). The Korle lagoon stretches along the Accra Korlebu high-way thus receiving heavy smoke from vehicles that move constantly on the road. Aside this problem at some distance from the lagoon, there is a slaughter house which also produces thick smoke that may have caused PAHs accumulation in the lagoon. It is also suspected that effluent from the Korlebu Teaching Hospital may get into the lagoon which may also contribute to the level of pollution. In general it is gratifying to note that the level of PAHs in Chemu lagoon is relatively higher than that of the Korle lagoon. This may be due to the dredging process that was ongoing during the time of sampling at the Korle lagoon. In spite of this reduction, all PAH compounds analyzed with the exception of Benzo (a) pyrene exceeded the WHO acceptable limits and thus consumption of fish or any other food substances from the lagoon may prove dangerous to the health of the consumers.

Table 4 showed a compilation of PAH concentrations from the Kpeshie lagoon. The average concentrations of PAHs in the waters of the Kpeshie lagoon range from 0.052μg/L for Pyrene to 4.703μg/L for Acenaphthylene. Other PAHs which recorded extremely high average values in the Kpeshie lagoon include Benzo (b) fluoranthene, Acenapththene, Chrysene, Benzo (ghi) perylene, Anthracene, Fluorine with average concentrations of 4,680μg/L, 4.003μg/L, and 4.374μg/L, 7.847μg/L, 3.364μg/L, 1.112ug/L respectively. Along the banks of the Kpeshie lagoon is stretch of mangroves which is used as hiding places for petty criminals therefore smoking of cigarettes and Indian hemp at these places is routine. Again some parts of the Kpeshie lagoon stretches along the Accra-Tema high way near La. It is interesting to note that just at the portion where the lagoon begins is also the starting point of a very serious traffic jam that has terrorized the inhabitants of Teshie and Nungua for years. Another very important consideration about the location of the lagoon its closeness to the Accra International Trade Fair Center. Waste discharged from the trade fair center to the lagoon might have also increased the level of PAH contaminations. It is therefore not far from right to say that these two major activities may have contributed to the PAH levels in the Kpeshie lagoon

The concentration levels of PAHs detected were slightly varied from the location. The commonly found PAH compounds in water samples were acenapthene, fluorine, phenanthene, fluoranthene, pyrene, benzo [b] fluoranthene. Naphthalene, acenaphthylene, benzo [a] pyrene and benzo [ghi] perylene were found in all samples taken from oblogo dumping site and it's environ. In the case of the three lagoons all PAHs were detected. There were huge variations between sites for some compounds (e.g., acenaphthene, acenaphthylene and benzo [a]pyrene), whereas the concentrations of the majority of

Table 4. Summary of PAH concentrations (µg/L) ±SD comparison from the Chemu, Korle and Kpeshie Lagoons.

PAH	CONCENTRATIONS (µg/L) ±SD		
	CHEMU	KORLE	KPESHIE
Naphthalene	0.781± 0.437	0.440±0.581	0.195±0.000
Acenaphthylene	9.146 ± 3.356	2.978±0.431	4.703±4.742
Acenapththene	0.552±1.006	1.021±1.254	4.003±4.505
Fluorine	2.877± 4.002	0.802±0.651	3.120±3.217
Phenanthrene	0.939±0.387	0.457±0.082	1.140±0.609
Anthracene	2.020±0.978	8.310±7.318	3.364±4.329
Fluoranthene	4.787±3.367	7.796±5.413	1.573±0.912
Pyrene	2.391±2.483	0.401±0.000	0.052±0.012
Benzo (a) anthracene	2.673±2.384	0.143±0.270	0.572±0.000
Chrysene	1.485±0.000	3.669±2.923	4.374±6.190
Benzo (b) fluoranthene	9.948±8.668	0.490±0.167	4.680±4.024
Benzo (k) fluoranthene	6.644± 9.739	0.412±0.326	2.327±2.547
Benzo (a) pyrene	1.142±1.357	0.000	0.372±0.656
Indeno(1,2,3-cd)pyrene	1.187±0.931	0.0713±0.00	0.839±0.721
Dibenz(a,h)anthracene	3.741±2.133	3.099±1.654	1.626±0.708
Benzo (ghi) perylene	11.399±10.311	8.800±6.188	3.697±2.492
TOTAL	61.712	38.889	34.091

Table 5. Summary of Correlation coefficients for seven different locations sample site for 16 PAHs (n =16).

	OBSW	LDRW	RD	WDS	CMU	KLE	KPSH
OBSW	1	0.228	0.208	0.708**	0.305	0.495*	0.208
LDRW		1	0.225	0.058	-0.203	0.013	0.186
DR			1	-0.017	-0.155	0.192	0.132
WDS				1	0.343	0.312	-0.034
CHM					1	-0.046	-0.091
KLE						1	0.083
KPSH							1

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level.

OBSW = Oblogo solid waste disposal site, LDRW= Leach diluted with rain water, RD=Riveer Densu, WDS= Weija Dam site, CHE= Chemu Lagoon, KLE= Korle Lagoon and KPSH= Kpeshi Lagoon.

compounds were comparable at the various sites which is similar to similar work by Kanchanamayoon and Tatrahun (2009) [19]. The highest PAHs were recorded by compounds with molecular weights ranging from 128–154 (i.e., naphthalene, acenaphthalene and acenaphthene) and those from 252–276 (i.e. [a] fluoranthene, perylene, benzo[a]pyrene, and benzo[g,h,i] perylene) which has also been reported by [20].

As far as the compositional pattern of PAHs is concern, the lagoon was generally dominated with all the PAHs. This relative abundance of low molecular weight PAHs (LPAHs) indicated that the PAHs were from petrogenic origin such as oil leakages or inadvertent oil spills [21].

Currently, there are no specific standards in Ghana for both inland and coastal waters for PAHs however evaluation of the toxicity that results from measured PAHs in the lagoons may be done by assessing their compliance with known international, national and provincial standards. According to the world health organization (WHO) the concentration of PAHs in water exceeding 0.05µg/L indicates some level of toxicity [22]. From Table 3 and 4 it can be observed that all the individual PAH compounds analyzed exceeded the WHO accepted value of 0.05µg/L and hence can be said that the Chemu, Korley and Kpeshi lagoon as well as Oblogo dumping site and it's environ are polluted with PAHs. Therefore consumption of fish or any other edibles from the lagoons, Densu River, and Weija Dam may prove detrimental to the health of consumers.

3.2. Source Assessments

The differences in the type of PAH compounds at the different sites indicate that there are potentially different sources of PAHs in the area; possibly including sewage outfalls, industrial wastewater, thermal combustion processes (e.g., cooking and heating oils, and coal buring) followed by atmospheric fallout, oil residues, vehicular emissions (e.g., automobiles and trucks), and biomass burning (e.g., fire woods, charcoal, etc) [20]. From inspection of the distribution of PAHs in the surface water alone, it is often difficult to differentiate between the sources of inputs. The ratios of specific parent PAH

Table 6. Summary of Correlation coefficients for PAHs compounds in the water samples at seven different locations (n = 13).

	NAP	ACL	AC	F	PH	AN	FL	PYR	BZA	CHR	BZB	BZK	BZaP	Ind	Dib	BZghi
NAP	1	0.064	0.303	-0.205	-0.052	-0.255	-0.504*	-0.225	-0.342	0.006	-0.059	-0.198	-0.105	-0.207	-0.113	-0.339
ACL		1	-0.368	0.209	-0.010	-0.057	-0.084	0.555*	0.528*	-0.111	0.762**	0.546*	0.570*	0.170	0.504*	0.046*
AC			1	-0.012	0.202	-0.098	-0.167	-0.249	-0.188	0.172	-0.160	-0.127	-0.093	-0.096	-0.460	-0.353
F				1	0.715**	0.171	-0.092	0.234	0.721**	-0.041	0.335	0.313	-0.093	-0.096	-0.460	-0.353
PH					1	0.186	-0.302	-0.232	0.165	-0.270	-0.150	-0.252	-0.237	0.353	-0.313	-0.358
AN						1	0.624*	0.043	0.018	-0.189	-0.127	-0.121	-0.190	-0.237	0.114	0.067
FL							1	0.447	0.155	0.072	0.133	0.270	0.207	-0.164	0.543*	0.640**
PYR								1	0.769**	0.090	0.805**	0.857**	0.881**	0.432	0.746**	0.833**
BZA									1	0.016	0.793**	0.807**	0.750**	0.678**	0.364	0.596*
CHR										1	0.216	0.399	0.411	0.176	0.074	0.241
BZB											1	0.927**	0.923**	0.514*	0.495*	0.671**
BZK												1	0.975**	0.574*	0.481*	0.728**
BZaP													1	0.560*	0.527*	0.709**
Ind														1	0.089	0.185
Dib															1	0.877**
BZghi																1

*Pearson Correlation is significant at the 0.05 level (1 tailed).
** Pearson Correlation is significant at the 0.01 level (1 tailed)
Naphthalene (NAP), Acenaphthylene (ACL), Acenapththene (AC), Fluorine (F), Phenanthrene (PH), Anthracene (AN), Fluoranthene (FL), Pyrene (PYR), Benzo (a) anthracene (BZA), Chrysene (CHR), Benzo (b) fluoranthene(BZB), Benzo (k) fluoranthene (BZK), Benzo (a) pyrene (BZaP), Indeno(1,2,3-cd)pyrene (Ind), Dibenz(a,h)anthracene (Dib), Benzo (ghi) perylene (BZghi).

Table 7. Summary of PAH ratios of water samples from sampling sites.

RATIO	OBSW	LDRW	RD	WDS	CMU	KLE	KPSH
AN/(AN+PH)	0.599	0.330	0.552	0.775	0.683	0.948	0.747
AN/(AN+F)	0.665	0.789	0.320	0.413	0.414	0.912	0.481
NAP/(NAP+ ACL)	0.185	0.465	0.647	0.426	0.079	0.129	0.040
NAP/(NAP+ AC)	0.461	0.122	0.322	0.973	0.586	0.301	0.046
FL/(FL+PYR)	0.985	1.000	0.931	1.000	0.667	0.951	0.912
BZA/(BZA+CHR)	0.000	1.000	0.699	1.000	0.372	0.039	0.116
BZaP/(BZghi)	0.104	0.000	0.000	0.136	0.100	0.000	0.101
BZB/(BZB+BZK)	1.000	1.000	0.937	1.038	0.599	0.543	0.659
Ind/(Ind+Dib)	0.310	0.00	0.950	0.000	0.241	0.02	0.327

Compound abbreviations in Table 6.

compounds have also been identified to be one approach to distinguish between different sources of PAH in a particular environmental matrix, [20] and this method is used in the present study to characterize the PAH sources to the lagoon. Correlation analyses can also provide information about associations between sites, between the individual PAH compounds, and between some specific PAH compounds and heavy metals to determine common origins.

3.3. Site Correlations

Correlation analyses between the sites' individual PAH compound levels (n = 16) Table 5, indicates no significant correlation between leach diluted with rain water, River Densu, Chemu, korle and kpeshi with any other site suggesting the unique origin of PAHs from these sites. Weija Dam Site correlates strongly with Oblogo solid waste site with significant coefficient of 0.708 at 0.01 levels. The correlation between the two sites for the individual PAH compounds is also reflected in the similarities of the compositional patterns at these two sites (see map).However, despite the distance apart of Korle lagoon to Oblogo solid waste disposal site, their correlation is only fair (0.495) at 0.05 level, suggesting that PAH origins from these sites are quite different to overcome the site proximity.

3.4. PAH Interrelationships

In order to assess PAH associations and their possible origins, correlation analyses were conducted among the concentration of the individual PAHs in the water samples. The results are summarized in Table 6. It is known that where two compounds have a common source, there is more likely to be a correlation between their concentrations [20]. Strong positive significant correlation was observed between individual PAHs. Benzo (a) Pyrene and Benzo (k) fluoranthene showed the highest PAH interrelationship with correlation coefficient of 0.975 followed by Benzo (b) fluoranthene/Benzo (k) fluoranthene and Benzo (a) Pyrene/Benzo (b) fluoranthene correlated with 0.927 and 0.923 respectively, significant at 0.01 levels. The following pairs also interrelated strongly at the significant level of 0.01: Benzo (a) Pyrene/ Pyrene (0.881), Dibenz (a,h) anthracene/Benzo (ghi) perylene (0.877), Benzo (k) fluoranthene/ Pyrene(0.857), Benzo (ghi) perylene/ Pyrene(0.833), Benzo (k) fluoranthene/ Benzo (a) anthracene(0.807), Benzo (b) fluoranthene/Pyrene (0.805), Benzo (b) fluoranthene/ Benzo (a) anthracene (0.793), Benzo (a) anthracene/pyrene (0.769), Benzo (b) fluoranthene/ Acenaphthylene (0.762), Benzo (a) Pyrene/ Benzo (a) anthracene (0.750), Pyrene/ Dibenz (a,h) anthracene(0.746±0.00), Benzo (ghi) perylene/ Benzo (k) fluoranthene(0.728), Benzo(a)anthracene/Fluorine(0.721), Fluorine/Phenanthren (0.715±0.03), Benzo (ghi) perylene/ Benzo (a) Pyrene (0.709), Indeno(1,2,3-cd)pyrene/ Benzo (a) anthracene(0.678), Benzo (ghi) perylene/ Benzo (b) fluoranthene(0.671), Benzo (ghi) perylene/ Fluoranthene(0.640).

At 0.05 level, significant positive correlation were also observed between PAHs with Anthracene/ Fluoranthene recording the highest correlation coefficient of 0.624 followed by Benzo (a) anthracene/ Benzo (ghi) perylene (0.596), Fluorine/ Indeno(1,2,3-cd)pyrene (0.588), Benzo (k) fluoranthene/ Indeno(1,2,3-cd)pyrene(0.574), Benzo (a) Pyrene / Acenaphthylene (0.570), Benzo (a) Pyrene/ Indeno(1,2,3-cd)pyrene (0.560), Pyrene/ Acenaphthylene (0.555), Benzo (k) fluoranthene/Acenaphthylene(0.546), Dibenz (a,h) anthracene/Fluoranthene(0.543), Acenaphthylene/ Benzo (a) anthracene (0.528), Dibenz (a,h) anthracene/ Benzo (a) Pyrene (0.527), Benzo (b) fluoranthene/ Indeno(1,2,3-cd)pyrene (0.514), Acenaphthylene/ Dibenz (a,h) anthracene (0.504), Benzo (b) fluoranthene/ Dibenz (a,h) anthracene(0.495), Benzo (ghi) perylene/ Acenaphthylene(0.486) and Benzo (k) fluoranthene/ Dibenz (a,h) anthracene (0.481) in that order. The results reveal that these compounds, and to a lesser extent pyrene, were possibly derived from a common anthropogenic origin. No significant correlation was identified between Acenapththene and chrysene compound with any of the other PAH compounds measured which indicate other source of these two PAHs. In one case, Fluoranthene (FL) (containing 3 fused aromatic rings) showed inverse correlation with Naphthalene (at 0.01 level) (Table 6) containing 2 fused aromatic rings. It is speculated that some fraction of these compounds could be from the biodegradation of Fluoranthene (FL) by natural occurring population of water microorganisms since Fluoranthene is a polycyclic aromatic hydrocarbon (PAH) consisting of naphthalene and a benzene unit connected by a four-membered ring. It is also known to occur naturally as a product of plant biosynthesis [27]. Further studies are required to verify this speculation.

3.5. PAH Isomer Pair Ratios as Diagnostic Source Indicators

The ratios of specific PAH compounds have been identified to possess the potential to distinguish natural and anthropogenic sources. [24-25]. To minimize confounding factors such as differences in volatility, water solubility, adsorption etc. ratio calculations are usually restricted to PAHs within a given molecular mass [24]. Yunker et al 2002 have summarized the literature on PAH ratios for petroleum, single-source combustion and some environmental samples and made the following conclusions. For mass 178, an anthrancene to anthracene plus phenanthrene (AN/{AN+PH}) ratio of >0.50 usually is an indication of biomass & coal combustion transition point. For mass 202, a fluoranthene to fluoranthene plus pyrene (FL/{FL+PYR) ratio of >0.50 seems to be the characteristic of grass, wood or coal (biomass) & coal combustion transition point, though not definite. For mass 228, a benzo[a]anthracene to benzo[a] anthracene plus chrysene ratio <0.20 imply petroleum, 1.2–5.0 indicates wood burning and coal burning [26], and >0.35 imply combustion [25]. The ratios of the above-specified PAHs in the Oblogo dumping sites, Leach diluted with rain water, Riveer Densu, Weija and Dam site as well as Chemu, Korle and Kpeshi lagoons were calculated and are shown in Table 6. The AN/AN+PH ratios are all >0.50, suggesting grass, wood or coal (biomass) & coal combustion sources of PAH from all eight sites. However, the smaller ratios (0.330) obtained for Leach diluted with rain water (LDRW) distinguishes it from the other sites. It appears there is mixed petroleum and combustion sources at this site. The BZA/(BZA+CRY), AN/(AN+F), FL/(FL+PYR), BZB/(BZB+BZK), Ind/ (Ind+Dib),mixed ratios of >0.01, 0.4–0.5 and ≥0.50 re-echo the predominance of grass, wood (biomass), coal and petroleum combustion are the main source of PAH from the Oblogo solid waste dumping site down stream to Weija Dam down to Densu River. This confirms the belief that the burning of solid waste at Oblogo solid waste dump site is polluting the environment with PAHs. At the Chemu, Korle and Kpeshi Lagoons NAP/(NAP+ACL) and BZaP /(BZghi) ratio of >0.10 suggests a combustion source which is said to be affluent from Tama oil refinery.

The BZA/ (BZA+CHR) ratios whose interpretations are said to be more definitive [24] provided more distinctions between the sites. Based on >0.35 as the transi tion ratio, the calculated 0.375 suggests a combustion source for Chemu Lagoon, mixed unburned petroleum and combustion sources for Korle and Kpeshi. The mixed petroleum and combustion sources at this site is confirmed from the Ind/(Ind+Dib) fraction, where ratios of 0.241 (Chemu Lagoon) and 0.327 (Kpeshi Lagoon), which falls within the generally observed mixed-source ratio of 0.2–0.35 for mixed petroleum/ combustion origin of pollution are observed. At Korle Lagoon ratio of >0.10 implying unburned petroleum source has also been observed.

Despite the lack of consistency in some cases, there seems to be a general consensus by all the ratio indicators that combustion is the dominant source of PAH input into the lagoon. Although not conclusive, there is also an indication of petrogenic source contributions to sites such as chemu, korle, kpeshi as well as Weija Dam (Table 6). Variations in additional input sources (e.g., high or medium temperature combustion processes, different fossil materials) may also account for the differences in the composition pattern of PAHs between sampling sites (Table 7) [27]. Despite the apparent dominance of combustion and wood/coal burning (pyrogenic origin) as the major source of anthropogenic PAH to the Oblogo solid waste dump site, weija Dam, River Densu, Chemu, Korle and Kpeshi Lagoons sites (using the ratio indicators above). The AN/(AN+F) and NAP/(NAP+ ACL) ratios suggests petroleum combustion for Waija Dam, Chemu and Kpeshi sites (Table 7). It is therefore possible that combustion of liquid fossil fuel is the major source of PAH to the lagoons and the other sites.

NB: Source Patterns from the literature [24-25]; >0.10: combustion source; <0.10: unburned petroleum source, >0.50: biomass & coal combustion, 0.4–0.5: petroleum combustion, <0.40: unburned petroleum, >0.35: combustion, 0.20–0.35: mixed petroleum/ combustion <0.2: unburned petroleum source, 1.2–5.0: wood burning and coal burning [26].

4. Conclusions

Results obtained from the study clearly demonstrated that the leach from Oblogo solid waste disposal site and its environs as well as Chemu, Korle and Kpeshi Lagoons are polluted by Polycyclic Aromatic Hydrocarbons with concentration ranging from below detection level to 14.587µg/L. However, seven carcinogenic PAHs were detected in different concentrations from the various sites. It is important that, those PAHs promulgated by USEPA to be toxic and need to be investigated in developing countries. Acenaphthene, Anthracene, Benzo [a]anthracene, Benzo[b]fluoranthene, Chrysene, Phenanthrene occurred at the various sites above the safety level set by WHO. It can be concluded that people living around the Oblogo solid waste disposal site, who swim and bath in the downstream of River Densu would be exposed to these PAHs and may be at risk of their harmful effects.

The average concentration of PAHs in the water ranged from 0.552µg/L, for Acenapththene to 11.399 µg/L for Benzo (ghi) perylene of the Chemu Lagoon, 0.00µg/L for Benzo (a) Pyrene to 8.800µg/L for Benzo (ghi) perylene (Korle Lagoon) and 0.052µg/L for Pyrene to 4.703ug/L for Acenaphthylene of the Kpeshi Lagoon.

Good site correlations shown by water samples from Oblogo solid waste site and Weija Dam which derive their source mainly from burning of biomass and coal and combustion processes demonstrate how open dumping and burning procedure used in Ghana can pollute the environment. Other site far apart seem to inter-relate in terms of their PAH levels. Close relationships were also found between all individual PAH compounds except Acenapththene and chrysene which did not show any correlation with other PAHs. Benzo (a) Pyrene and Benzo (k) fluoranthene showed the highest PAH-PAH associations. The correlation and ratios of PAHs results revealed that these compounds were possibly derived from a common anthropogenic origin. There seems to be a general consensus from some three PAH-PAH ratio indicators that combustion and burning of biomass are the dominant source of PAH input into the Oblogo dumping sites down stream and the three lagoons studied. Although not conclusive, there is also an indication of petrogenic source contributions from some sites especially, the Chemu, Korle and Kpeshi Lagoons. Particularly in the vicinity of the Tema oil refinery.

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ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN STREET SOIL DUST IN KUMASI METROPOLIS OF GHANA

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Abstract. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in street soil dust from streets in Kumasi Metropolis in the Ashanti Region of the Republic of Ghana have been measured in this study. The concentrations of the various types of PAHs identified in this study are as follows: Naphthalene (m/e 128) – 41,700 μg/kg, Acenaphthylene (m/e 152) – 99,300 μg/kg, Acenaphthene (m/e 154) – 111,200 μg/kg, Fluorene (m/e 166) – 8,900 μg/kg, Carbazole (m/e 167) – 3,500 μg/kg, phenanthrene (m/e 178) – 12,900 μg/kg, Anthracene (m/e 178) – 5,400 μg/kg, Fluoranthene (m/e 202) – 16,200 μg/kg, Pyrene (m/e 202) – 15,000 μg/kg, Benzo[a]anthracene (m/e 228) – 13,800 μg/kg, Chrysene (m/e 228) – 33,600 μg/kg, Benzo[k]fluoranthene (m/e 252) – 45,700 μg/kg, Benzo[a]pyrene (m/e 252) – 27,900 μg/kg, Perylene (m/e 252) – 57,200 μg/kg and Benzo[g, h, i]perylene (m/e 276) – 47,000 μg/kg. The results of the study shows that road users, like resident living in buildings within these areas, those engaged in commercial activities like hawking, and the general public are at risk of exposure to the toxic effects of the various types of PAHs from the exhaust of vehicles into the environment. According to these results, there is the potential for exposure to high levels of PAHs for road users and those living in urban environments or along highways.

Keywords: Kumasi, p–terphenyl–d10 (m/e 244), PAH.

1. Introduction

High urbanization and industrialization growth have made Kumasi one of the most densely populated cities in Ghana. This has resulted in an increase in the number of vehicles that ply the metropolis each day. Uncontrolled emissions from industries and exhaust of vehicles have increased the levels of pollutant in the metropolis. Emissions from vehicles contain a variety of toxic chemicals such as platinum and palladium from catalytic converters, lead from vehicles that run on leaded fuels, nickel from vehicles that also run on diesel, cadmium and zinc from vehicular tyres and copper from brakes linings and electrical wires. In addition to the above toxic chemicals from vehicular fallouts is that of polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons (PAHs) occur ubiquitously in the environment and can be found in sediments, soils and water either in solution or adsorbed on particulate material (Alloway and Ayres, 1993). Most PAHs in the environment are from incomplete burning of carbon – containing materials like oil, wood, garbage or coal. Many useful products such as mothballs, blacktop, and creosote wood preservatives contain PAHs. They are also found at low concentrations in some special – purpose skin creams and anti–dandruff shampoos that contain coal tars (Wisconsin Department of Health, 2000).

Automobiles exhaust, industrial emission and smoke from burning of wood, charcoal and tobacco contain high levels of PAHs. It is in the light of this that this study was conducted to determine the levels and the various types of PAHs in vehicular fallouts in the Kumasi metropolis.

Automobile exhaust from the combustion of fossil fuels releases large concentrations of different types of PAHs into the ambient air in Kumasi along highways or high, low or medium vehicular densities.

The PAHs released from the fallouts of vehicular movement in Kumasi may be inhaled by road users such as hawkers, or are deposited on nearby vegetations or soils, buildings, food stuffs sold along these traffic points. Some of the PAHs may also settle on the skin of resident road users in Kumasi, which may cause redness, blistering and peeling (Wisconsin Department of Health, 2000).

Studies conducted in developed countries such as USA, Japan, etc, have revealed that the concentration of Bezo[a]pyrene in vehicular fallout is between 0.0063ppb to 1.9×10^{-6} ppb. Kuniko (1988), measured the BaP and PAH in airborne particulates near a high way in Tokyo, Japan during December, 1984 within 60 m radius from a crossing point of two high ways. The BaP concentration in precipitated dust was 1.49×10^{-4} to 1.3×10^{-4} ppb. However, no studies have been conducted in Ghana to measure the concentrations of PAHs in ambient air in municipal and metropolitant cities. It is in light of this that this study was conducted. The following health effects may occur after several years of exposure to PAHs such as benzo[a]pyrene:

- Reproductive effects: reproductive problems and problems in unborn babies' development have occurred in laboratory animals that have been exposed to benzo[a]pyrene. The health effects of other PAHs on reproductive organs of human beings and laboratory animals are not well known.
- Other organs and systems of human beings can be damaged after long exposure to benzo[a]pyrene and other PAHs whose mode of action is not well known (Wisconsin Department of Health, 2000).

This study was designed to measure the concentrations of the various types of PAHs that are deposited in soil dusts taken from different traffic point in Kumasi metropolis.

The main thrust for this study is to:

- Identified the various types of PAHs from vehicular movement in Kumasi metropolis.
- Determine the concentrations of each type of PAH identified from the fallout due to vehicular movement in Kumasi metropolis.

- Compare the concentrations of the various types of PAHs obtained in this study with permissible standards recorded in other countries.

2. Materials and Methods

2.1. SAMPLING TECHNIQUES

Random sampling technique was adopted in obtaining soil samples from road dusts from each of the major traffic points in the metropolis. In all 128 soil samples were taken from different streets in Kumasi Metropolis.

The soil samples were put together after which a representative sample (laboratory sample) was obtained from the composite sample.

2.2. SAMPLE COLLECTION AND PREPARATION

The samples were obtained from street dust from each of the four zones. The samples were put into amber glass containers and sealed with an aluminium foil. The samples were stored in an ice – chest at 4°C and conveyed to the laboratory. In the laboratory the samples were freed from stones and other foreign materials. The samples were then air – dried to a constant weight, ground with motor and pestle and then sieved through a 200 μm mesh.

2.3. ANALYSIS OF PAHS

10 g of a crushed, air – dried and homogenized soil sample was put into of a soxhlet thimble. The sample was cautiously spiked by adding 1.00 mL of working deuterated surrogate standard solution (i.e., 100 g of deuterated p – terphenyl) to the soil in the thimble. The thimble was then placed in a clean soxhlet funnel. 120 mL of dichloromethane was put into a round bottom flask. The soxhlet apparatus was assembled and the spiked soil sample was extracted for PAHs for 6 hours. The soxhlet apparatus was cooled to room temperature before removing the solvent.

For high level contaminated samples, the solvent was carefully and quantitatively transferred from the round–bottom flask into a stoppered measuring cylinder. The flask was rinsed with 2 mL dichloromethane and added to the content of the measuring cylinder. The contents of the measuring cylinder were thoroughly mixed. 5 mL of this solution was pipetted into 50 mL beaker and 0.5 g of activated alumina was added to it. The content of the beaker was swirled and then allowed to evaporate. A glass – fritted chromatographic column was set up containing activated silica gel to a depth of 60 mm, covered with 0.5 g of activated alumina containing 5 mL of the PAH extract to a depth of 30 mm. the column was conditioned by passing 20 mL of pentane through the column. The pentane eluate was discarded, after which 25 mL of dichloromethane was added to the silica gel column. The eluate was collected and was quantitatively transferred into a rotary evaporation apparatus. The flask was rinsed with 10 mL of dichloromethane and was then added to the soxhlet apparatus. The volume was reduced to 1.0 mL, it was quantitatively transferred to a GC-MS vial. 200 μL of working deuterated p – terphenyl PAH internal standard was added to the GC-MS vial. The vial was sealed tightly with a crimp top for the chromatographic determination of various types of PAHs.

For low level contaminated samples, the solvent in the round – bottom flask was quantitatively transferred into a rotary evaporation apparatus. The flask was rinsed with 2 mL of dichloromethane and the solvent was added to the rotary evaporation apparatus. The contents of the rotary evaporatory were rinsed with 10 mL of dichloromethane and the solvent was added to the beaker. The alumina residue was transferred from the beaker to the top of the column containing the alumina and silica gel and eluted with 20 mL of pentane, the pentane eluate was discarded. A clean rotary evaporation apparatus was placed beneath the column and the PAHs eluted from the column with 25 mL of dichloromethane. The eluate was collected. The extract was rinsed with 2 mL of dichloromethane and then the solvent added to the rotary evaporatory apparatus. The volume was reduced to 1.0 mL, after which the solution was quantitatively transferred to GC – MS vial. 200 μL of working deuterated p – terphenyl standard was used as an internal standard was added to the GC – MS vial. The vial was sealed tightly with crimp top for the chromatographic determination using the GC – MS chromatogram. The efficiency of the solvent extraction process was determined as 67.54%. Recovery and reproducibility studies were conducted. 95.6% recovery was recorded in the recovery and reproducibility studies.

3. Results and Discussion

The results of the various types of PAHs identified from vehicular fallout in Kumasi metropolis and their concentrations have been presented in Table I below.

From Table I, it was realized that 15 different types of PAHs were identified in the fallouts of vehicular movement in Kumasi metropolis. The concentrations of the various types of PAHs identified ranged from 3,500 μg/kg (Carbazole) to 111,200 μg/kg (Acenaphthene).

The concentration of acenaphthene was the highest (i.e., 111,200 μg/kg), suggest that there is high persistence of this type of PAH in the environment. Though health effects of breathing high concentrations of acenaphthene is not known, contact with the skin can cause several disease such as blistering or redness of the skin which may lead to peeling of the skin. Much concerted effort is required to reduce the levels of acenaphthene in Kumasi environment.

Again from Table I, the concentration of bezo[a]pyrene was 27,900 μg/kg. Benzo[a]pyrene is a common PAH and is known to cause lung and skin cancer in laboratory animals. The United States of America Environmental Protection

TABLE I
Mean results of various types of PAHs in vehicular fallouts in Kumasi Metropolis and their concentrations

Compound	Molecular mass (m/e) of analyte	Concentration of analyte (μg/kg)
Naphthalene	128	41,700
Acenaphthylene	152	99,300
Acenaphthene	154	111,200
Fluorene	166	8,900
Carbazole	167	3,500
Phenanthrene	178	12,900
Anthracene	178	5,400
Fluoranthene	202	16,200
Pyrene	202	15,000
Benzo[a]anthracene	228	13,800
Chrysene	228	33,600
Benzo[k]fluoranthene	252	45,700
Benzo[a]pyrene	252	27,900
Perylene	252	57,200
Benzo[g, h, i]perylene	276	47,000

*The calculations were based on the values in appendix I.

Agency (USEPA, 1990) has classified PAHs with benzo[a]pyrene indicator species as a class B 2 pollutant that means a probable human carcinogen with sufficient evidence from animal studies but inadequate evidence from human studies.

The background soil concentrations of PAHs in USA soils set by the Agency for Toxic Substance and Disease Registry have been presented in Table II below.

From Tables I and II, it is clear that benzo [a] pyrene concentration in Kumasi environment is very high. That is, the concentration of benzo[a]pyrene in vehicular fallouts in Kumasi metropolis is higher than the permissible range of background concentration of benzo[a]pyrene in urban soil. It is 169.1 times higher than the background concentration. According to WHO (1987), no safe level can be recommended for benzo[a]pyrene due to its carcinogenicity. Complete removal of PAH from the environment is impossible, but they can be controlled. Therefore standards have to be set for benzo[a]pyrene a known carcinogen in Ghana.

A sample is said to be contaminated if the concentration of the pollutant in the sample is three times higher than the background concentration.

From Table II below, concentrations of acenaphthene, acenapthylene, anthracene, fluorene and phenathrene are not major PAHs pollutant in USA urban soils. This suggests that, these pollutants are not heavily release from vehicular fallouts into the environment. PAHs also occur in the atmosphere in both the particulate phase and the vapour phase. Three–ring PAH compounds are found in the atmosphere primarily in the gaseous phase, whereas, five– and six – ring PAHs are found mainly in the particle phase; four–ring PAH compounds are found in both

TABLE II
Background soil concentrations of polycyclic aromatic hydrocarbons (PAHs) in urban soils

Compound	Concentrations (μg/kg) range
Acenaphthene	–
Acenaphthylene	–
Anthracene	–
Benzo[a]anthracene	169–59,000
Benzo[a]pyrene	165–220
Benzo[b]fluoranthene	15,000–62,000
Benzo[e]pyrene	60–14,000
Benzo[g, h, i]perylene	900–47,000
Benzo[k]fluoranthene	300–26,000
Chrysene	251–640
Fluoranthene	200–166,000
Fluorene	–
Ideno (1, 2, 3-c, d)pyrene	8,000–61,000
Phenathrene	–
Pyrene	145–147,000

phase. To fully characterize atmospheric PAH levels in an urban environment as in Kumasi or cities in USA, both particle – and vapour – phase samples must be collected. The absence of acenaphthene, acenapthylene, fluorene and phenathrene in the USA background urban soil values suggest that, these PAHs because of their low volatility were volatilized quite easily and because only particulate samples were also collected from highways in USA cities, thus no background concentration values recorded in USA urban soils for these PAHs.

However, their presence in urban soil obtained from highways in Kumasi soils calls for more elaborate study to fully understand the mechanism of volatilization of low molecular weight PAHs in an urban environment such as Kumasi.

PAHs can be harmful to health under several circumstances. Several of the PAHs, including benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene, have caused tumors in laboratory animals when they breathed these substances in the air, when they ate them, or when they had long periods of skin contact with them. Studies of people show that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can also develop cancer.

Mice fed with high levels of benzo[a]pyrene during pregnancy had difficulty reproducing and so did their offspring. The offspring of pregnant mice fed with benzo[a]pyrene also showed other harmful effects, such as birth defects and decreased body weight. Similar effects could occur in people, but we have no information to show that these effects do occur (USEPA, 1990).

Studies in animals have also shown that PAHs can cause harmful effects on skin, body fluids, and the body's system for fighting disease after both short- and long-term exposure (USEPA, 1990).

4. Conclusion

Concentrations of various types of PAHs have been measured in this study. The results obtained suggest that, the concentration of benzo[a]pyrene a common PAH obtained in this study is higher than the recommended safe limit values set by WHO and the Netherlands ambient air quality standards. Since benzo[a]pyrene is a class B.2 human carcinogen according to USEPA, there is the need to reduce the levels of set safe limit for this pollutant in Ghana, so as to protect road users like drivers, hawkers and other road users in Kumasi metropolis from exposure to toxic effects of benzo[a]pyrene and other PAHs whose health effects are not well known.

It is clear from the results of the study that road users in Kumasi and other major cities in Ghana are exposed to harmful health effects of PAHs in street soil dust. The interesting thing about this study is that most of the vehicles imported into Africa and for that matter Ghana are overage vehicles from Europe and other developed countries, their engines might have run down and therefore releases large amount of toxic pollutants such as PAHs. Much work should be conducted in Ghana to determine the health effects from exposure to PAHs from vehicular movement.

APPENDIX I

Calculation of concentrations of PAHs in the samples

Compound	M/e	Retention time	Peak Area	Response Ratio	Conc. ppm
Naphthalene	128	10.213	253998	0.0072	0.0417
Acenaphylene	152	19.793	150799	0.1246	0.0993
Acenaphthene	154	16.969	122983	0.1016	0.1112
Fluorene	166	18.906	10983	0.0091	0.0089
Carbazole	167	23.503	27859	0.0007	0.0035
Phenanthrene	178	22.625	156072	0.0041	0.0129
Anthracene	178	22.748	51257	0.0013	0.0054
Fluoranthene	202	27.184	17099	0.0052	0.0162
Pyrene	202	27.997	18293	0.0056	0.0150
Benzo [a]anthracene	228	32.731	12851	0.0039	0.0138
Chrysene	228	32.880	24594	0.0075	0.0336
Benzo[k]fluoranthene	252	36.682	48422	0.0151	0.0457
Benzo[a]pyrene	252	37.720	14766	0.0046	0.0279
Perylene	252	38.003	49458	0.0154	0.0572
Benzo[g,h,I]perylene	276	41.947	69433	0.0216	0.0470

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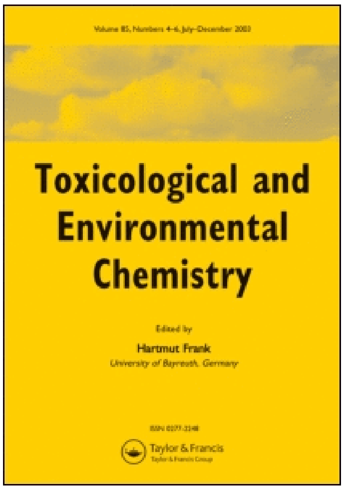

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Distribution, levels, and risk assessment of polycyclic aromatic hydrocarbons in the soot of some kitchens in the Cape Coast Metropolis of Ghana

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Distribution, levels, and risk assessment of polycyclic aromatic hydrocarbons in the soot of some kitchens in the Cape Coast Metropolis of Ghana

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The effect of using firewood for cooking, baking, and heating in poorly ventilated kitchens on the formation of polycyclic aromatic hydrocarbons (PAH) in kitchen soot in the Cape Coast Metropolis of Ghana has been studied. The kitchens in Ghana, especially those in the rural areas, are simple clay hut structures with small doors. The kitchens have little or no openings for ventilation and, as a result, the cook is exposed directly to high doses of smoke containing different compounds including PAH. In this study, a total of 42 soot samples were collected for 6 weeks from seven kitchens and analyzed using gas chromatography with flame-ionization detection (GC/FID). The average PAH concentration in the kitchen soot samples ranged from 0.7 to 445 $\mu g\,kg^{-1}$. The unit risk of PAH associated with the dermal contact/inhalation of the kitchen soot occurred at 7.4×10^{-3} in children and at 4.8×10^{-5} in the adults, showing the impact. However, the high level of PAH measured in this work especially that of benzo[a]pyrene (B[a]P) may cause cancer in the women who are exposed to the smoke. The study was therefore designed to find out the level of PAH in kitchen soot and their contributions as the monitoring tools in the assessment of risks and hazards of PAH in Ghana.

Keywords: polycyclic aromatic hydrocarbons; soot; risk assessment; Cape Coast Metropolis; kitchens

Introduction

In Ghana and in most of the developing world, wood burning (firewood) has been the main source of energy in the preparation of food, baking, and heating for ages. People are therefore exposed to smoke from the wood-burning activity which contains some amounts of polycyclic aromatic hydrocarbons (PAH) (Raiyani et al. 1993). Meanwhile, contrary to the western type of kitchens, which have effective ventilation systems, most Ghanaian kitchens, especially those in the rural areas, are simple clay hut structures with small doors that only allow the cooks to bend and squeeze themselves into it. The kitchens have little or no openings to aid in ventilation and as a result, the cook is directly exposed to the high doses of smoke.

PAH have received considerable attention as environmental organic pollutants (xenobiotics) in many continents such as the US, Europe, and Asia. A great number of

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PAH have been identified and quantified in virtually all segments of the environment due to their carcinogenicity, mutagenicity, and cytotoxicity at very low concentrations (Davis, Fellin, and Otson 1987).

Exposure to smoke from wood burning in the kitchen can be detrimental; a report submitted by Freeman and Cattel (1990) indicated that wood burning can generate high PAH concentrations. According to their findings, a total concentration of 3000 pg m^{-3} PAH can be generated from wood burning and concentrations of 60 p gm^{-3} for benzo[a]pyrene (B[a]P) have been measured from fuel emissions from small residential wood-burning stoves.

Also, emission studies from residential fireplaces and wood stoves were carried out by Gullet, Touati, and Hays (2003) in the San Francisco Bay area in which a total of 32 PAH compounds ranging from 0.06 to 7.00 mg kg^{-1}, amounting to between 0.12% and 0.38% of particulate matter mass. Additionally, the PAH level of ambient air can be increased by contribution from tobacco smoking (Sakai et al. 2002) while the use of heaters such as gas cookers and firewood heaters can increase PAH concentration in the indoor air (WHO 1987).

As indicated by Liu, Zhu, and Shen (2001), indoor air quality is of particular interest in the world nowadays. Exposure to PAH concentration in indoor air can be in the bedroom, kitchen, living room, and the balcony. The level depends on the ventilation conditions; indoor air of kitchens tends to be more polluted by PAH. They further indicated that if good cooking practice is not employed, cooking oil fumes could make a significant contribution to the PAH concentrations indoors (Moret and Conte 2000).

A recent study by Smith (2006) to assess the household's pollution problems in Ghana clearly indicated that the wood users are the most exposed to hazards with the poorer households standing at a higher risk (Smith 2006). The report indicated that the exposure to air pollution from cooking fires can have long-term health effects and lead to diseases such as cancer, respiratory infection among children, and chronic respiratory problem among women (McGranaham 1994). This may be responsible for the recent increase in the case of breast and cervical cancer diseases among Ghanaian women as reported by Awuah et al. (2004). For example, it was indicated that over 588 breast cancer cases have been recorded at the Komfo Anokye Teaching Hospital in Kumasi alone in 1 year as against 157 cases in the previous year (Awuah et al. 2004; Gray 2008).

The nature of the Ghanaian kitchen and the kind of heating stoves employed during cooking (Figures A.1 and A.2) does not allow for the complete combustion (Smith 2006) and often contains a substantial quantity of PAH (Raiyani et al. 1993). This is because the process of generating the kitchen soot is similar to the way PAH are generated from other sources; both of which result from the incomplete combustion (oxygen limited condition) of the fossil fuels. This may expose the women or men who use the kitchen directly to all kinds of PAH in the smoke, i.e. light, medium, and heavy molecular weight PAH (Freeman and Cattel 1990). PAH from the fire can bind to the ashes and move long distances through the air, especially those that are lighter before the soluble ones get dissolved in water and get into rivers and ground water sources (Sarrazin et al. 2006). However, this is the first investigation being undertaken in Ghana to estimate the distribution of PAH in the indoor (kitchen) environments particulate deposition (Appendix 1).

This study was carried out in the Cape Coast Metropolis of Ghana with about 100,000 inhabitants of whom the majority is engaged in using firewood for cooking, heating, and fish smoking. The purpose of this study therefore was to determine the concentrations of PAH in the soot deposited on the cooking pots from kitchen wood burning and to use the results to quantify the toxicological effect of PAH in the kitchen soot sampled in Ghana. The study does not seek to estimate or compare the amount of PAH produced by the various kinds of firewood as employed by Stumpe-Vıksna et al. (2008); therefore, the correlation between the water content of the fuel woods and the amount of PAH was not considered in this study.

Materials and methods

Sample collection

Random sampling technique was adopted to select kitchens in seven deprived but populated areas in the Cape Coast Metropolis. One sample was collected from each kitchen every week for 2 months between December 2007 and February 2008. Thus, a total of 42 samples were collected for the entire 2-month period from all the seven kitchens. The samples were collected from the cooking pots using a clean blunt knife and a new aluminum foil sheet. The soot deposits were carefully scrapped off the cooking pots onto clean aluminum sheets. This method was employed because having this study as the first of its kind in Ghana; the idea was to determine the level of the various PAH compounds present in the soot generated from the kitchen wood-burning activity and to use the result to estimate how much of such soot particles might have been inhaled by the cook taking into consideration the nature of the kitchens and the heating stoves employed.

However, although difficult, subsequent studies will focus on the use of modern trapping techniques as well as the analysis of soil samples from these kitchens (Figures A.1 and A.2). The samples from the sampling sites were wrapped in aluminum foils and sent to the laboratory in a black aluminum container. In the laboratory, the samples were air dried for 2 h at room temperature. Each soot sample was ground in a laboratory porcelain mortar and sieved through a 450 μm mesh. The homogenized samples were placed in glass sample bottles and kept in a dark locker at room temperature for extraction. Dichloromethane was the main solvent used in the extraction of PAH from the deposited soot samples. The solvents were of analytical grade and those which were not analytically graded were distilled in glass before use.

Extraction of PAH from soot

The extraction procedure employed for the kitchen soot samples in this work is a modification of the method described by Lee et al. (2006). A 10 g aliquot of each of the homogenized soot sample was weighed and transferred into a Soxhlet extraction thimble ($24.5 \times 26.0 \times 60.0$ mm). Each soot sample was then spiked with a deuterated PAH standard solution of 100 $\mu g\, mL^{-1}$ (deuterated *p*-terphenyl) and fitted to the bottom of a multiple Soxhlet extractor. The extractor was then connected to a Grant W14 water circulator operating at 1°C. The contents were vigorously extracted with 60 mL dichloromethane. The above extraction procedure was repeated for the residual sample with another 50 mL of dichloromethane. The two extracts were combined in the same flask and concentrated at 30°C to a volume of 2 mL using a rotary evaporator (Rotavapor R-114, BUCHI Water-bath B-480). Each crude extract was kept in a desiccator at room temperature for a chromatographic clean-up.

Clean-up procedure

About 2 mL of each of the concentrated soot extract was purified using column chromatography. A glass tube, 1.5 × 50 cm^2, was packed with 20 g of silica gel to a height of 30 cm. Before loading the column, the silica gel was activated by heating in a laboratory oven for 2 h at 150°C. The column was conditioned with 30 mL *n*-hexane. The concentrated soot extract was dissolved in 5 mL dichloromethane and applied onto the silica column containing glass wool and about a 0.5 cm layer of sodium sulphate on the top. During the elution, the first 10 mL eluent was collected and discarded. The PAH were eluted from the chromatographic column with 30 mL of dichloromethane. The elution was repeated twice with 25 mL each of dichloromethane. The eluates were combined and concentrated to 2 mL using a rotary evaporator at 30°C for the analysis by the US EPA Method 8100 (1989). The above process was repeated for all the 42 soot samples. The idea for the elution was not to collect separate bands or components of PAH, but to remove impurities such as aliphatic hydrocarbons that pose major problems in the identification of PAH.

Instrumentation

The identification of PAH was conducted using Agilent 6890N gas chromatograph interfaced with Agilent 6890N flame ionization detector (FID) operating in a selective split mode. The injection was done manually. A SLB5$^{\mathrm{TM}}$-MS fused capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) and helium carrier gas at a flow rate of 1.5 mL min^{-1} were used for separation. The make-up flow of helium was 20 mL min^{-1}, and an airflow of 300 mL min^{-1}. The temperature was programmed as follows: oven set point was 60°C, hold for 2 min, 40°C min^{-1} to 170°C, 10°C min^{-1} to 220°C, 5°C min^{-1} to 290°C, hold for 10 min. The injections of 2 µL were performed in the split mode, and the split valve was opened after 2 min. The split ratio was 50 : 1. Sample peaks were identified based on the retention times on the target ion chromatograms and in relative abundance of the qualifier ions selected for each PAH in comparison with PAH standards.

Analytical quality controls

A modified extraction procedure of Chen and Lin (1997) and Lee et al. (2006) was employed in the recovery studies. Two recovery study procedures were conducted to test the efficiency of the extraction system as well as GC/FID. The first recovery study involves random spiking of the soot samples with deuterated *p*-terphenyl surrogate standard solution before extraction. PAH standard solution of 100 µg mL^{-1} was applied to the samples and extracted in the same way as the nonspiked samples. The extracted samples were analyzed and the recoveries were calculated from the differences in total amounts of PAH standard spiked and the amount realized after analysis. Several deuterated PAH standards were used, but only deuterated *p*-terphenyl was chosen for the recovery calculation as directed by the method employed (MEWAM 2003).

The second recovery study involves the use of PAH certified reference materials (soil sample) from the National Institute of Standards and Technology (NIST, USA). This certified soil sample has 24 different standard PAH. The soil control sample was used because it was difficult to obtain a related soot sample standard. About 2.69 g of soil sample was weighed and subjected to the same extraction procedure as applied for all soot samples. Recoveries were calculated from the differences in PAH certified concentrations and the concentrations obtained after analysis using GC/FID.

Recovery results

In this study, similar procedures employed by many researchers in obtaining a final solution of purified PAH, liquid–liquid extraction, and column chromatography were employed. The importance of these differences can only be evaluated in terms of figures on recovery. Fritz (1971) reported about 80% recovery of B[a]P whilst Grimmer and Hildebrandt (1967) obtained recoveries ranging from 87% to 98% for B[a]P, B[b]P, B[a]A and chrysene.

The average recovery for the spiked deuterated *p*-terphenyl surrogate standard in the soot was calculated to be 69%. Table 1 shows the codes of the randomly selected spiked samples, the concentrations of *p*-terphenyl after analysis, and the percent recovery in the soot samples. The results shown in Tables 2 and 3 do not, however, suggest that this difference in the clean-up and recovery had any major effect on the PAH levels determined. The recoveries were calculated from the differences in PAH certified concentrations and the concentrations obtained after analysis by GC/FID. Table 4 shows the PAH concentration from the analyzed (NIST) standard material and the percent recovery results.

The results from the NIST reference material shows high recovery of PAH, ranging from 65% to 102%, with an average PAH recovery of 83%. The use of these recovery results, which were from standard soil samples to assess the efficiency of extraction of PAH from the kitchen soot matrix, is highly contentious since the two samples are of different matrices. However, the values could be used to establish the reliability of the extraction system as well as the efficiency of the GC/FID instrument.

Calculation of the carcinogenic risk

The human health evaluation computerized software-RISC 4.02 (USEPA 1989) was used in the evaluation of the cancer and noncancer risk assessment. Carcinogenic risks are

Table 1. Recovery results for the randomly spiked soot samples with *p*-terphenyl surrogate standard solution (100 $\mu g\,mL^{-1}$).

Sample	*p*-terphenyl ($\mu g\,L^{-1}$)	Recovery (%)
KC3	0.15	68
KA4	0.15	67
KB6	0.21	47
KE3	0.20	50
KE6	0.14	72
KF5	0.14	73
KA1	0.13	76
KA3	0.13	76
KA4	0.12	81
KB6	0.15	66
KE4	0.13	75
KF3	0.13	80
KG2	0.13	76

Notes: K represents kitchen and A–G, sample alphabets.

Table 2. Average PAH concentration in the kitchen soot samples ($\mu g\,kg^{-1}$).

PAH	Averages	SD	Variance
Naphthalene	0.7	0.8	0.6
Acenaphthylene	2.5	1.5	2.4
Acenaphthene	3.0	1.2	1.4
Pyrene	16	8.8	78
Fluoranthene	9.2	5.1	26
Fluorene	7.7	3.2	10
Phenanthrene	3.6	1.7	3.0
Benzo[a]anthracene	31	12	156
Chrysene	2.4	1.0	0.94
Anthracene	9.8	5.4	29
Benzo[b]fluoranthene	79	48	2352
Benzo[k]fluoranthene	85	72	5114
Benzo[a]pyrene	73	33	1058
Indeno(1,2,3-cd)pyrene	26	19	377
Dibenz[a,h]anthracene	450	34	1156
Benzo[g,h,i]perylene	173	11	115

Table 3. Summary of the comparison of the result obtained with other studies.

	Carcinogenic PAH[a]	[BaP] in soot[b]	Carcinogenic PAH in the fly ash[c]	Carcinogenic PAH[d]
Individual	2.4–450 $\mu g\,kg^{-1}$	6–35 $\mu g\,kg^{-1}$	0.06–1.00 $\mu g\,kg^{-1}$	–
Total	750 $\mu g\,kg^{-1}$	48 470 $\mu g\,kg^{-1}$	–	950–1830 $\mu g\,kg^{-1}$
Total PAH	210–1840 $\mu g\,kg^{-1}$	–	8500 $mg\,kg^{-1}$	–

Notes: [a]This work; [b]Stumpe-Vıksna et al. 2008; [c]Kakareka, Kukharchyk, and Khomich 2005; [d]Zou, Zhang, and Atkiston 2003.

estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen. This risk is referred to as the individual excess lifetime cancer risk (IELCR) or just carcinogenic risk. The published values of the chemical carcinogenic toxicity (slope factor) are used to calculate the risk from the lifetime average daily dose (LADD):

$$\mathrm{IELCR}_{ij} = \mathrm{SF}_{ij} \cdot \mathrm{LADD}_{ij}, \tag{1}$$

where IELCR_{ij} is the individual excess lifetime cancer risk for chemical i exposure route j (dimensionless), SF_{ij}, the slope factor for chemical i exposure route j $(\mathrm{mg/kg\text{-}d})^{-1}$, and LADD_{ij}, the lifetime average daily dose for chemical i exposure route j (mg/kg-d).

Calculation of the hazard index

The human health evaluation computerized software-RISC 4.02 (USEPA 1989) was used in the evaluation of the cancer and noncancer risk assessment. The potential for noncarcinogenic effects was evaluated by comparing an exposure level over the exposure duration (maximum of 70 years) with a reference dose derived for a similar

Table 4. Percent recovery analysis of the NIST reference material (dry-mass basis).

PAH (reference)	Concentration ($\mu g\, g^{-1}$)	Recovery (%)
Naphthalene	0.68	80
Pyrene	0.60	102
Fluoranthene	0.42	65
Fluorene	0.08	91
Phenanthrene	0.40	99
Benzo(a)anthracene	0.23	68
Chrysene	0.24	84
Anthracene	0.17	93
Benzo(b)fluoranthene	0.46	102
Benzo(a)pyrene	0.31	85
Indeno(1,2,3-cd)pyrene	0.23	68
Dibenz(a,h)anthracene	0.05	85
Benzo(g,h,i)perylene	0.25	81

exposure period. This ratio of exposure to toxicity for an individual pathway and chemical is called a hazard quotient. The hazard quotients are usually added across all chemicals and routes to estimate the hazard index. Some, however, will argue that it is more appropriate to only sum the hazard quotients for chemicals that affect the same target organ (e.g. liver or blood). The noncancer hazard quotient assumes that there is a level of exposure below which it is unlikely that even sensitive populations would experience adverse health effects (USEPA 1989).

Results and discussion

PAH concentration in kitchen soot

In homes where the occupants do not smoke cigarettes or use candles or incense, residential wood smoke may be of great concern to their health because it is repetitive on successive day-to-day preparation of food and heating. Table 2 shows the average level distribution of PAH in the seven kitchens investigated in Cape Coast Metropolis between December 2007 and February 2008.

In this study, the average distribution of PAH in the seven kitchens ranged from the lowest 0.7 $\mu g\, kg^{-1}$ (naphthalene) to the highest 450 $\mu g\, kg^{-1}$ of dibenz[a,h]anthracene. The results from Table 2 shows that dibenz[a,h]anthracene and benzo[g,h,i]perylene are the predominant PAH in the kitchen soot.

Despite the fact that the concentrations of PAH from the various kitchens are comparable, some of the PAH were predominant at some specific kitchens though some others either decreased or increased across the kitchens. The least PAH concentration of 0.1 $\mu g\, kg^{-1}$ (naphthalene) came from kitchen KF, whereas the highest PAH concentration of 1088 $\mu g\, kg^{-1}$ (dibenz[a,h]anthracene) came from kitchen KE as given in Table 5. A close observation of the above results shows that the use of different woods for smoke generation may be responsible for the variation in PAH concentration. One type of wood species observed in kitchen KE is dried acacia, while in kitchen KF, dried coconut peels.

In a work undertaken by Kakareka, Kukharchyk, and Khomich (2005), the content of the most carcinogenic PAH, benzo[a]pyrene in fly ash and soot was found to range from

0.06 to 1.00 μg kg^{-1}. They also reported the total 16-PAH in the fly ash and soot to be 8500 mg kg^{-1}. Stumpe-Vıksna et al. (2008) found that one of the critical parameters in controlling the level of PAH is the choice of wood for the smoke generation. According to them, spruce wood was found to produce the highest level of individual and total PAH with benzo[a]pyrene from 6 to 35 μg kg^{-1} and total PAH from 48 to 470 μg kg^{-1} (Stumpe-Vıksna et al. 2008).

A similar work done by Zou, Zhang, and Atkiston (2003) gave a pine wood the highest total carcinogenic PAH concentration of 950 μg kg^{-1} and 1830 μg kg^{-1} under fast- and slow-burning conditions, respectively. Similar differences in the PAH concentration were observed from one kitchen to the other in this work even though the statistical test conducted showed no significant differences in the PAH concentrations from the seven kitchens. The differences in concentration may be attributed to the use of different woods in each of the seven kitchens as has been stated above. However, different species of wood and the amount of smoke generated as well as the moisture content of the various woods were not considered in this work.

Comparing the results from this work with the above-reported values, it was realized that the total average carcinogenic PAH concentration in this work (750 μg kg^{-1}) is lower than the lowest average total carcinogenic PAH obtained by Zou, Zhang, and Atkiston (2003). However, the results from this study are relatively far higher than those reported from fly ash and soot. The difference in the results may be due to the methods of sample collection, temperature, and the method of smoke generation. It is important to note that the levels of PAH concentration obtained from the kitchen soot may be high enough to cause cancer-related illnesses (Mazumdar, Redmond, and Sollecito 1975).

It was also realized that 5-ringed PAH were found to be more predominant in the kitchen soot from all the seven kitchens. The high levels of 5-ringed PAH suggests that the soot produced from these kitchens may be hazardous to the human health because Grimmer (1983) indicated that PAH containing four or more rings are more susceptible to inducing malignant tumors than those containing two or three rings (Grimmer 1983). From Table 5, the high levels of PAH obtained from kitchen KE may be linked to the use of partly dried wood by the women as was observed during the sampling that partly dried wood produces soot with high PAH than the fully dried ones (Stumpe-Vıksna et al. 2008).

Table 6 shows the seven kitchens (i.e. KA–KG) and their total PAH concentrations. The highest total PAH concentration was obtained from kitchen KE (1840 μg kg^{-1}) followed by kitchen KF with the least total PAH concentration realized in kitchen KC (210 μg kg^{-1}). Kitchens KD and KA also showed considerably higher total PAH concentration than those from kitchens KC and KB. The variations in the measured total concentration of PAH from the kitchens can be attributed to factors such as the kind of firewood used, the temperature at which the smoke was generated, and the state of the firewood used (i.e. whether fully dried, partly dried, or wet; Stumpe-Vıksna et al. 2008). Other contributing factors of concern are the nature of the kitchen, the type of heating stove employed, and the ventilation system of the kitchen.

Risk assessment of PAH pollution in kitchen soot (carcinogenic and noncarcinogenic PAH)

Figure 1 shows the distribution of total individual carcinogenic and noncarcinogenic PAH. The total carcinogenic PAH was generally higher than the noncarcinogenic ones except for chrysene which had a low concentration similar to those of noncarcinogenic PAH. The low

Table 5. The PAH concentration in kitchen soot samples ($\mu g\,kg^{-1}$).

PAH	KA	KB	KC	KD	KE	KF	KG	Averages	SD	Variance
NA	0.8	0.3	0.2	0.2	0.8	0.1	2.3	0.7	0.8	0.6
Acyl	2.0	3.2	1.4	5.7	1.3	2.2	1.7	2.5	1.5	2.4
Ac	3.5	1.9	2.3	4.2	1.7	4.9	2.9	3.0	1.2	1.4
Py	13	9.5	1.5	22	17	27	23	16	8.8	77
Fl	8.6	6.2	4.2	10	9.2	20	5.8	9.2	5.1	26
F	11	4.3	3.8	6.2	9.2	12	7.5	7.7	3.2	10
Phe	2.7	1.7	2.6	3.2	3.6	4.0	7.1	3.6	1.7	2.9
B[a]A	21	22	12	40	33	45	42	31	12	144
Chy	1.7	2.9	1.2	3.1	2.8	4.0	1.9	2.4	0.9	0.9
An	5.5	13	2.1	12	7.4	18	10	9.8	5.4	29
B[b]F	61	21	15	94	140	120	103	79	49	2351
B[k]F	37	15	19	110	65	204	147	85	71	5114
B[a]P	64	70	13	64	96	85	116	72	32	1058
Ind	24	14	3.6	22	65	33	23	26	19	376
D[a,h]A	381	109	96	435	1088	416	588	445	34	1156
Bg,h,i	207	42	29	162	303	287	181	173	11	121

Notes: Compound abbreviations: naphthalene [NA], acenaphthylene [Acyl], acenaphthene [Ac], Fluorene [F], phenanthrene [Phe], anthracene [An], fluoranthene [Fl], pyrene [Py], chrysene [Chy], benzo[a]anthracene [BaA],benzo[a]fluoranthene [BaF], benzo[a]pyrene [BaP], benzo[g,h,i]perylene [Bghi], benzo[k]fluoranthene [BkF], Dibenz[a,h]anthracene D[a,h]A, and Indeno[1,2,3-cd]pyrene [Ind].

Table 6. Total PAH distribution in soot from the seven kitchens.

Kitchen	Total PAH ($\mu g\,kg^{-1}$)
KA	840
KB	340
KC	210
KD	990
KE	1840
KF	1280
KG	1260

Notes: Letters A–G represent the various seven kitchens.

values for the noncarcinogenic PAH may be linked with degradation by heat during the extraction process. However, the highest total PAH concentration (benzo[a,h]anthracene, 3110 $\mu g\,kg^{-1}$) was among the carcinogenic PAH and the lowest total PAH concentration (naphthalene, 4.6 $\mu g\,kg^{-1}$), the noncarcinogenic PAH. The high carcinogenic PAH concentrations recorded from the kitchens may invariably put individuals (especially mothers and children) at a high risk of cancer-related illnesses. It was also acknowledged that the low concentration of the noncarcinogenic PAH, especially those of low molecular weight, could be as a result of the close proximity of the cooking pots to the cooking fire which might have exposed the highly volatile PAH in the soot to high temperatures.

In the risk assessment studies, PAH carcinogenic risk and hazard assessment were conducted on seven individual average PAH concentrations by employing central

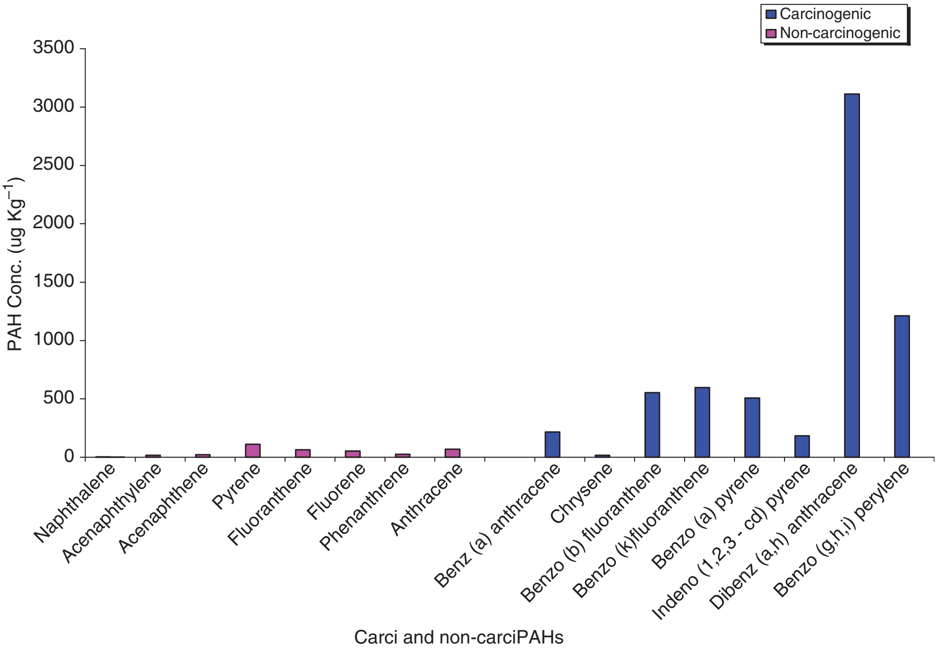

Figure 1. Comparison of carcinogenic and noncarcinogenic PAH in kitchen soot.

tendency exposure (CTE), in accordance with the USEPA's Risk Assessment Guidance for Superfund (RAGS; USEPA 1989). The unit risk was estimated considering a lifetime of 70 years for adults and up to 2 years for children using the Human Health Evaluation Computerized software-RISC 4.02 (USEPA 1989). Table 7 shows the results of the carcinogenic-PAH risk assessment for inhalation route in humans for dibenz[a,h]anthracene, benzo[b]fluoranthene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, chrysene, and indeno[1,2,3-cd]perylene (Anuj-Bhargava et al. 2004). The total PAH carcinogenic unit risk for inhalation is calculated as 4.8×10^{-5} in adults and 7.4×10^{-3} in children. The result implies that about 5 out of every 100,000 adults may suffer from cancer-related diseases through inhalation of the kitchen soot in their lifetime. In children, the results indicate 7 out of every 1000 children may suffer from cancer-related diseases through inhalation of the kitchen soot in their lifetime (Gray 2008; USEPA 1995).

Hazard Assessment was also conducted by using hazard quotients for kitchen soot as shown in Table 8 for acenaphthene, anthracene, fluoranthene, fluorene, and pyrene. The total PAH hazard quotients for dermal contact in adults and children are 9.1×10^{-5} and 6.1×10^{-4}, respectively. The hazard quotients indicate that at least 9 out of every 100,000 adults may suffer from some noncancer-related illnesses in their lifetime through inhalation or dermal contact with the kitchen soot. For children, the incidence of noncancer-related diseases is 6 out of every 10,000 (USEPA 1995).

The values of CTE-PAH were used to estimate the corresponding lifetime health risks associated with the typical exposure to the constituents of concern (COCs). With respect to the health risk via the inhalation route, the World Health Organization (WHO) suggested the unit risk of 8.7×10^{-5} for a lifetime (70 years) of PAH exposure (Ohura et al. 2004). Some of the values from this work especially those for children have exceeded the

Table 7. Summary of PAH carcinogenic risk for kitchen soot.

PAH	Inhalation of PAH (soot) Adult	Inhalation of PAH (soot) Child
Benzo[a]anthracene	2.4E−07	3.7E−05
Benzo[a]pyrene	5.7E−06	8.9E−04
Benzo[b]fluoranthene	6.8E−07	1.1E−04
Benzo[k]fluoranthene	8.2E−08	1.3E−05
Chrysene	1.9E−10	2.9E−08
Dibenz[a,h]anthracene	4.1E−05	6.4E−03
Indeno[1,2,3-cd]perylene	2.4E−07	3.7E−05
Total	4.8E−05	7.4E−03

Table 8. Summary of hazard quotients for the kitchen soot.

PAH	Dermal contact of PAH in soot Adult	Dermal contact of PAH in soot Child
Acenaphthene	4.4E−06	2.9E−05
Anthracene	2.9E−06	1.9E−05
Fluoranthene	2.1E−05	1.4E−04
Fluorene	1.6E−05	1.1E−04
Pyrene	4.8E−05	3.1E−04
Total	9.1E−05	6.1E−04

health-based guideline level (10^{-5}; Boströn et al. 2002). It can therefore be said that there is some health risk of noncancer-related illnesses for women who cook and their children who stay with them during cooking.

Conclusion

The results from previous works (such as Chen and Lin 1997) and this study confirm the presence of PAH in the soot and suggest that the practice of burning wood in kitchens as a source of energy for cooking and heating may pose serious health effects to the cook and children who stay with them during cooking.

The analysis of PAH concentration revealed that Dibenz[a,h]anthracene showed the highest concentration in the soot sample. It was also observed that the carcinogenic PAH were higher in concentration than the noncarcinogenic ones. This difference may be attributed to the fact that some of the PAH with low molecular weight might have been lost during storage and extraction because of their susceptibility to oxygen, heat (lost due to high temperature of the cooking pot) and light degradation and might have been responsible for the reduction in the noncarcinogenic PAH (Chen, Wang, and Chiu 1996; Gomma et al. 1993). The statistical comparison (ANOVA) of the independent variables in the soot showed certain deviations from the expected result. For instance, the samples collected from different kitchens were expected to show a significant difference in PAH concentration from one kitchen to another based on the suspicion that different firewood might have been used in the various kitchens. The insignificant differences observed in the results may be attributed to the fact that well-dried wood were mostly used in all the seven kitchens.

Correlation analysis conducted showed positive and strong correlation relationships between the PAH from the seven kitchens, confirming the common origin of the PAH in the soot (wood smoke). Even though the results from this work show high PAH levels, especially those of carcinogenic PAH, it cannot be used hitherto to correlate the amount of PAH that enters the body of individuals through inhalation and the dermal passage because the amount of PAH inhaled or contacted during cooking and heating is relative from kitchen to kitchen depending on the method of fire set, kind of firewood used, how long one stays in the kitchen, and the ventilation system of the kitchen. As the results from these kitchens are relatively high, minimization of these compounds into human system is required through adoption, enacting, and enforcement of legislations on smoke pollution in Ghana. The womenfolk should also be educated on the health risks associated with the use of firewood during cooking as well as actions that help reduce the impact.

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Appendix

Figure A1. A cook in contact with direct smoke emanating from locally made cooking stove.

Figure A2. Typical process of smoking fish in Ghana (Smith 2006).

Suppliment 5

Levels and Distribution of Polycyclic Aromatic Hydrocarbons (PAHS) in some water bodies in Esbjerg, Denmark

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ABSTRACT

The levels and distributions of 6 polycyclic aromatic hydrocarbons (PAHs) in 6 selected water bodies in Esbjerg, Denmark were studied. In all, 12 water samples were collected from the 6 water bodies and the PAHs present were extracted with Isolute solid phase extraction (SPE) columns and analysed using GC/MS/MS with ion trap detector (TCD). There were some levels of the individual as well as the total PAHs in the lake water samples (referred to as retention points) and also, all 6 PAHs were generally not well distributed in all the water samples. The most abundant components were flourene and fluoranthene. The total of the 6 PAHs in the water bodies ranged from 26.8 to 105.5 μg L-^{1} with an average of 68.4 μg L-^{1} whiles the mean benzo(a)pyrene (BaP) concentration is 2.6 μg L-^{1}. In fact, the PAH levels in the study cannot be compared with ground water limit because the two scenarios are not the same. With regard to the river, the PAHs levels obtained in this study are within acceptable limit. However, the study shows that there are some depositions of PAH on the Esbjerg water environment which needs attention. Carcinogenic PAH levels in water bodies in Esbjerg is hitherto a scarcely explored problem as a result, more studies are ongoing to strengthen this database and investigate the range and profile of carcinogenic PAHs content in the Esbjerg environment.

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[1]

Key Words; polycyclic aromatic hydrocarbons, water bodies, source assessment, Esbjerg

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) comprise the largest class of chemical compounds, known to be genotoxic agents (SCF, 2002). They are formed whenever wood, coal or oil is burnt. Owing to their mode of formation, PAHs are almost ubiquitous in the environment and therefore enter into the food chain, via air, water and soil (Falco et al. 2003; Šimko 2002; Tfouni et al. 2007*)*. Out of the, billions of poisonous chemicals in the environment, PAHs accumulate and with time pose an imminent threat to public health, mostly water pollution. Also, the PAHs in water get adsorbed onto fish skins, which pose serious health problems to man since it is a source of food (Binková and Srám, 2004; Berrojalbiz et al., 2009).

Water supply, urban drainage and wastewater treatment systems were originally designed to solve just conventional problems such as supply of potable water, flooding prevention and sanitation. The main problem within the conventional urban water cycle approaches now is the absence of designs to deal with xenobiotics. There has been an increased focus nowadays on rainwater use, wastewater reclamation and reuse in industrial and as well in domestic sector which may increase the exposure to xenobiotics. Innovative approaches are therefore needed to prevent xenobiotics from being discharged into surface waters where they may give rise to impacts on the chemical water quality and ecological status of receiving waters as it is already recognized by the EU-Water Framework Directive (Hlavinek et al., 2007). As a result, surface waters, such as rivers, lakes and seas, receive large quantities of waste water from industrial, agricultural, and domestic sources, including municipal sewage treatment plants which contain a lot of xenobiotics. These surface waters, which contain many unknown compounds, are used as a source of drinking water, as well as for agricultural, recreational and religious activities around the world. Consequently, water pollution can be a serious public health and aquatic ecosystem problem as it transports mutagens (Ohe et al., 2004)

One of the primary aims of environmental quality studies is to understand the impacts of anthropogenic compounds such as organic micropollutants on the ecosystem, in order to minimise or prevent adverse effects. Organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) may enter the water environment from many different sources including road runoff, atmospheric precipitation, sewage outfalls, leachates from land filling and maritime transport (Zhou and Maskaoui, 2003)

Anthropogenic input from incomplete combustion, oil spills, urban runoff, domestic and industrial wastewater discharges, as well as atmospheric fallout of vehicle exhaust and industrial stack emission have caused significant accumulation of PAHs in the environments (Simpson et al., 1996; Zakaria et al., 2002). Nielsen (1996) reported that motor vehicle emissions alone could account for as much as 90% of the particle-bound PAH mass in the air in downtown Copenhagen and that PAH levels varied both temporally and spatially as a function of traffic patterns. Due to their toxic, mutagenic, and carcinogenic characteristics, PAHs are considered to be hazardous to the biota and environment. Because of their low water solubilities and high partition coefficients, these compounds are strongly sorbed onto the surface of particles associated with the organic compounds of solid phase matrix and can be deposited to the underlying sediments (Kim et al., 1999; Doong and Lin, 2004).

PAHs are known for their carcinogenic, mutagenic (gene mutation causing agent) and teratogenic (chemicals that affect the normal development of foetus) properties (Luch, 2005). Some people who have breathed or touched mixtures of PAHs and other chemicals for long periods of time have developed cancer. A research conducted by the Agency for Toxic Substances and Disease Registry under the Canadian department of Health and Human services in the year 2007, ranked PAHs as the seventh most hazardous substance among a number of 275 compounds on which the research was conducted (Aynankora et al., 2005; ASTDR, 2007). PAHs have also been reported to disrupt endocrine systems in humans (Zakaria et al., 2005). Hence, their presence/distribution/source in the environment and potential human health risks has become the focus of much attention in recent times.

Esbjerg is a Danish harbour city on the west coast of the Jutland peninsula in southwest Denmark. Esbjerg with a population of 71,025 (2009) is the fifth largest city in Denmark (Esbjerg Kommunen, 2009). The condition of the environment in the city of Esbjerg is affected by a few types of pollution sources. Besides the fishing industry, Esbjerg is also an important port for the Danish North Sea oil offshore activity, which influences the quality of the environment. The city of Esbjerg is also a large transport hub for road, water and rail traffic therefore attracting big companies such as Mærsk Oil & Gas, Ramboll Oil & Gas, ABB A/S, Schlumberger, COWI and Atkins Denmark. All of these companies have offshore related activities in Esbjerg (Danish Offshore Database, 2009). The largest particulate matter (PM) emission sources are the residential sector (55%), followed by road traffic (18%) and other mobile sources (13%), and the rest comes from industrial and other sources (OECD, 2007).

The objective of this paper is to measure PAH concentrations and distribution in the local surface waters in Esbjerg and identify major contributing sources. This paper is part of a wider research programme concerning particulate matter pollution of the Esbjerg environment.

MATERIALS AND METHODS

Sample collection

The samples were collected from twelve sampling points from six water bodies in Esbjerg, Denmark. The six water bodies are;

1 Spangbjerg møllebæk (River)
2 Gamelby møllevej lake 1
3 Gamelby møllevej lake 2
4 Gamelby møllevej lake inlet
5 Rørkær lergravsparken lake
6 Nordskræntene v. Granlunden lake

Two samples were taken from each water body labelled ‘a’ and ‘b’. The label ‘a’ refers to up-stream sample and ‘b’ downstream water samples. The sampling sites have been indicated on the map below with a red circle and their respective numbers. The water samples were collected into 1.0 L amber bottles and sent to the laboratory for immediate extraction and analysis.

Fig. 1: Map of Esbjerg showing the sampling sites (Courtesy; Google Earth)

Sample analysis

Dichloromethane, isooctane and cyclohexane solvents were of chromatographic grade and purchased from Sigma-Aldrich, Germany. The stock reference standard of 6 PAHs (not a mixture) from Sigma-Aldrich, Germany includes fluorene, fluoranthene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, and benzo(ghi)perylene at 98% purity.

The Isolute solid phase extraction (SPE) columns were conditioned with 5 mL methanol under vacuum, then with 5 mL of deionized water. 10 mL of deionized water was subsequently passed through the column with the flow rate of 1 mL min-^{1}. Ten millimetres of isopropanol alcohol was added to the filter water samples (filtered using a 0.2-µm pore size PTFE) before it was run through the Isolute solid phase extraction (SPE) column (Isolute SPE column USA: Isolute PAH 1.5 g/6mL Part #

927-0150-C). The column was allowed to dry completely after the extraction and dichloromethane (DCM) was used to elute the PAH fractions from the SPE (Kanchanamayoon and Tatrahun 2009). The DCM extract was evaporated to dryness under a gentle stream of pure nitrogen after adding 3 mL of isooctane and then dissolved to 3 mL with internal standard Methylheptadecanoic acid (IS, MHD) in cyclohexane for analysis of the PAHs. The final concentrated extracts from the water samples were analyzed using Varian 8200 Cx Auto Sampler and Varian 3800 GC coupled with Varian Saturn 2000 GC/MS/MS with ion trap detector (TCD).

Quality control analysis

The analytical precision was checked by the analysis of PAH standards and each of the triplicate results were not significantly different at the 95% confidence level. The internal standard was also run along with the samples to ensure accurate readings. Limits of Detection (LOD): [fluorene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(ghi)perylene] = 0.001mg L^{-1} and [fluoranthene] = 0.005 mg $L-^{1}$ [nd = below detection limit]

RESULT AND DISCUSSIONS

The total PAHs in the analysed water bodies in Esbjerg city were from 26.8 µg $L–^{1}$ to 105.5 µg $L–^{1}$ and the mean total concentration of PAHs was 68 µg $L–^{1}$ for the ∑6 PAHs. High molecular weight PAHs with 4–6-rings had elevated levels of the total dissolved PAHs in the created lakes (retention points) of Esbjerg city (Figs. 2 and 3).

Table 1: Mean PAH levels in the water bodies in µg/L

Sample	Spangbjerg møllebæk	Gamelby møllevej lake 1	Gamelby møllevej lake 2	Gamelby møllevej lake inlet	Rørkær lergravsparken lake	Nordskrænten v. Granlunden lake
Fluorene	10.8	5	22	25.5	3.5	25
Fluoranthene	16	54	49	50	48	72
Benzo(k)fluoranthene	0	0.5	0	0	1.5	5
Benzo (b) fluoranthene	0	0.5	0	0	1	3.5
Benzo(a)pyrene	0	4	3.5	2	6	0
benzo(ghi)perylene	0	0	0	0	2	0
Total	**26.8**	**64**	**74.5**	**77.5**	**62**	**105.5**

The mean benzo(a)pyrene (BaP) concentration is 2.6 µg L-^{1}. However, the PAH levels in the study cannot be compared with ground water limit because the two scenarios are not the same. This shows that there are some PAH deposition into the Esbjerg created lake water (retention points) environment which needs some attention. The highest concentrations of the 6 selected PAHs were identified in the created lakes which also receives effluent from the community. Influences from most PAH sources (road run-offs, industries and transport) are evident.

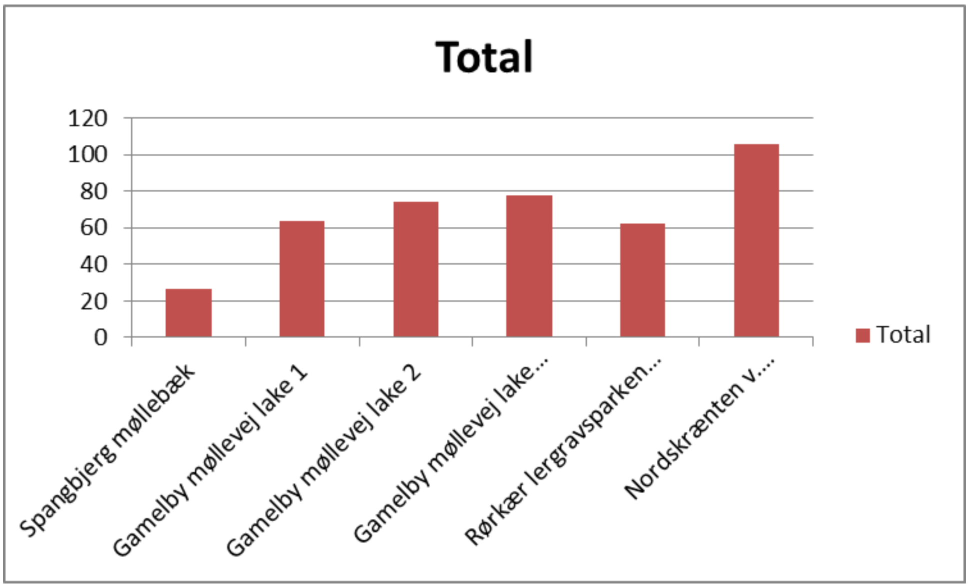

Fig. 2: Mean total PAHs levels in the monitored water bodies in Esbjerg

Distribution of PAHs in the surface water bodies

Two of the 6 PAHs analysed, fluorene and fluoranthene were present in all the water samples (Fig. 3). However, fluoranthene was generally higher than the other PAHs in almost all the twelve (6) water bodies. The other four benzo(a)pyrene, benzo(k)fluorathene, benzo(b)fluoranthene and benzo(ghi)perylene were not very high compared to fluorene and fluoranthene, however, their presence in the created lakes is significant. A similar study conducted in Nigeria (Okoro, 2008) reported similar levels except for that of fluorene and fluoranthene which had elevated values in our study. The benzo(a)pyrene levels in this study is lower than that of the Jiulong River Estuary, China studied by Maskaoui et al., (2002).

Six of the PAHs were found not very well distributed in all the water bodies analysed and their values ranged, fluorene (3.5 – 25.5) μg/L, fluoranthene (16 – 72) μg/L, benzo(k) fluoranthene (BD – 5) μg/L, benzo(b) fluoranthene (BD – 3.5) μg/L, benzo(a) pyrene (BD – 6) μg/L and benzo(ghi)perylene (BD – 2) μg/L. However, most of the carcinogenic PAHs were below the detection limit (BD) (<0.001 μg/L) of the Varian Saturn 2000 GC/MS/MS employed in the analysis. The distribution of PAHs in this study followed a similar pattern as that obtained by Essumang et al., (2009). The heavy molecular mass PAHs were only scarcely found in most of the water samples.

The levels of benzo(a)pyrene in the water may be an indication of both pyrogenic and petrogenic sources of PAH pollution on the environment (Denissenko, 1996).

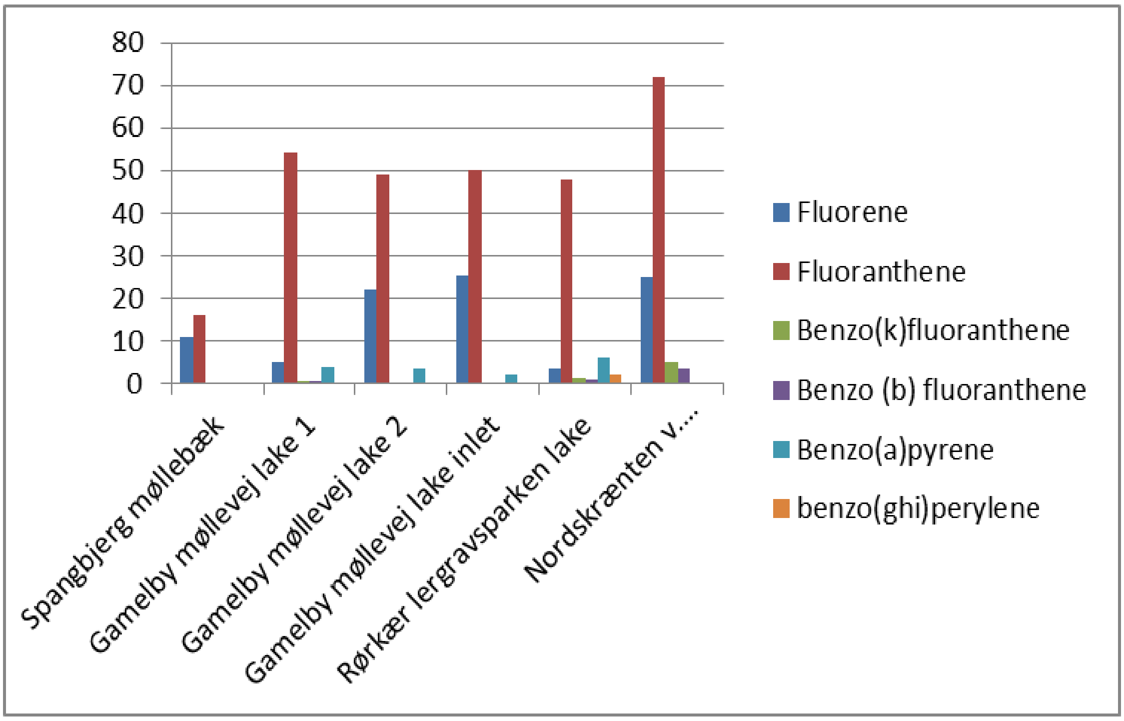

Fig. 3: Distribution of mean PAH levels in the monitored water bodies in Esbjerg

Correlation Analysis

In order to investigate the relationship between the twelve sampling points, correlation analysis of the PAHs data was conducted using Pearson's method. The result is presented in Table 2. All the sampling sites (1a-6b) were strongly positively related ($r > 0.7$, $p < 0.05$) to each other with regards to the monitored PAHs. This result may suggest that all the sampling sites are almost equally affected by these pollutants from their source(s) or the pollutants to these sites may come from the common source. The highest correlation was seen between 2b and 5b (0.999) at 0.01 levels. Sample 1b strongly correlated positively (0.946-0.998) with most sites (2a, 2b, 3b, 4a, 5b, 6a, and 6b) all at 0.01 level. Again, 1b correlated with 3a, 4b and 5a (0.883-0.15) at 0.05 levels. Most of the sites correlated positively, with the exception of sites 1a which only correlated with 3b and 4b with 0.821 and 0.971 at 0.05 and 0.01 levels respectively. This may mean that all the water bodies receive their PAHs from pyrogenic as well as petrogenic depositions.

Table 2: Pearson Correlation matrix of the water samples N=6

samples	a1	b1	a2	b2	a3	b3	a4	b4	a5	b5	a6	b6
a1	1											
b1	0.75	1										
a2	0.50	.946**	1									
b2	0.60	.974**	.990**	1								
a3	0.74	.915*	.857*	.916*	1							
b3	.821*	.994**	.906*	.947**	.917*	1						
a4	0.59	.974**	.994**	.995**	.875*	.944**	1					
b4	.971**	.883*	0.689	0.773	.866*	.929**	0.756	1				
a5	0.43	.914*	.996**	.977**	.831*	.865*	.981**	0.625	1			
b5	0.60	.969**	.989**	.999**	.925**	.941**	.991**	0.769	.977**	1		
a6	0.69	.987**	.959**	.974**	.866*	.972**	.981**	.827*	.929**	.965**	1	
b6	0.79	.998**	.928**	.962**	.912*	.998**	.961**	.905*	.891*	.956**	.984**	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

PAHs interrelationships

The result of a relationship check between the examined PAHs with Pearson's correlation procedure is shown in Table 3. The outcome of the analysis showed that most of the PAHs are not correlated, indicating they might come from a different factor or source. The only PAHs that correlated are BbF and BkF (0.995) at 0.01 levels. These PAHs are isomers and however, their source may be the same.

Table 3: Pearson Correlation matrix of the PAHs (N=12)

PAH	Fluorene	Fluoranthene	BkF	BbF	BaP	BghiP
Fluorene	1					
Fluoranthene	0.442	1				
BkF	0.008	0.316	1			
BbF	-0.014	0.285	.995**	1		
BaP	-0.293	-0.237	-0.157	0.137	1	
BghiP	-0.329	0.032	0.244	0.21	0.362	1

**. Correlation is significant at the 0.01 level (2-tailed).

CONCLUSION

The result obtained from this study clearly demonstrates that the influences from most PAH sources (industrial, energy and transport) are evident. The total of the 6 PAHs in the water bodies ranged from 26.8 to 105.5 µg L-^{1} with an average of 68.4 µg L-^{1} whiles the mean benzo(a)pyrene (BaP) concentration is 2.6 µg L-^{1}. Most of the water bodies analysed was lakes which do not flow all year round. The only river (Spangbjerg møllebæk) sampled had most of the PAHs below the detection limit of the instrument. All the 6 PAHs analysed generally were present in the water bodies at significant levels but not very well distributed. The correlation analysis identified mixed petrogenic and pyrogenic sources as the main contributors of PAHs on the Esbjerg environment.

Carcinogenic PAHs pollution in Esbjerg owing to vehicular, thermal and industry on water bodies is hitherto a scarcely explored problem. More studies are ongoing to strengthen this database and to investigate the range and profile of carcinogenic PAHs content in the Esbjerg environment.

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Suppliment 6

Distribution, Levels, and Source Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the particulate matter (PM) of some indoor environment in Esbjerg, Denmark

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ABSTRACT

Six polycyclic aromatic hydrocarbons (PAHs) compounds with some known to be carcinogenic in air particulate matter (PM) collected on Spider web (accumulated for over six months) from eight domestic kitchens of Esbjerg, Denmark were measured in this study. In all, 21 spider web PM were collected and the PAHs present were extracted with dichloromethane and analysed using GC/MS/MS with ion trap detector (TCD). There were some levels of the individual as well as the total PAHs in the PM samples and also, all 6 PAHs were present in all the collected samples due to the very long exposure time. The total 6 PAH concentrations in indoor PM ranged from 0.942 to 8.219 mg kg^{-1} d.w, with an average of 3.391 mg kg^{-1} d.w. The benzo(a)pyrene (BaP) levels in the various kitchens were also from below detection to 0.583 mg kg^{-1} with an average value of 0.191 mg kg^{-1} d.w. The diagnostic ratios and the correlation analysis identified pyrogenic (cooking sources: oil-fumes, grilling and smoking) as the main source of indoor PAHs with some amount from petrogenic sources (outdoor). In Esbjerg, most of the residential areas are very close to major roads hence, the influence of outdoor PAHs on the indoor environment. PAH pollution in Esbjerg owing to indoor air PM is hitherto a scarcely explored problem. More studies are ongoing to strengthen this database and to investigate the range and profile of carcinogenic PAHs content in the Esbjerg indoor environment.

Key Words: Petrogenic, pyrogenic, indoor-PAHs, particulate matter, oil-fumes, grilling

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INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are known to be genotoxic and carcinogenic to humans according to the International Agency for Research on Cancer (IARC, 1985; Samanta 2002). Concerns about the potential carcinogenic properties of some PAHs have led to an increased need to determine the extent of pollution caused by this group of compounds in recent times (Denton 2006). PAHs have been identified as very important among the organic hazardous air pollutants due to their carcinogenicity and mutagenicity (Castro et al. 2010; Mannino and Orecchio, 2008).

Epidemiological studies showed an elevated incidence of cancers among non-smoking population exposed to smoke from wood-burning activity which contains some amounts of PAH (Raiyani et al. 1993).

A number of air pollutants, associated with particulate matter, are generated in the indoor environment from human activities such as cooking, cleaning, smoking and burning of candles among others. Indoor air of kitchens is polluted by PAHs that come from emission sources such as cooking, using liquefied petroleum gas, ovens (during grilling) and some home appliances. Even though there are extractors fixed in most kitchens in Europe yet this does not take care completely of indoor emissions. For example, ovens are opened on the sideway and this does not allow the extractor to take all the emissions coming out of it. As a result, thick fumes (oil-fumes) are sometimes generated during grilling and when a food item put in the oven get burnt making significant contribution to PAH concentrations of indoor air (Castro et al. 2010; Moret and Conte 2000).

A report indicated that the exposure to air pollution from cooking fires can have long-term health effects and lead to diseases such as cancer, respiratory infection among children, and chronic respiratory problem among women (McGranaham 1994). Also, emission studies from residential fireplaces and wood stoves were carried out by Gullet, et al., (2003) in the San Francisco Bay area in which a total of 32 PAH compounds ranging from 0.06 to 7.00 mg kg-^{1}, amounting to between 0.12% and 0.38% of particulate matter mass were identified. Additionally, the PAH level of ambient air is known to be increased by contribution from tobacco smoking (Sakai et al. 2002) while the use of heaters such as gas cookers and firewood heaters can increase PAH concentration in the indoor air (WHO 1987). A study by Castro et al, (2010) in Paranhos district of Oporto city in Portugal puts tobacco smoking (with heating temperature greater than 700^{o}C) contribution to indoor ambience total PAH to about 8 times that of non-smoking indoor environment.

As indicated by Liu et al., (2001), indoor air quality is of particular interest in the world nowadays. Exposure to PAH concentration in indoor air can be in the bedroom, kitchen, living room, and the balcony. The level depends on the ventilation conditions but indoor air of kitchens tends to be more polluted by PAH. They further indicated that if good cooking practice is not employed, cooking oil fumes could make a significant contribution to the PAH concentrations indoors (Moret and Conte 2000).

Women (cooks) exposed to long-term cooking oil-fumes and kitchen air were found to have had increased levels of cancers (an excessive bladder cancer) (Schoenberg et al., 1984; Zhu and Wang, 2003).

It has been indicated that the two, three, and four-ring PAHs were predominant in the vapour phase due to their low molecular weight ($MW < 220$). While the five-ring PAHs (high molecular weight PAHs) were primarily associated with the particulate phase or remain in particle-bound fractions due to their low vapour pressure and high actanol air partition coefficient values (Jones et al. 1992; Kaupp, 1996). The fraction of PAHs in vapour phase will increase with the increase of temperature with the release of abundantly high molecular weight PAHs (MW > 202) (Liu et al., 2001). It has been also established that petroleum – derived residue contain relatively high abundances of lower molecular weight PAHs (MW<202) (Mai et al. 2003, Halek and Kianpour-rad 2010). Petroleum derived PAHs are preferentially biodegradable as compared to combustion derived ones (Jones et al, 1986; Singh et al. 2008). In contrast, production or release of PAHs through combustion processes usually favours the release of unsubstituted or less-alkylated forms of PAH over more highly alkylated forms, and the proportion of alkylated to unsubstituted PAHs varies as a function of combustion temperature (Aboul- Kassim, and Simoneit, 2001, CCME, 2008).

Several studies indicated that PAH concentrations in indoor air can be higher than in outdoor air with certain combustion sources (Liu et al. 2001). Because people spend more than 80% of their time in indoor environments (homes, schools, offices and restaurants and particularly in the kitchen) there is a special interest in analysing the exposure to PAHs in indoor environments and evaluating the influence of the main indoor emission sources. In this study, the levels, distribution and sources of 6 PAHs were examined in 8 kitchen environments in Esbjerg.

MATERIALS AND METHODS

Particulate matter (PM) deposited on natural spider web from 8 kitchens was monitored in Esbjerg, Denmark. Spider web act as a filter as such, as air passes over it, it’s able to take all the PM present in it. It is therefore a good keeper of PM that is found in the air (Passive sampler). The collected samples were the total suspended particulate matter (TSPM). These spider webs had been formed at hidden places where normal cleaning is not done regularly in those kitchen areas (eg behind the heaters in the various kitchens, around the cabinet, in the heater area, behind refrigerators etc.). The first PM samples collected had formed over a period of over 6 months whilst the second were collected after eight weeks. The period of sampling was between April and June, 2010 (during the spring). These sampling areas could be categorized into 2 groups. The first group is made up those who use electrical heaters without smoking occupants. The second group is also made up of those who use liquefied petroleum gas (LPG) for heating and some of their occupant smoke cigarettes or other smoking objects. In all, 21 samples were collected over the period. Among the 21 samples, 15 were using electrical heaters, 3 from individuals who were using LPG together with 2 smokers and 3 were using electrical heaters but very close to road/main train station which operate as a semi-public facility as well.

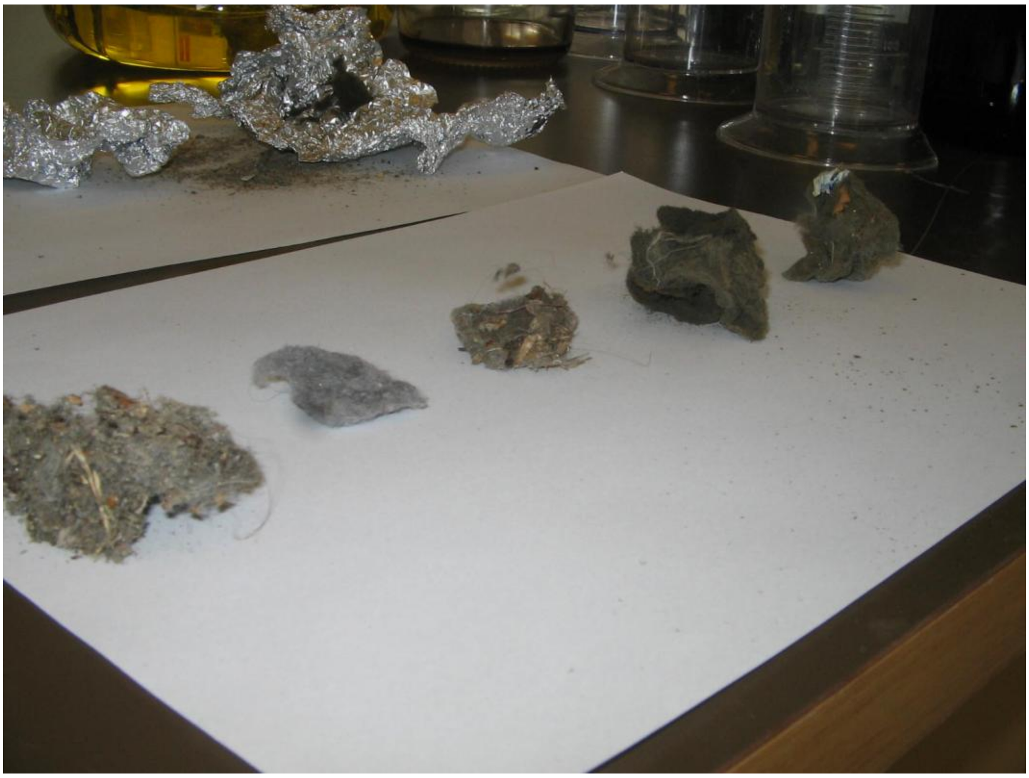


Plate 1: Spider web with the Particulate Matter collected from some kitchens

Sample Collection

The standard method to measure PAHs in ambient air is by active samplers. Active sampling is also the most common method, often considered as the “gold standard”, within occupational hygiene to measure and monitor human exposure to PAHs in workplaces and homes. The use of the spider web is entirely a new passive sampling approach for PAHs which has not been validated on uptake rate, exposure time geometry and structure which might influence the presented approach. Even though, most passive samplers like the spider web, have high contaminant retention (high uptake), low sampling rate and long exposure times, the sensitivity to the pollutants to be analysed and its insensitivity to interfering matrix components have not been validated and which may influence the spider web approach which invariably may affect the levels of the result (Bohlin, 2009).

The objective was to collect respirable PM from breathing zone and the surrounding area during cooking and grilling for indoor-air PAHs estimates. In this study, PM that gets trapped by spider web in the kitchen area (sampled at 2 – 4 points) was collected and composited. All the samples were immediately wrapped in an aluminium foil, transported to the laboratory and kept in the fridge prior to analysis of PAHs.

Sample analysis

Dichloromethane, acetone, acetonitrile, isooctane and cyclohexane solvents were of chromatographic grade and purchased from Sigma-Aldrich, Germany. The stock reference standard of 6 PAHs (not a mixture) from Sigma-Aldrich, Germany includes fluorene, fluoranthene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, and benzo(ghi)perylene at 98% purity.

About 10 g dry weight (d.w.) of the PM together with the spider web samples were weighed precisely and were then covered with 50 mL dichloromethane (DCM) and sonicated for 72 hours at room temperature (Allen et al., 1996; Jorgensen, 1999; Guerin, 1999). The particle/liquid suspension and additional DCM used to rinse the jar were filtered using a 0.2-μm pore size PTFE filter. The solvents were removed by rotary evaporation after adding 5 mL of isooctane and 3 mL internal standard Methylheptadecanoic acid (IS MHD). This was further concentrated (at 55°C) to approximately 2 mL prior to clean-up. The samples were cleaned up using solid phase extraction (SPE) columns (Isolute SPE column USA: Isolute PAH 1.5 g/6mL Part # 927-0150-C). Dichloromethane was used to elute the PAH fractions from the SPE and finally evaporated to almost dryness under a gentle stream of pure nitrogen, then dissolved to 3 mL with cyclohexane for analysis of the PAHs. The final concentrated extracts from the samples were analysed using Varian 8200 Cx Auto Sampler and Varian 3800 GC coupled with Varian Saturn 2000 GC/MS/MS with ion trap detector (TCD).

Quality Control

To evaluate the precision of the analysis, three replicates of field samples and standards were analysed. The relative standard deviations of the replicates on the concentrations of individual PAHs ranged from 6% to 19% and were satisfactory for determinations at the μg m-^{3} level (Mannino and Orecchio, 2008).

RESULTS AND DISCUSSION

Appendix A (table 1) summarizes the mean PAH concentration of triplicate analyses of weeks one and eight samples obtained for all indoor PM collected at some kitchens in Esbjerg. Sources of the PAHs in the environment under investigation have been estimated, in similar way to that reported for other matrices by Mannino and Orecchio, 2008. The total 6

PAH concentrations in indoor PM ranged from 0.942 to 8.219 mg kg^{-1} d.w, with an average of 3.391 mg kg^{-1} d.w. These levels recorded in this study do not reflect the normal indoor daily PM-PAH levels because, the samples had gathered for over six months. This however, only gives an indication that there is some PM-PAH emission in the indoor environment which needs to be investigated further. The PAH concentrations found in the PM samples indicates almost homogeneous sources of contamination in the investigated indoor environments (Mannino and Orecchio, 2008). The total PAH levels in indoor PM for smoking household where tobacco was burnt (7) and a semi-commercial facility (6) were higher than the others as reported in literature (Castro et al, 2010; Bayram and Muezzinoglu, 1996). Furthermore, for each PAH studied, the highest levels (except fluoranthene) were recorded in smoking household PM as reported in similar studies by Castro et al. (2010), Bayram and Muezzinoglu, (1996). Kitchen number 7 (Roust near Esbjerg) from fig. 1 generally had the highest PAHs levels. LPG is what was being used for heating and most of the occupants were cigarette smokers as well.

Distribution of PAHs

All the six PAHs analysed were present in the PM samples from the various kitchens at various levels. The individual PAHs ranged from below detection for benzo(b)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene from kitchens 2, 5 and 6 respectively to 4.555 mgkg-^{1}fluoranthene (Mannino and Orecchio, 2008). This high PM-PAH levels is due to the fact that, the exposure time is over six months period.

In general, fluoranthene and fluorene levels were quite high (fig. 1), but the general distribution of PAH seems similar to results obtained in a similar study in Palermo (Mannino and Orecchio, 2008). It is evident from the result that, cigarette smoking indeed (may) adds some amount of PAHs into the indoor environment. Kitchen 7 which housed those who smokes generally had high levels of PAHs. Castro et al. (2010), Bayram and Muezzinoglu, (1996) in their report also stated the contribution of PAHs from cigarette smoke.

Benzo(*a*)pyrene (BaP) contributed quit significantly. Maximum concentrations of indoor PM benzo(*a*)pyrene >0.5 mg kg^{-1} d.w with an average level of 0.191 mg kg^{-1} d.w was found in the study. The average BaP concentration is high but the PM in the spider web had gathered for (accumulated over a long period of time) over six months. Hence these higher BaP and other PAH levels cannot be compared with data from other Danish cities (benzo(a)pyrene 4.4 ± 1.2 ng m^{-3}) by Nielsen et al. (1996) because the samples used are not under the same conditions.

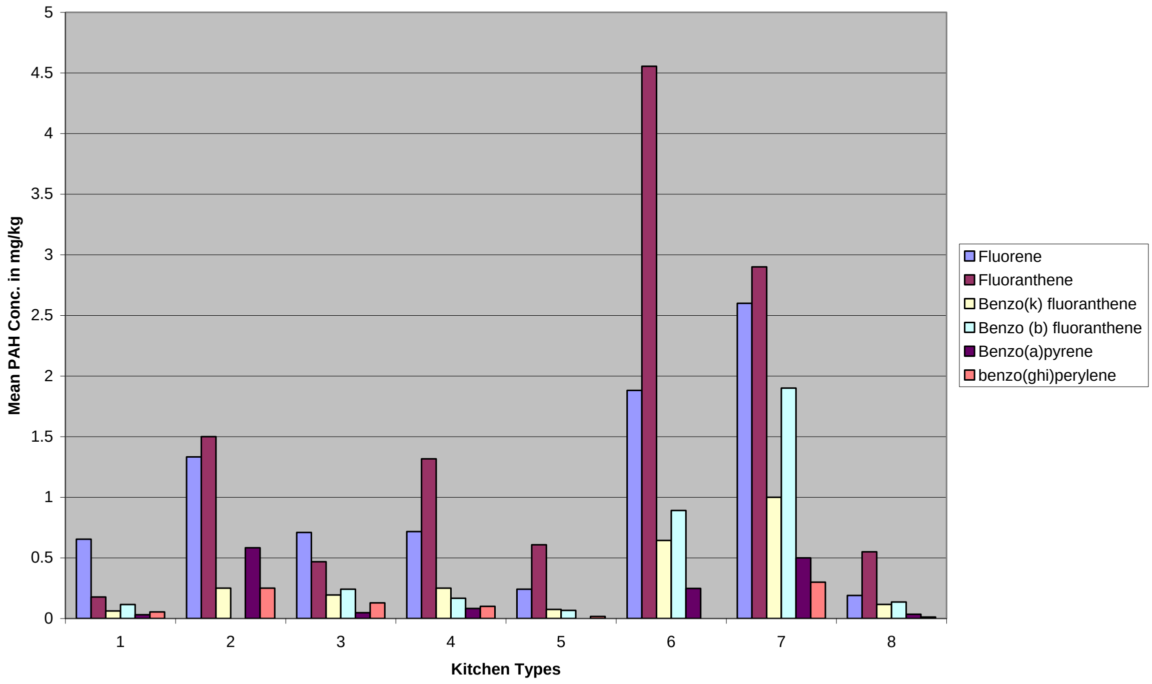


Fig. 2: Mean PAH concentrations in indoor particulate matter in some kitchens in Esbjerg.

PAH diagnostic ratio analysis

Diagnostic ratios of selected PAH compounds are generally considered to be a good indicator of their sources and the mechanism of transport in the environment (Zhu and Wang (2004); Mai et al., (2003); Yunker (2002)) however, some reviewers do not share such generalisation (Galarneau, 2008). The ratios Indeno (1,2,3 - cd) pyrene/(Indeno (1,2,3 - cd) pyrene + Benzo(g,h,i)perylene) Ind/(Ind+BghiP) and Fluorathene/(Fluoranthene + Pyrene) FTH/(FTH+Pyr) are often used to distinguish between pyrogenic and petrogenic sources. The ratio of LMW/HMW could be an index used to apportion the anthropogenic sources of PAHs. For example, a value of Ind/(Ind+BghiP) > 0.5 indicates grass/coal/wood combustion sources. Values of FTH/(FTH+Pyr) > 0.4 indicates pyrogenic sources, and we can distinguish between the values 0.4-0.5 for fuel combustion and values > 0.5 for grass/coal/wood combustion sources. The ratio of (LMW/HMW) BaP(252)/BghiP(276) as stated above can also be used as an indicator for the determination of traffic and non-traffic sources, when the value (> 0.6) is characteristic of traffic sources (Maliszewska-Kordybach et al., 2008; Yin et al, 2008). The B[bk]Fs/B[ghi]Pe ratio has also been proposed by Cretney et al., (1985), for use in discriminating automobiles (0.21–0.28) from domestic fires (2.6–14 in coal/wood soot) table 2 in Appendix B.

The diagnostic ratios of the above-specified PAHs in the particulate matter were calculated and are shown in Table 2. Traffic source of PAHs is also evidenced at kitchen 2,4,6,7 and 8 with their BaP/BghiP ratios > 0.6 (Table 2). There seems to be outdoor air influence on the indoor air as demonstrated by ratios designate as traffic source. Studies revealed that the presence of potentially carcinogenic PAHs (4-6 rings) in indoor air can be strongly associated with infiltration of PAHs from outdoor air originated mainly by vehicle emissions (Fischer et al., 2000; Sanderson and Farant, 2004).

Rogge et al., (1993) and Dickhut et al., (2000) have also reported that benzo(b)fluoranthene/benzo(k)fluoranthene (BbFL/BkFL), can also indicate pyrolytic or petrogenic origin of the PAHs. Thus, the calculated BbFL/BkFL ratio of <1 is consistent with range of BbFL/BkFL ratio from wood burning (0.47 – 0.92).

Table 2: Sample sites/PAH Ratios

Ratios	Traffic	Pyrogenic	From the result	References
BaP(252)/BghiP(276)	< 1.2	1.2–5.0:	0 - 3	Maher and Aislabie 1992 (Maliszewska-Kordybach et al. 2008
B[bk]Fs/B[ghi]Pe	0.21–0.28	2.6–14	0.5 -1.1	Cretney et al., (1985)
BbF/BkF	1.1–1. 5	0.4–1.1	0.35 -1	Dickhut et al., 2000 Rogge et al., (1993)

[F = Fluorene, FTH = fluoranthene, BkF = benzo(k)fluoranthene, BbF = benzo(b)fluoranthene, BaP = benzo(a)pyrene and B(ghi)P = benzo(ghi)perylene]

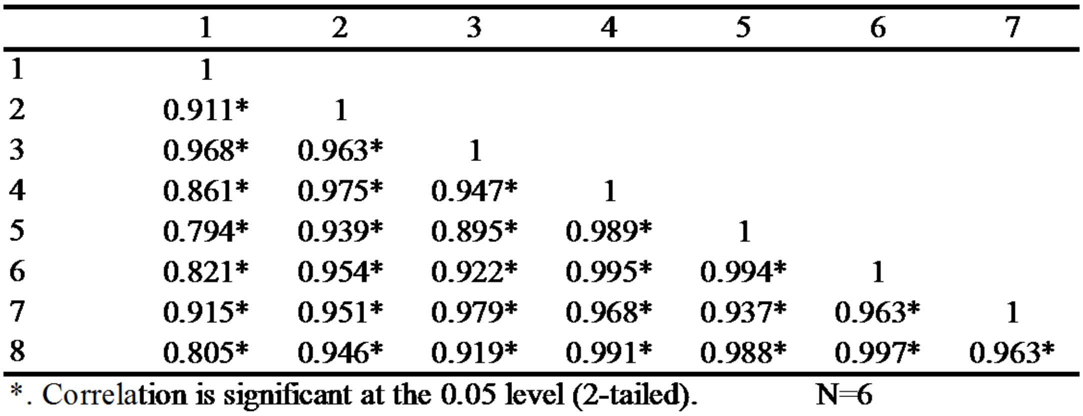
Despite the lack of consistency in some cases, there seems to be a general consensus by all the ratio indicators that combustion is the dominant source of PAH input in the indoor particulate matter of the studied kitchens. Although not conclusive, there is also an indication of some petrogenic source contributions to indoor PAHs as was also observed by Castro et al, (2010).

High or medium temperature combustion processes and different fossil materials may have also accounted for the differences in the composition pattern of PAHs between sampling sites (Table 3) (Zhou and Maskaoui, 2003). Despite the apparent dominance of combustion as the major source of anthropogenic PAH to the particulate matter (using the ratio indicators above), the BaP/BghiP ratios suggests wood and coal burning only for sites 2, 7 and 8 (Table 5) with ratios from 1.2 to 5. The average ratios also predict predominance of combustion source of PAH with one showing wood and coal burning. It is therefore possible that combustion of liquid fossil fuel (e.g. burning of oil and fat from grilling of chicken and meats and cooking using butter or oil) is the major source of PAH to the indoor environment of the kitchens studied.

Spatial similarities with cluster analysis

In order to investigate the relationship between the eight sampling points, a preliminary correlation analysis of the PAHs data was conducted using Pearson's method. Pearson's method was selected for the test since the data was generally normally distributed (parametric data). The result is presented in Table 3. All the sampling sites (1-8) were strongly positively related ($r > 0.7$, $p < 0.05$) to each other with regards to the monitored PAHs. This result may suggest that all the sampling sites are almost equally affected by these pollutants from their source(s).

Table 3: Pearson's Correlation matrix of sampling sites



	1	2	3	4	5	6	7
1	1						
2	0.911*	1					
3	0.968*	0.963*	1				
4	0.861*	0.975*	0.947*	1			
5	0.794*	0.939*	0.895*	0.989*	1		
6	0.821*	0.954*	0.922*	0.995*	0.994*	1	
7	0.915*	0.951*	0.979*	0.968*	0.937*	0.963*	1
8	0.805*	0.946*	0.919*	0.991*	0.988*	0.997*	0.963*

*. Correlation is significant at the 0.05 level (2-tailed). N=6

Cluster analysis (CA) was performed on PAH data set to confirm and ascertain spatial similarities among the various sampling sites. The Q-mode CA defines groups (clusters) sampling points of a particular air quality in terms of the examined PAHS. The data was normalized using Ward's method of linkage with squared Euclidean distance as a measure of similarity (Anicic et al., 2009; Vega et al., 1998; Zhang et al., 2008; Hussain et al., 2008). Cluster analysis used all the variance or information contained in the original dataset. Ward's method was selected for sampling site classification because it possesses a small Space distortion effect, uses more information on cluster contents than other methods, and has been proved to be extremely powerful grouping mechanism (Anicic et al., 2009; Vega et al., 1998).

The Q-mode CA reveals two distinct sampling groupings (Fig. 3), which show spatial variation in air quality of the studied kitchens. Group 1 includes sampling sites 1-5 and 8. Group 2 consists of sampling sites 6 and 7 (7 is where LPG is used with tobacco smoking whiles 6 is a semi-public facility and also very close to the main Esbjerg station).

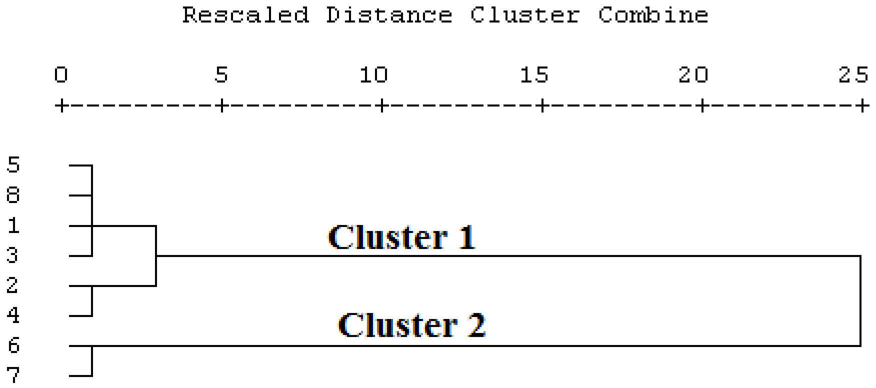


Fig. 3: A dendrogram showing clustering of the sample sites.

PAHs source identification with Cluster analysis

The result of a preliminary relationship check between the examined PAHs with Pearson's correlation procedure is shown by Table 4. The outcome of the analysis showed that most of the PAHs are correlated, indicating they might come from a common factor or source.

Table 4. Pearson’s Correlation matrix of examined PAH

	Fluoren	Fluoranthen	Benzo(k) fluoranthene	Benzo (b) fluoranthene	Benzo(a)pyrene	benzo(ghi)perylene
Fluoren	1					
Fluoranthen	0.811*	1				
Benzo(k) fluoranthene	0.951**	0.817*	1			
Benzo (b) fluoranthene	0.876*	0.688	0.964*	1		
Benzo(a)pyrene	0.764*	0.708*	0.649	0.509	1	
benzo(ghi)perylene	0.632	0.136	0.534	0.48	0.512	1

*. Correlation is significant at the 0.05 level (2-tailed). N=8

Cluster analysis (CA) was performed on the dataset to identify the underlying factors responsible for the PAHs in the sampled particulate matter. Cluster analysis in R-mode was performed on the PAHs dataset and 2 distinct groups or clusters were revealed. Cluster 1 contains benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, and benzo(k)fluoranthene. The PAHs, fluorene and fluoranthene are grouped in Cluster 2 (Fig. 4). These sources are indicative of mixed pyrogenic and petrogenic which is likely to come from both traffic and combustion (cooking, grilling and cigarette smoking).

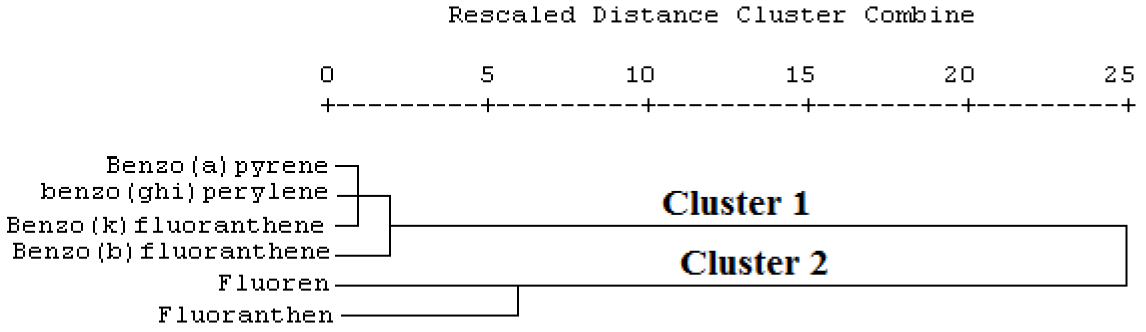


Fig.4. A dendrogram of the measured PAH in particulate matter

CONCLUSION

In this study, the levels of 6 PAHs have been examined in 8 kitchen environments in Esbjerg. The result showed some levels of the six PAHs analysed. The result clearly demonstrates that the influences of smoking impacted heavily on PAH levels in the indoor environment. The average concentration of PAHs in the particulate matter ranged from below detection of benzo(b)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene from kitchens 2, 5 and 6 respectively to 4.555 mg kg-^{1} fluoranthene. Most of these PAHs have been classified as carcinogenic and therefore their presence in the indoor environment ought to be minimized. All the 6 PAHs analysed were present in the particulate matter at significant levels which could expose people to the harmful effects of these chemicals. The diagnostic ratios gave combustion as the dominant source but also with some amount of distinct mixed petroleum (traffic from the outdoor) situations (Zhu et al. 2004; Yunker et al. 2002). The correlation analysis identified pyrogenic sources as the main contributors of PAHs on the Esbjerg indoor environment. Even though not conclusive from the diagnostic ratios, it is evident that outdoor and cigarette smoking contributed PAHs significantly to that of the indoor PM.

Polycyclic Aromatic Hydrocarbon pollution in Esbjerg owing to indoor kitchen PM is hitherto a scarcely explored problem. More studies are ongoing to strengthen this database and investigate the range and profile of carcinogenic PAHs content in the Esbjerg indoor environment.

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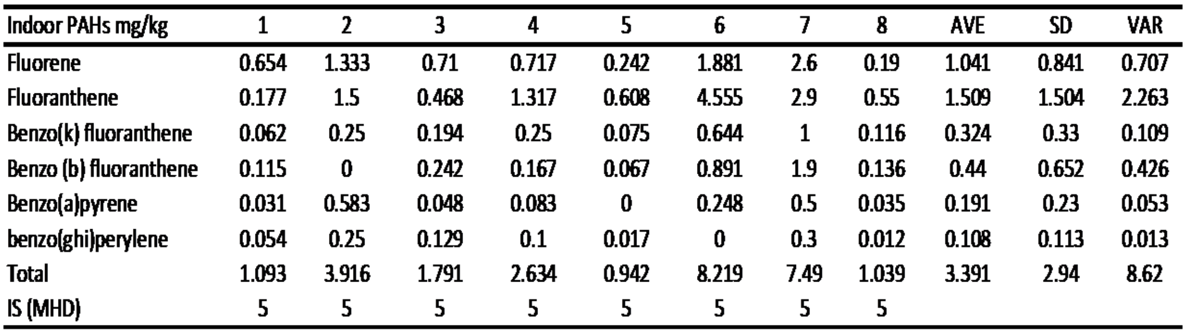
APPENDIX A



Indoor PAHs mg/kg	1	2	3	4	5	6	7	8	AVE	SD	VAR
Fluorene	0.654	1.333	0.71	0.717	0.242	1.881	2.6	0.19	1.041	0.841	0.707
Fluoranthene	0.177	1.5	0.468	1.317	0.608	4.555	2.9	0.55	1.509	1.504	2.263
Benzo(k) fluoranthene	0.062	0.25	0.194	0.25	0.075	0.644	1	0.116	0.324	0.33	0.109
Benzo (b) fluoranthene	0.115	0	0.242	0.167	0.067	0.891	1.9	0.136	0.44	0.652	0.426
Benzo(a)pyrene	0.031	0.583	0.048	0.083	0	0.248	0.5	0.035	0.191	0.23	0.053
benzo(ghi)perylene	0.054	0.25	0.129	0.1	0.017	0	0.3	0.012	0.108	0.113	0.013
Total	1.093	3.916	1.791	2.634	0.942	8.219	7.49	1.039	3.391	2.94	8.62
IS (MHD)	5	5	5	5	5	5	5	5			

Limits of Detection (LOD): [fluorene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(ghi)perylene] = 0.01μg m-^{3} and [fluoranthene] = 0.05 μg m-^{3} [0 = below detection limit]

APPENDIX B

Traffic related	Wood related	References
anthracene to anthracene plus phenanthrene (An/178) ratio<0.10 usually is taken as an indication of petroleum	anthracene to anthracene plus phenanthrene, ratio>0.10 indicates a dominance of combustion	Placha´ et al. 2009 Pies et al. 2008; Zhang et al. 2006
The Fl/Fl+Py ratio is below 0.50 for most petroleum samples	The Fl/Fl+Py ratio is above 0.50 in kerosene, grass, most coal and wood combustion samples and creosote	Yunker et al. 2002; Zhu and Wang 2004 Placha´ et al. 2009
indeno[1,2,3- cd]pyrene plus benzo[ghi]perylene (IP/IP+Bghi) a ratio below 0.50 has been attributed to low temperature diagenesis	indeno[1,2,3- cd]pyrene plus benzo[ghi]perylene (IP/IP+Bghi) over 0.50 has been taken to indicate combustion	(Maliszewska-Kordybach et al. 2008 Placha´ et al. 2009
BaA/(BaA+Chr) 0.20–0.35: mixed petroleum/ combustion <0.2: unburned petroleum source	BaA/(BaA+Chr) 0.35: combustion	(Mark et al., 2002) Pies et al. 2008; Zhang et al. 2006 Placha´ et al. 2009
BaP/(BghiPl) < 1.2	BaP/(BghiPl) 1.2–5.0: wood burning and coal burning	(Maher and Aislabie 1992 (Maliszewska-Kordybach et al. 2008 Yin et al. 2008
BbF/BkF 1.1–1. 5	BbF/BkF 0.4–1.1	Dickhut et al., 2000 Rogge et al., (1993)

B[bk]Fs/B[ghi]Per 0.21–0.28	B[bk]Fs/B[ghi]Pe r 2.6–14	Cretney et al., (1985)