Atmospheric Pollution Assessment from a Mountainous Environment in Southern Ghana: Case Study of Abetifi

This dissertation is submitted to the University of Ghana, Legon in partial fulfilment of the requirement for the award of **PhD Nuclear & Environmental Protection degree**.

By

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DECLARATION

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DEDICATION

This work is dedicated most especially to the Holy Spirit without whom, I may never have made it in this life. Sweet Spirit of God, you are more than enough to me. You just are everything to me. With you, my life has been luxuriantly fruitful, and full of glorious fortunes and increase. I love you with passion.

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LIST OF ABBREVIATIONS

ATSDR	Agency for Toxic Substances and Disease Registry
COP	Conference of the Parties
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DL-PCBs	Dioxin-like polychlorinated biphenyls
DRINS	Cyclodien pesticides
EI	Electron ionization
EPA	Environmental Protection Agency
EU	European Union
FTOHs	Fluorotelomer alcohols
GC–MS	Gas chromatography with mass spectrometer
GMP	Global Monitoring Plan
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography

IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
IUPAC	International Union of Pure and Applied Chemicals
LOD	Limit of detection
LOQ	Limit of quantification
LRAT	Long Range Atmospheric Transport
MONET	Monitoring network
MS	Mass spectroscopy
NAAQS	National Ambient Air Quality Standards
ND	Not detected
NIP	National Implementation Plan
NIST	National Institute of Standards and Technology
NTP	United States NTP
OCPs	Organochlorine pesticides
PAHs	Polycyclic Aromatic Hydrocarbons
PAS	Passive air sampling/sampler
PBBs	Polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDDs/Fs	Polychlorinated dibenzo-*p*-dioxins/furans

PeCB	Pentachlorobenzene
PFASs	Perfluoroalkyl sulfonates
PFCAs	Perfluorinated carboxylic acids
PFCs	Perfluorinated compounds
PFOS	Perfluorooctane sulfonate
POPs	Persistent organic pollutants
PUF	Polyurethane foam
QA/QC	Quality assurance/quality control
RECETOX	Research Centre for Toxic Compounds in the Environment
S/N	Signal to noise ratio
SRM	Standard Reference Material
SC	Stockholm Convention
TEF	Toxic Equivalence Factor
TEQ	Toxicity Equivalency
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds
WHO	World Health Organization

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ABSTRACT

In the pursuit to improve man's livelihood, human activities which include emission of heavy metals from various industries and sectors, as well as the past use of chemicals such as pesticides, polychlorinated biphenyls and flame retardants have often mobilized and redistributed natural substances and anthropogenic pollutants into the atmosphere, predisposing it to relatively high concentrations of such pollutants even in pristine areas in the environment.

This study assessed the level of atmospheric pollution, contributing sources and human health exposure risk of persistent organic pollutants (POPs) along with selected heavy metals with focus on Abetifi, one of the highest altitude environments in Ghana. Passive sampling with polyurethane foam (PUF) as adsorbent was employed. Samplers were deployed every 84 days for two years. A total of 65 polyurethane foams were deployed and twelve (12) groups of analytes were considered together with their various isomers. High resolution gas chromatographic technique coupled with high resolution mass spectrometry (HRGC-HRMS) and electron capture detectors (ECD) were used in the analysis of the POPs. Besides, high performance liquid chromatography (HPLC) coupled with MS was employed in analysing the perfluorinated compounds (PFCs) while the heavy metals were analysed using Atomic Absorption Spectrometer (AAS). Principal Component Analysis (PCA) and UNMIX model were used to group pollution source contribution of all analytes (POPs and heavy metals) in this study. Diagnostic isomer and other predictive ratios were also employed for source apportionment of various individual analyte groups.

Results revealed that polychlorinated dibenzo-furans gave with the least total mean concentration (0.074 pg/m^3) for the sampling period and polybrominated biphenyls gave the highest (55 pg/m^3). The pesticide group gave values in the order of DRINs

(53 pg/m^3) > DDT (41 pg/m^3) > HCHs (28 pg/m^3). Data for perflourinated compounds (PFCs) in the atmosphere at Abetifi was recorded with a maximum total concentration (Σ_8) of 15 pg/m^3. The human exposure level to dioxin-like chemicals in the air at the study location was 0.0067 pg TEQ/kg bw per day. The atmospheric pollution source observed at Abetifi was a mixed one consisting of agricultural, vehicular and from burning of biomass. Agricultural source was basically as a result of re-volatilization from polluted sinks (a secondary pollution source).

CHAPTER ONE

INTRODUCTION

1.1 Background

The production of many different chemicals (household, pharmaceutical, agrochemicals) for the progress of man's livelihood has ended up polluting the environment particularly the atmosphere. Various atmospheric pollutants including heavy metals, particulate matter, aerosols and persistent organic pollutant (POPs) have, therefore, become a major concern.

Once released into the atmosphere, these pollutants become extremely difficult to control (UNEP, 2001; 2002) Owing to their nature, persistent organic pollutants (POPs) are among global chemicals whose management concern places a demand on governments, industry, civil society and the international community as a whole to help reduce their impact on human health and the environment. On the basis of this, national and international agencies have made series of enforceable air pollution abatement laws, regulations and programmes. For example, the United States Environmental Protection Agency (USEPA) has established air quality standards such as the National Ambient Air Quality Standards (NAAQS) to protect public health and welfare and the ecosystems (Daly and Zannetti, 2007). The United Nations Economic Commission for Europe (UNECE) also put forward a Convention to reduce long-range trans-boundary air pollution (UNECE, 1998). Likewise, the United Nations Environment Programme (UNEP) put forth the Stockholm Convention on Persistent Organic Pollutants to protect human health and the environment from persistent organic pollutants by reducing or eliminating their releases into the environment (MONET, 2013; UNEP, 2001). Equally, the Ghana Environmental Protection Agency

act 490 (1994) encapsulates the air quality guidelines in Ghana. Ghana is signatory to the Stockholm Convention (UNEP, 2001) as such, has the obligation to protect human health and the environment from POPs by helping reduce or eliminate their releases into the environment and to monitor their levels.

In Ghana, research works have been conducted on many air pollutants (heavy metals, particulate matter, sulphate and nitrate aerosols and persistent organic pollutants) with focus on non-mountainous urban areas (Safo-Adu *et al.*, 2014a,b; Ofosu *et al.*, 2013; Quansah *et al.*, 2012; Adu-Kumi *et al.*, 2010a,b). However research shows that mountains can act as a convergence zone for organic pollutants (Choi *et al.*, 2009). The transport mechanism that pertains in mountainous areas (where there is decrease in the rate of re-volatilisation of the pollutants) is principally responsible for this (Choi *et al.*, 2009; Levy, 2008). Therefore, mountainous or high altitude areas are well suited for monitoring of atmospheric contamination particularly, persistent organic pollutant (POPs).

It is worth noting that over the years, the atmospheric pollution studies undertaken in most areas in Ghana had engaged the use of active air volume samplers, a technique which is energy (power) supply based (Safo-Adu *et al.*, 2014a,b; Ofosu *et al.*, 2013; Ofosu *et al.*, 2012). Active samplers are very useful as they can take up high volume of air samples within a short time. They have the ability to be programmed to record the following parameters: sampling date, time, sampling pressure and rate of sampling including sampling duration (Chaemfa *et al.*, 2008). Despite its advantages, this classical technique is not always logistically possible, especially in places where power supply is either unreliable and/or expensive or unavailable. Besides their energy supply need and regular maintenance, active samplers are also very bulky and create practical

restrictions on the number and frequency of sampling and monitoring, as well as on the number of geographical sites/locations suitable for active sampling (Levy, 2008).

In view of these challenges, focus is being directed towards alternative sampling techniques. Passive air sampling is seen as a capable alternative to the active volume sampling. They uptake compounds by means of passive mass transfer, based on the free flow of compounds from the air to an accumulation matrix (for example polyurethane foam) (Levy, 2008; Harner *et al*., 2006 a,b). Passive air samplers are cost-effective, i.e. cheaper in implementation and manipulation in addition to easier maintenance and can be operated in the absence of power. In air pollution and monitoring studies, different types of passive samplers have been and are being employed; natural and man-made samplers (Levy, 2008). In "natural passive sampling", plants such as lichens, spruce needles and mosses are used for air monitoring (Boamponsem *et al.,* 2010; Yenisoy-Karakas and Tuncel, 2008; Nyarko *et al.,* 2006; Lehndorff and Schwark, 2004) and in "man-made sampling", there is the use of sampler which contains either a semi-permeable membrane device (SPMD), a coated stir bar or polyurethane foam (Klanova *et al*., 2009; 2008; Henkelmann *et al*., 2007; Harner *et al.,* 2004; Ockenden *et al.,* 2001).

The man-made passive samplers have the advantage of having a standardized design, contrary to the natural passive samplers, whose uptake capacity are climatic and geographically-restricted and are dependent on the age of plants used. It is important to note that these natural samplers (e.g lichens, spruce needles and mosses) are not easily movable from one location to another. One type of passive air sampler which employs the use of polyurethane foam (PUF) in a passive air sampling dome chamber has been effectively explored (Cheng *et al*., 2013; Klanova *et al*., 2009; 2008; Harner *et al.,* 2006a; 2004; Jaward *et al.,* 2004a,b; Holoubek *et al.,* 2001, 2000). These ones

are less expensive and their design is reproducible. This type of man-made passive air sampler consists basically of two dome chambers (one big and one small) and was developed by Kohoutek *et al*. (2006) for use for organic pollutants. The sampler has been modified by other researchers (Chaemfa *et al.*, 2008; Hazrati and Harrad, 2007; Harner *et al.*, 2006b) and the results obtained have suggested that the sampling bowl design does not have an important influence on the accumulation of chemicals (i.e. concentration of the pollutants).

1.2 Problem statement and justification

Air quality improvement which is achieved by means of preventing the atmosphere from the effect of polluting substances, is a significant aspect of promoting sustainable environment and human health. Nonetheless, the atmosphere has been negatively affected by such human activities as emission from various industries and other working sites, which often mobilize and redistribute natural substances and other chemicals particularly organic chemicals in the environment. Most of these organic pollutants and heavy metals have been found to cause several deleterious effects such as neurological, developmental, endocrine, renal and immunological toxicity in humans (Naja and Volesky, 2009; WHO, 1988). Some other effects known to be associated with these pollutants are dullness, restlessness, irritability, hallucinations, and loss of memory (Begum *et al*., 2009; Sarojam, 2009; Farghaly and Ghandour, 2005).

Many scientists have put in frantic efforts to provide data on the pollution status in various matrices and environmental media in Ghana. Blankson-Arthur *et al.* (2012) provided data on meat whiles Kuranchie-Mensah *et al.* (2012; 2011) and Essumang *et al.* (2009) provided data on fish, water and sediment. Atiemo *et al.* (2012; 2011)

worked on water and road dust. Palm *et al.* (2011) produced data on smoked fish whereas Adu-Kumi *et al.* (2010a) worked on fresh fish. All these data provision is a very useful evaluation process for drawing national programmes and coming up with regulations towards the mitigation of pollution. However only few of such efforts have been focussed on the atmospheric medium even though it is suitable for estimating temporal changes in concentrations of pollutants (Adu-Kumi *et al.*, 2010b; UNEP, 2009; Jaward *et al.*, 2004a,b; Holoubek *et al.*, 2001, 2000).

It is worth mentioning that, for many research centres, universities and other relevant institutions in Ghana, very few air samplers are available for such air pollution and monitoring studies (hence the probable little attention on air sampling). And in such places, active samplers are the most available which inherently have energy-supply need. In recent years therefore, the use of passive air samplers has emerged as a promising alternate tool for air monitoring. Granting that passive air samplers (PAS) have great advantages however, they are also very limited in quantity in the country due to importation cost implications. Based on these limitations, there is need for PAS to be produced or fabricated locally using tools available in the country, to make it accessible for use in pollution studies.

1.3 Hypothesis

Primary atmospheric emission sources have reduced over the past decades (UNEP, 2009a) with the ban on some industrial chemicals and the application of new atmospheric pollution preventive measures (Kukucka, 2012) as well as being committed to best practices. However, the existence of secondary pollution sources (cycling of previously emitted chemicals) (UNEP, 2009a) can not be ignored. Additionally, the influence of meteorological factors prevailing in a mountainous environment must be considered in assessing atmospheric pollution.

It is therefore proposed that:

i. secondary source pollution constitutes a higher percentage to the general atmospheric pollution at Abetifi than the local source.
ii. meteorological data have positive correlation with the concentration of atmospheric pollutants at Abetifi.

1.4 Objective

The main objective of this study is to assess the level of atmospheric pollution and its human health exposure/risk in Abetifi using polyurethane foam (PUF) in locally fabricated passive air sampling dome chambers for sample collection.

Specific Objectives:

1. To generate baseline data on atmospheric persistent organic pollutants (POPs) concentration from a mountainous environment by employing a method of polyurethane foam (PUF) in a locally fabricated passive air sampler (PAS).
2. To ascertain the temporal trends of POPs in air by accessing the changing concentrations of POPs over a two-year period from a mountainous environment, Abetifi.
3. To identify atmospheric pollution sources and evaluate their contributions.
4. To assess human health exposure caused by dioxin and dioxin-like chemicals/pollutants in ambient air from a mountainous environment.
5. To ascertain the suitability of using a locally-prepared polyurethane foam in passive air sampler (PAS) to sample heavy metals in air.

1.5 Scope

This study is designed to collect data from a key location in Ghana, Abetifi on the atmospheric pollution level caused by persistent organic pollutants (POPs) and heavy metals using both imported and locally-fabricated polyurethane foam disk (PUF) in passive air samplers (PAS). The focus of the study will subsequently be to collect data on levels of POPs at a location not easily influenced by local pollution sources. As such, primarily, the characterization of various POPs present in the atmosphere at a mountainous rural environment will be done using passive air sampling method that uses polyurethane foam (PUF) disks.

Secondly, exposure assessment will be done considering three groups of pollutants (dioxins, furans, and dioxin-like PCBs). In addition, various source apportioning models (UNMIX, PCA, diagnostic isomer ratios) will also be applied and finally, the study will look at the feasibility of using locally prepared polyurethane foam in locally fabricated passive air sampling dome chambers to sample heavy metals in ambient air for analyses which is an innovative area.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter describes air pollution and provides an overview of some work done on air toxicants which includes organochlorine pesticides, brominated flame retardants, perflourinated compounds, polycyclic aromatic hydrocarbons, dioxins and furans, and heavy metals. Their physical and chemical properties and their occurrence in the atmospheric environment are also considered.

2.2 Atmospheric pollution

Atmospheric or air pollution has nowadays become a major environmental health problem, affecting both developed and developing countries around the world. The vitality of air to humans and their environment demands that air quality issues be of uttermost importance to all and that air quality standards are upheld (Vallero, 2007). According to the United States Environmental Protection Agency (2009), air pollution is “the presence of contaminants or pollutants or substances in the air that interfere with human health or welfare, or produce other harmful environmental effects”. The same agency also defines air pollution as “the degradation of air quality resulting from unwanted chemicals or other materials, which are higher than its own natural concentration, occurring in the atmosphere that may result in adverse effects on humans, animals, vegetation, and/or materials” (USEPA, 2009). An air pollutant, therefore, is any substance in the air that can cause harm to humans or the environment.

The pollutants may either be natural or manmade and may take the form of solid particles, liquid droplets or gases. These pollutants are divided by the USEPA into various groups including particulate matter, volatile organic compounds (VOCs) and halogen compounds. The others include lead, mercury and asbestos (USEPA, 2009).

Based on the definition above, countless pollutants have been identified and grouped by various organizations over the years. This includes persistent organic pollutants (POPs), a group of pollutants identified by the United Nations Environment Programme (UNEP) under the Stockholm Convention (UNEP, 2002). Under the Convention, a total of twelve (12) target chemicals called the "dirty dozen" or the Legacy POPs were initially listed considering the challenges they posed to humans and the environment (Gh EPA, 2007; UNEP, 2002). At its fourth meeting, held in May 2009 in Geneva, Switzerland, the Conference of the Parties, by its decisions SC-4/10 to SC-4/18, amended Annexes A, B and C to the Convention (Stockholm Convention on POPs) to include additional chemicals grouped as New/ Emerging POPs.

2.3 Hierarchy of atmospheric pollutants under review

Two major groups of pollutants are reviewed; organic and inorganic pollutants and their sub-groups. The organic pollutants are grouped into legacy POPs and new/emerging POPs. The legacy POPs include groups of pesticides, industrial chemicals and unintentionally produced pollutants. The new POPs cover groups of flame retardants, perfluorinated compounds and polycyclic aromatic hydrocarbons with the flame retardants comprising polybrominated diphenyl ethers, hexabromocyclodeodecane and polybrominated biphenyls. The inorganic pollutants are heavy metals. This can best be visualized in scheme presented in Figure 2-1.

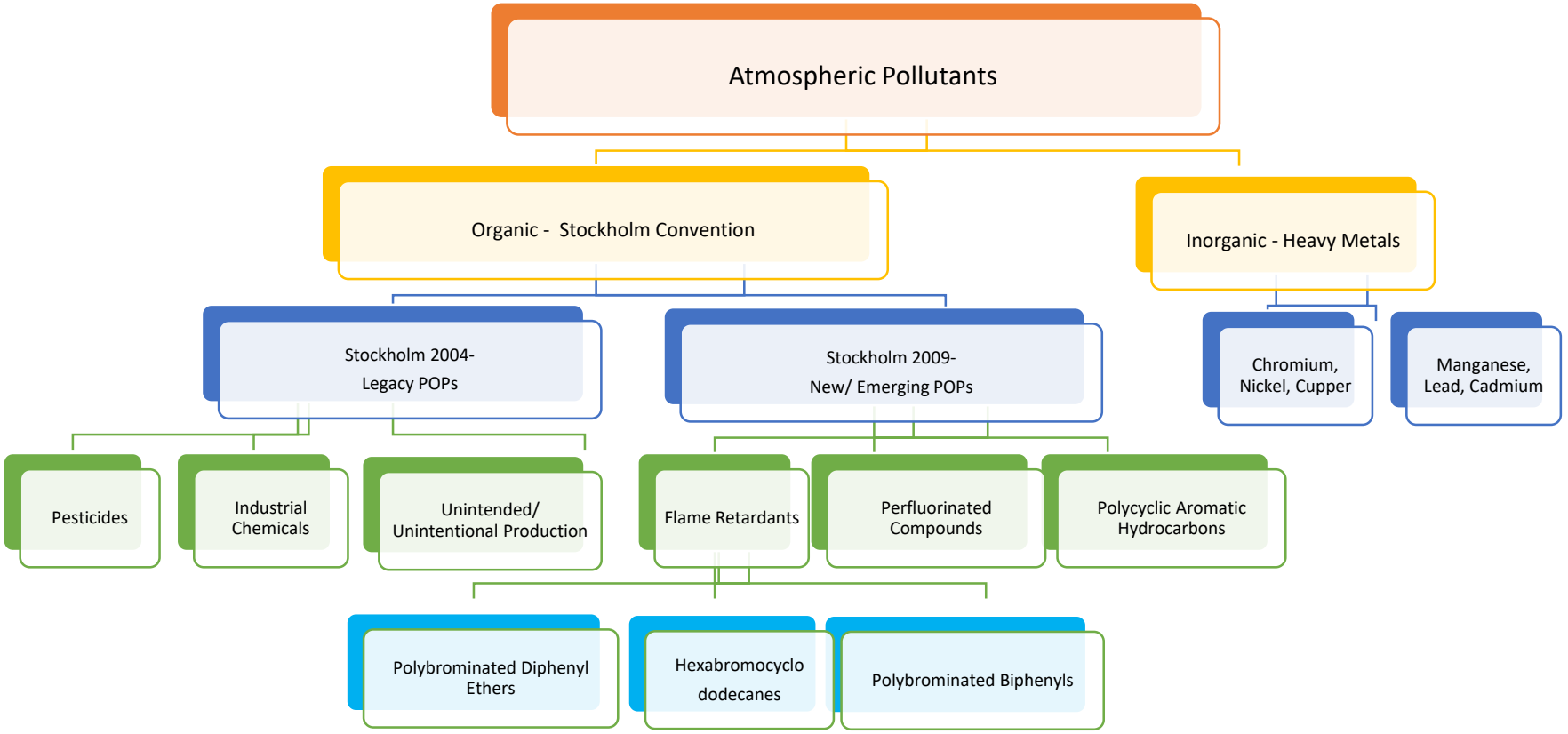


Figure 2-1: Hierarchy of atmospheric pollutants under review (author's design).

2.3.1 Persistent organic pollutants in the environment

Persistent organic pollutants (POPs) are organic chemical substances possessing peculiar physico-chemical properties such as water solubility, vapour pressure (P) (Covaci *et al.*, 2006) octanol-water partition coefficient (K_{ow}) and the organic carbon-water (K_{oc}) and Henry's law constant (H) (IPCS, 1995) which allow them to remain in the environment for long and become widely dispersed. These dispersions are mostly by natural processes involving soil, water and air in particular. These chemical substances bioaccumulate in fatty tissues of living organisms and magnify in concentration along the trophic chain (UNEP, 2001; UNEP, www.pops.int). One of the characteristics of these substances is their toxicity to both humans and wildlife; where they have been identified to have carcinogenic, mutagenic and endocrine disruption potentials (ATSDR, 2013, 2005; Baird, 2000). Persistent organic pollutants can be emitted from various primary and secondary sources with atmospheric transport being the main route for delivery of these POPs to both aquatic and terrestrial ecosystems within the immediate vicinity of the POPs sources. Aditionally, they are also transported over great distances which is known as long-range atmospheric transport (LRAT). The LRAT property of these persistent organic pollutants is usually referred to as "grass-hopper" effect (Adu-Kumi, 2010a,b; Wania, 2003; Klanova *et al*., 2006; UNEP, 2001).

2.3.1.1 Legacy POPs

The Stockholm Convention has three categories for the first set of listed chemicals ("Legacy POPs") which they banned:

i. pesticides

ii. industrial compounds

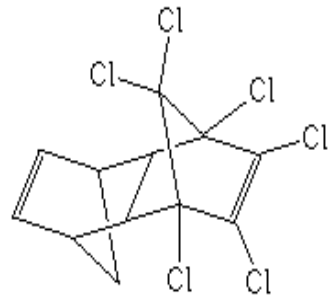
iii. by-products or unintentional production.

The legacy POPs are a total of twelve (12) chemicals including aldrin, dieldrin, endrin, chlordane, dichlorodiphenyl trichloroethane (DDT), heptachlor, mirex, toxaphene, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). HCB belongs to all three categories. It is a pesticide (fungicide), a by-product of industry as well as an unintended by-product of combustion process (UNEP, 2002; Gh EPA, 2007). Under the Convention, there are nine (9) chemicals that are pesticides. These are aldrin, dieldrin, endrin, DDT, chlordane, HCB, heptachlor, mirex, and toxaphene. Five out of the nine were analysed for in this study.

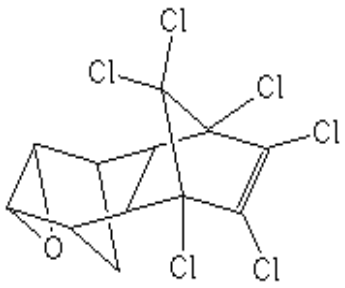
2.3.1.1.1 Aldrin, dieldrin and endrin pesticides

Aldrin, dieldrin and endrin with structures shown in Figure 2-2a, Figure 2-2b and Figure 2-2c respectively are pesticides and collectively known as DRINs or cyclodiene pesticides with a basic chemical structure revolving around dimethanonaphthalene structure. Their physical and chemical properties, their production history, use and environmental contamination are discussed in this work with portions in Appendix iia (Gh EPA, 2007; UNEP, 2002).

Aldrin, dieldrin and endrin were commercially manufactured in 1950 and used throughout the world up to the early 1970s. Both aldrin and dieldrin were used to control soil pests such as corn rootworm, wireworms, rice water weevil, and grasshoppers (Gh EPA, 2007).



[A]



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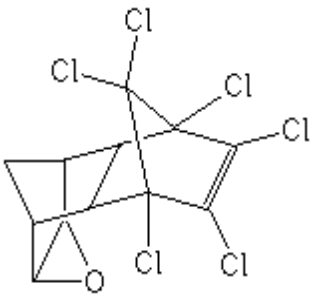


[C]

Figure 2-2: Structure of Aldrin [A], Dieldrin [B] and Endrin [C]

Aldrin was additionally used specifically to protect wooden structures from termites whiles dieldrin was used against cat worms. The much more toxic but structurally similar to the two, endrin was used as a rodenticide and also against a wide range of agricultural pests, mostly on cotton but also on rice, sugar cane, maize and other crops (Gh EPA, 2007; Mariussen and Fonnum, 2006; UNEP, 2002).

As target POP chemicals, aldrin, dieldrin and endrin are very persistent with endrin being the most persistent (Appendix iia). Under certain conditions, aldrin metabolises either directly or by transformation to dieldrin to form aldrindiol. In the atmosphere, aldrin decomposes to form photoaldrin or photodieldrin by transformation to dieldrin (Gh EPA, 2007; UNEP, 2002).

Aldrin and dieldrin have both been banned in many countries. Ghana banned them in 1985 (Gh EPA, 2007; UNEP, 2002). Years after their ban, these chemicals are still being detected in various environmental matrices due to their persistence and probably illegal use (Xu *et al*., 2013; Klanova *et al*., 2011; UNEP, 2009; Alegria *et al*., 2000). In agricultural areas, the mean concentration of aldrin and dieldrin were found to be 1-2 ngm^{-3} with a maximum of 40 ngm^{-3} (EHC 91, IPCS; WHO, 1989). Levels of DRINs from other countries are represented in Figure 2-3 (Xu *et al*., 2013; Klanova *et al*., 2011; UNEP, 2009; Daly *et al*., 2007a; Shen *et al*., 2005; Alegria *et al*., 2000).

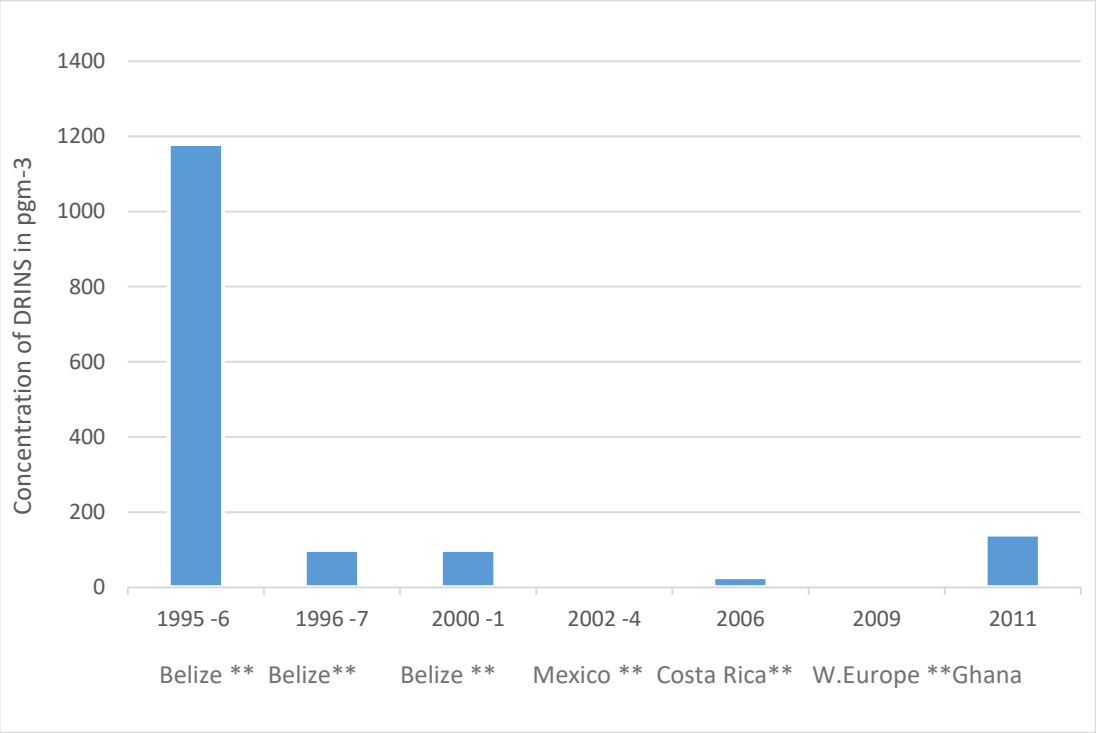
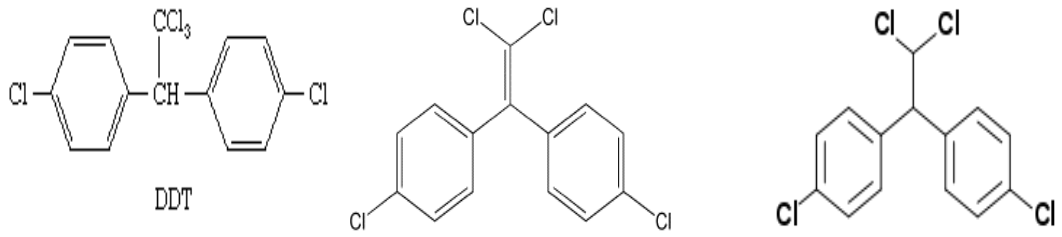


Figure 2-3: Maximum atmospheric concentration of DRINs in pgm^{-3}

2.3.1.1.2 Dichlorodiphenyltrichloro ethane, dichlorodiphenyldichloro ethylene and dichloro diphenyldichloro ethane

Dichlorodiphenyltrichloroethane (DDT) is an insecticide widely known for its usefulness in the health and agricultural sectors. DDT (Figure 2-4a) and its metabolites or degradation products; dichlorodiphenyldichloroethylene (DDE) (Figure 2-4b) and dichlorodiphenyldichloroethane (DDD) (Figure 2-4c) are relevant in the area of human and environmental toxicology. DDT and its metabolites have two isomers each known as ortho-para (o,p'-) and para-para (p,p'-). Their production history and use are discussed below whiles their physico-chemical properties and environmental contamination are tabulated in Appendix iia.



[A] [B] [C]

Figure 2-4 Structure of DDT [A], DDE [B] and DDD [C]

DDT has been widely used for malaria control and in agriculture to control pest insects that spread diseases such as dengue fever and typhus in many countries including Ghana. The technical composition of this product is a mixture of about 85% p,p'-DDT and 15% o,p'-DDT isomers (Pozo *et al.*, 2011; Linderholm, 2010; Gh EPA, 2007; UNEP, 2002). The global production of DDT for vector control was estimated to be 6,269 metric tons in 2005 being produced in two countries; India and China (Klanova *et al*., 2009; UNEP, 2007). DDT was officially used as the main insecticide against cocoa capsids and for malaria and filariasis control programmes by the Ghana Cocoa

Board and Ministry of Health respectively especially at Akwadum and Adonkwanta areas in Eastern Region (Gh EPA, 2007; Ntow, 2001).

DDT degrades to DDD under anaerobic conditions and to DDE in aerobic environments (Hitch and Day, 1992). The ratio, DDE/DDD has been used to trace the environment of decomposition of DDT and the ratio (DDD + DDE)/DDT, is used to trace whether there is new or fresh input of DDT into the environment (Liu *et al*., 2009). When released to the environment especially in an atmospheric medium, about 50% of DDT and its degradation products will be found adsorbed to particulate matter and the rest in the vapour phase (Bidleman, 1988). Where these chemicals are particulate-bound, they are not expected to undergo rapid photooxidation as such they may be subject to long-range transport (ATSDR, 2002). Exposure to high doses of DDT can affect the central nervous system, and other toxicological effects (Appendix iia).

Atmospheric concentration has been observed to be varied in different locations, possibly due to its different usage. A 10-year monitoring (1996 - 2005) in Czech Republic revealed concentrations of 0.08 to 0.17 ng/m^3 of DDT with highest concentrations observed in 1997 and 2004 (Dvorska *et al.,* 2008). According to Klanova *et al.* (2009) the highest air levels measured as the sum of p,p'- and o,p'-DDT, DDE and DDD, was 8970 ng $sample^{-1}$ (median 2580 ng $sample^{-1}$), detected at the Kitengela pesticide dump site, Kenya in a 2008 air monitoring campaign. Interestingly, the lowest concentration (1-2 ng/sample) was also detected in Kenya (Mount Kenya) including other such countries as Tombouctou in Mali and in the Republic of South Africa (background sites).

2.3.1.1.3 Hexachlorobenzene and pentachlorobenzene

Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) as shown in Figure 2-5a & Figure 2-5b respectively, belong to the group of chlorobenzenes. These are characterised by a benzene ring in which the hydrogen atoms are substituted by one or more chlorines. The chlorobenzenes are neutral, thermally stable compounds with increasing stability and higher melting and boiling points with increasing chlorine substitution (UNEP, 2007; UNEP, 2002; Van de Plassche *et al.,* 2002). Their physical and chemical properties and their abundance in the environment are listed in Appendix iia, iib and v of this work (Gh EPA, 2007; UNEP, 2007; USEPA, 2000).

[A] [B]

Figure 2-5: Stricture of Hexachlorobenzene [A] and Pentachlorobenzene [B]

HCB was first introduced in 1945 and used for seed treatments of grain crops, and used to make fireworks, ammunition, and synthetic rubber. Today HCB is mainly a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, solvents and several pesticides. It may also be from being by-product in waste streams of chlor-alkali plants and wood preserving plants and inadequate incineration of chlorine-containing wastes (Dvorska *et al.*, 2008; Gh EPA, 2007; UNEP, 2002).

Pentachlorobenzene (PeCB) on the other hand was introduced as a component in polychlorinated biphenyl (PCB) products, in dyestuff carriers, as a fungicide and a flame retardant. It was also used as a chemical intermediate for exaample in the

production of quintozene or pentachloronitrobenzene, a fungicide. Total estimated annual global emissions of PeCBs based on the US Toxics Release Inventory database were 85,000kg/yr (ICCA/WCC, 2007). Nowadays pentachlorobenzene enters the environment chiefly as a by-product of incomplete combustion, and it is the most important source of concern to the human and environmental toxicology (UNEP, 2007).

Hexachlorobenzene (HCB) is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries. It is very slow to break down in air and is subject to long-range transport in the atmosphere. It tends to adsorb to suspended particles. Pentachlorobenzene (PeCB) is also subject to long range transport eventhough PeCB can be photo-oxidized in the atmosphere, largely through reactions with hydroxyl (OH) radicals. HCB has a relatively high bioaccumulation potential and long half-life in biota. HCB is a toxic organochlorine that has been shown to cause death and other toxicological effects. Test animals exposed to PeCB have also shown various toxicological effects (Appendix iib) (ATSDR, 2013; Gh EPA, 2007; UNEP, 2007; CEPA, 1993).

Hexachlorobenzene (HCB) is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries. HCB concentration in air is usually detected at low levels typically in ngm^{-3} range (ATSDR, 2013). Table 2-1 shows concentrations in ngm^{-3} of HCB & PeCB from selected countries.

Table 2-1: Concentrations (ngm^{-3}) of HCB & PeCB from selected countries

Pesticide type	Country	Year of measurement	Min. Conc.	Max. Conc.	References
HCB	Czech Republic	1996 -2005	0.0005	0.835	Dvorska et al., 2008
	Europe**	1996 -2005	0.03	0.17	Farrar et al., 2006
	North America	2000 -2001	0.017	0.136	Shen et al., 2005
PeCB	Germany	-	0.031	0.286	ICCA/WCC, 2007
	Grt Lakes	-	0.072*	0.072*	ICCA/WCC, 2007
	Ghana	2008	0.005	0.015	Klánová et al., 2009

NB: * - Average concentration ** - Other parts of Europe

According to Shen *et al.* (2005), small spatial variabilities were observed in the study across the study area (Northern Hemisphere) and that was an indication that PeCB has a very long atmospheric residence time, which allows it to become widely distributed in the global hemisphere.

2.3.1.1.4 Hexachlorocyclohexane

Hexachlorocyclohexane (HCH) as shown in Figure 2-6 is an organochlorine pesticide. HCH isomers are brownish to white crystalline powders with a penetrating musty odour (NTP, 2011). Other physical and chemical properties and their presence in the environment are discussed in Appendix iib.

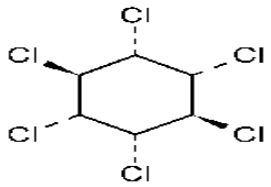


Figure 2-6: hexachlorocyclohexane

Technical-grade hexachlorocyclohexane (HCH) is produced as a mixture of isomers primarily the alpha (α), beta (β), gamma (γ), delta (δ), and epsilon (ε) isomers with proportions being α-HCH (65-70%), γ-HCH (14-15%) and β-HCH (7-10%) (Linderholm, 2010). The only identified use for HCH-containing products are based on the insecticidal activity of the γ-isomer and this was marketed under the trade name lindane in Ghana. This product is stable under normal temperature and pressure (Akron, 2009; HSDB, 2009). The use of lindane has been greatly restricted around the world (UNECE, 998) however, lindane continues to be manufactured in India and used for crop protection (Pozo *et al.,* 2011) even though in 1997, the technical HCH was banned completely there (Li *et al.,* 2003).

Lindane was primarily used in the treatment of wood and wooden structures, seed grains and live-stock (HSDB, 2009; ATSDR, 2005). In Ghana it was predominantly used for cocoa against such pests as cocoa capsids or mirids. Lindane was so much used in Ghana that by 1978, the annual use of Lindane was of the order of 900,000 litres per year. However, at the end of 2002, the use of lindane on cocoa was discontinued in Ghana in accordance with a directive from the European Union Advisory Committee on Pesticides (Adu-Kumi, 2010 a,b). Lindane as an insecticide was banned in the EU since 1995, in the United Kingdom, 2004 (Shitta-Bey, 2009) and in Ghana, since 2008 (Owusu-Ansah *et al.,* 2010).

The isomer ratio of alpha- to gamma-HCH (α-/γ-HCH) is often used to apportion pollution sources of either fresh input of the chemical or an effect of a long-range transport. For a technical-grade HCHs (55 - 80% α-HCH, 5- 14% β-HCH, 8- 15% γ-HCH, and 2- 16% δ-HCH), the values of the ratio α-/γ-HCH ranges from 3 to 7. Owing to the lower air-water partitioning coefficient (K_{aw}) of γ-HCH compared to α-HCH and

the photolytic isomerization from γ-HCH to α-HCH during long range transport the value tends to increase over time. The isomer α-/γ-HCH ratio tends to decrease as a signature of continuous application of technical-grade lindane (99% γ–isomer) (Zhu *et al.*, 2014; Zhu *et al.*, 2014 cited Walker *et al.*, 1999; Zhu *et al.*, 2014 cited Malaiyandi and Shah, 1984; HSDB, 2009).

Lindane has been observed to be transported over long distances in the air. It has been found in Arctic air, distant from any sources of use. Most sources of lindane in the atmosphere are fugitive dust particles from wind, erosion of contaminated soil, volatilization from treated agricultural soil and volatilization from plant foliage sprayed with lindane and others occurring due to releases from stockpiles or other sources (Pozo *et al.*, 2006; Sang *et al.*, 1999). Figure 2-7 below, shows the concentrations of α- and γ-HCHs (pgm^{-3}) in some cities in India.

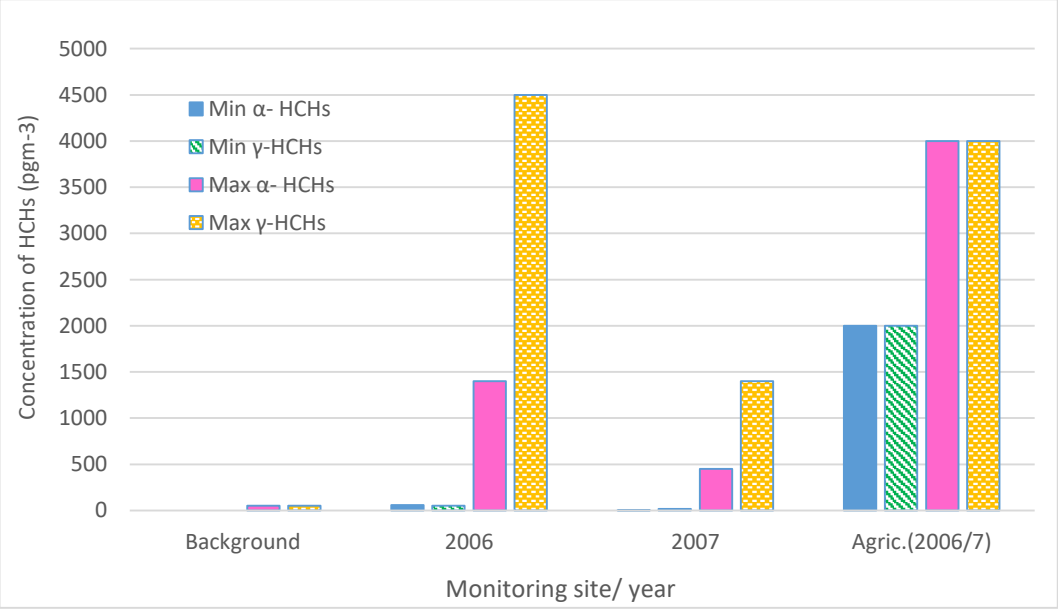


Figure 2-7: Concentrations of α- and γ-HCHs (pgm-3) in some cities in India.

In Ghana very little is known about atmospheric concentrations of lindane or other HCHs, however other environmental compartments such as soil, water and sediment

(Yeboah *et al.,* 1997) and other matrices such as plants, fish and breast milk have been well researched on. In breastmilk, gamma-HCH was detected to contain an average concentration of 4.2 ng/g (Osei Tutu *et al.*, 2011), in fruits concentrations were averaging 0.02 ug/g (Bempah *et al*., 2011), in fish, total HCH was detected was in the range of 0.72 ng/g to 4.38 ng/g (Kuranchie-Mensah *et al*., 2012; Adu-Kumi *et al.*, 2010a,b).

2.3.1.1.5 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) as shown in Figure 2-8 are aromatic compounds formed in such a manner that the hydrogen atoms on the biphenyl molecule (two benzene rings bonded together by a single carbon-carbon bond) may be replaced by up to ten chlorine atoms as such, they have a chemical formula of $C_{12}H_{(10-n)}Cl_n$, (where n is 1-10) (Gh EPA, 2007; UNEP, 2005).

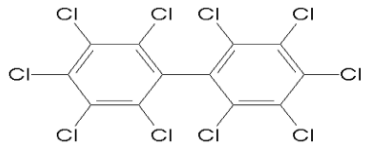


Figure 2-8: Polychlorinated biphenyl structure

The PCB compound can be separated into groups that have the same number of chlorine atoms attached to the biphenyl ring (i.e. a group of congeners that have the same degree of chlorination). These are called “homologues”. For example, four, six chlorine attachments to the biphenyl ring will belong to the group of tetra-, hexa-suffix homologue respectively (ODC and AQMD, 2001). The physical and chemical properties of PCB homologues are summarised in Appendix iic and vi. However, suffice to mention that PCBs are practically fire resistant because of their high flash points (170–380 °C). They form vapours which are heavier than air but are not explosive, they have low electrical conductivity, high thermal conductivity and high

resistance to thermal degradation (i.e. non-flammability properties). Pure individual PCB congeners are colourless and often crystalline. Commercial PCB mixtures are clear to light yellow oils or resins or waxy solids and they do not crystallize, even at low temperatures (Gh EPA, 2007; UNEP, 2005; WHO, 1993).

Polychlorinated biphenyls (PCBs) theoretically have a total of 209 possible congeners but only about 130 of these are likely to occur in commercial products (Gh EPA, 2007; Holoubek, 2000). Typically, four to six of the ten possible substitution sites are occupied by a chlorine atom (Environment Canada, 1988). The total global production of PCBs between 1930 and 1993 has been estimated to be 1.3 million tonnes (Brevik *et al*., 2002a). PCBs were used both for nominally closed and open-end applications. In open-end applications, they were vitally added for example in small quantities to ink, plastics, paints, flame retardants, adhesives, microencapsulation of dyes for carbonless duplicating paper, pesticide extenders, plasticizers, wire insulators and metal coatings. In closed applications, they were used in formulations of up to 70% PCBs in hydraulic fluid, transformer fluid and heat exchange fluids. In addition, they were used as capacitor oils, lubricating and cutting oils (UNEP, 2005).

All congeners of PCBs are lipophilic and their lipophilicity increases with increasing degree of chlorination (UNEP, 2005). Congeners with a lower degree of chlorination are more volatile than those with a higher degree of chlorination which are virtually insoluble in water and highly resistant to degradation. They are chemically stable as such resistant to chemical degradation as such they have excellent longevity (UNEP, 2005; WHO, 1993).

Some studies have been conducted to measure ambient air levels of PCBs and concentrations appear to differ markedly between locations (WHO, 2000a). Figure 2-

9 shows atmospheric PCB concentrations from various countries. In some studies, it was found out that indoor air values were higher than that of outdoors. In the USA, indoor levels ranged from 44 to 240 ng/m^3, while maximum outdoor levels were 18 ng/m^3. The levels of airborne PCBs were two times higher (457 ng/m^3) in buildings with PCB transformers than those without them (229 ng/m^3).

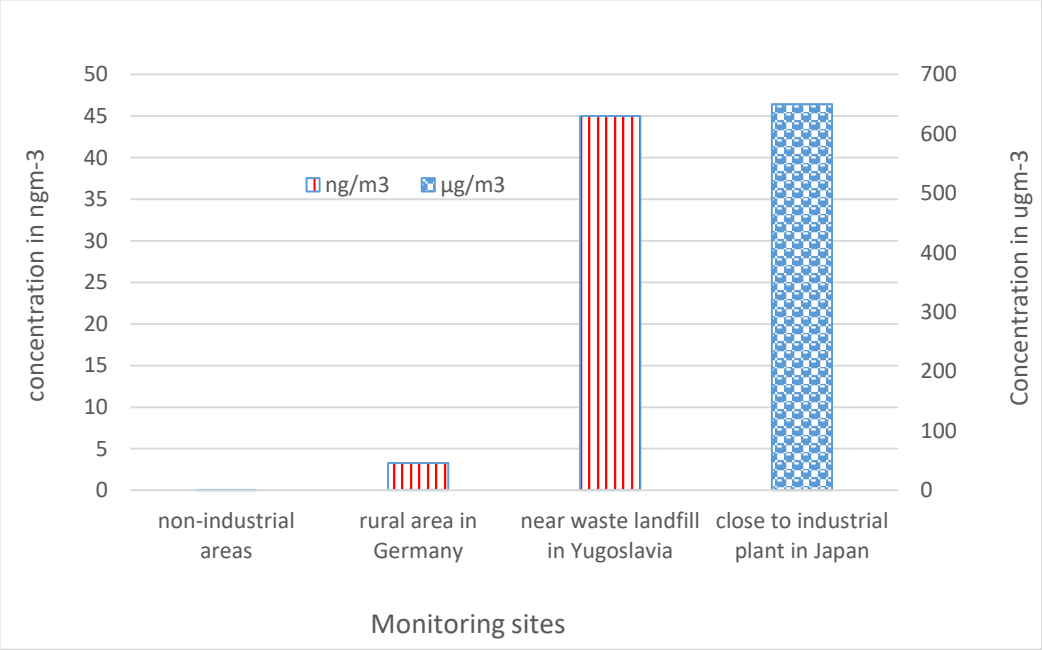


Figure 2-9: Atmospheric PCB concentrations from various sites

The highest indoor levels (up to 7500 ng/m^3) have been reported in buildings constructed from pre-fabricated concrete elements sealed with elastic materials containing PCBs (Balfanz *et al.*, 1993). In a related study, 39% of over 120 German buildings suspected to be contaminated, had PCB levels exceeding 300 ng/m^3 and in Sweden, indoor PCB concentration of 80 ng/m^3 was measured in an apartment while those with few or no PCB-containing materials had levels of 1.9 – 3.6 ng/m^3. Outside these buildings had levels of 0.5–4.6 ng/m^3. It was observed that, indoor PCB levels were inversely related to the degree of chlorination of the PCB mixtures used (WHO 2000a; Balfanz *et al.*, 1993; WHO, 1993).

In Ghana, very limited data exists for PCBs in air expect for Adu-Kumi *et al.* (2010b) and Klanova *et al.* (2009) where values in an urban environment was found to be between 0.069 ng/m^3 and 0.203 ng/m^3. Other environmental media however, have been worked on showing high concentrations, which might help in identifying some sources of exposure to the atmosphere. Asante *et al*. (2011) found in human breast milk, the sum of 62 PCB congeners (Σ_{62}PCB) to average 160 ng/g. In 2011, Kuranchie-Mensah *et al*. (2012) also found total of nine PCB congeners in fish from the Volta Lake to be 12.36 ng/g whereas Adu-Kumi *et al.* (2010a) had values as high as 1200 ng/g for the sum of six PCB congeners also in fish from the Volta Lake. Additionally, work done in 2009 in soil at Electricity Company of Ghana (ECG), a site considered to be contaminated with PCBs had values ranging between 45 ug/g and 154 ug/g when a sum of seven indicator PCBs were measured (Li *et al*., 2011).

2.3.1.1.6 Indicator and Dioxin-like Polychlorinated biphenyls

A proposed numbering system for the PCB congeners which has been adopted by the International Union of Pure and Applied Chemists (IUPAC) is shown in Appendix iii (Ballschmiter *et al*., 1992). Seven PCB congeners have been selected as indicators in several countries. These indicator PCBs include PCBs 28, 52, 101, 118,138, 153, and 180. The quantitation of the 7 indicator PCBs are used to determine whether PCB levels in food products, air, waste mineral oils, and environmental levels comply with the maximum levels permitted by legislation. There are also twelve PCB congeners for which the World Health Organization has assigned toxicity equivalency factors because they exhibit dioxin-like toxicity (coplanar PCBs) (WHO, 2000a; UNEP, 2005). These include PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and PCB 189 (MONET, 2014).

2.3.1.1.7 Polychlorinated dibenzo-p-dioxins & polychlorinated dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are important air pollutants created unintentionally during combustion processes. The polychlorinated dibenzo-p-dioxins are simply called dioxins. They have the chemical formula as $C_{12}H_{(8-n)}Cl_nO_2$ (Figure 2-10a) while the polychlorinated dibenzofurans are called furans. Furans have the chemical formula $C_{12}H_{(8-n)}Cl_nO$ (Figure 2-10b).

[A] [B]

Figure 2-10: Structure of Dioxin [A] and Furan [B]

These chemicals may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively. Like the PCBs, the dioxin and furans compounds (congeners) can be separated into groups that have the same degree of chlorination (homologues). Each homologue varies in its chemical, physical, and toxicological characteristics. There are eight (8) homologues of dioxins and furans (ODC and AQMD, 2001).

Dioxins and furans belong to the group of unintended by-products suggesting, they have not been deliberately manufactured except on a laboratory scale. They are by-products resulting from the production of other chemicals and from the low temperature combustion and incineration processes (Vallero, 2007). The use of

pentachlorophenol is considered to be a major source of PCDDs and PCDFs in many industrialized countries (WHO, 2000b). Other sources of PCDD and PCDF formations are from waste incineration combustion processes, iron and steel production (Rappe, 1994), chlorine bleaching of pulp and paper and other chlorine-alkali plants which used graphite electrodes (Rappe, 1991). Additionally car exhausts, mainly exhausts from leaded petrol in which chlorinated solvents have been used as so-called "scavengers", also produce these compounds (WHO, 2000b).

Dioxins and furans are characterized by their lipophilicity, semi-volatility and resistance to degradation and to long-range transport. They are also known for their ability to bio-concentrate and biomagnify under typical environmental conditions (Gh EPA, 2007). They are highly toxic compounds. The most toxic form is the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) isomer. Other isomers with the 2,3,7,8 configuration are also considered to have higher toxicity than those with different chlorine atom arrangements (Gh EPA, 2007).

Studies conducted to measure ambient air levels of dioxins (PCDDs) and furans (PCDFs) are few, basically, owing to the low detection limits required to quantify the expected low concentrations of specific congeners of these chemicals. Studies show that a higher proportion of lower chlorinated congeners are found in the vapour phase due to their higher vapour pressure (Duarte-Davidson *et al*., 1994). Some examples of the available data are summarized in Table 2.2 (WHO, 2000b).

Table 2-2: ΣTEQs of PCDDs/PCDFs in air reported for various locations

Country	Site	Sum of toxic equivalent (ng/m^3)
Belgium:	Ambient air, 6 sites	0.02 - 0.59
Netherlands	Air from North sea	0.005
	Local Background	0.010–0.015
	Downwind of municipal waste incinerator	0.14
Germany	Rural	<0.07
	Urban	0.07 -0.35
	Close to major sources	0.35-1.6
	Rural, 1 site	0.05
	Industrial/rural with industries, 5 sites	0.08 -0.15
Sweden	Urban/suburban	0.013 -0.024
	Remote/coastal	0.003 - 0.004
	Long-range transport:	
	– from the United Kingdom	0.055
	– from Germany	0.0056
	– from Iceland	0.0033
United Kingdom	Urban, 4 sites:	
	– median (range)	0.10 (not detected- 1.8)
	– mean	0.17
United states	Mean value, coastal environment (winter)	0.1
Japan	Mean (range):	
	– urban (summer)	0.79 (0.4 - 1.3)
	– urban (winter)	1.46 (0.3 -2.9)
Australia	Sydney, 4 sites	0.02 -0.06

Total toxicity equivalency (ΣTEQs) of dioxins and furans (PCDDs/PCDFs) in air reported for various locations (TSD, 2010).

2.3.1.2 Toxicity of PCDDs, PCDFs and dl-PCBs

The World Health Organisation (WHO), has established toxicity equivalent factors (TEFs) for seventeen 2, 3, 7, 8-substituted-dioxins/furans, out of the 210 known congeners. Inaddition, it has further identified twelve PCB congeners to be similar in toxicity to the PCDD/Fs (EC, 2002). These "WHO-PCBs" also called "dioxin-like PCB" congeners (dl-PCBs), can adopt structural conformations most resembling that of 2, 3, 7, 8- tetrachlorodibenzo-*p*-dioxin (TCDD) which leads to high binding

affinities to the aryl hydrogen receptor (AhR) producing toxicological effects (TSD, 2010). The dioxin-like PCBs include four (4) co-planar or non-ortho PCBs (PCBs No. 77, 81, 126, 169) and eight (8) mono-ortho congeners (PCBs No. 105, 114, 118, 123, 156, 157, 167, 189) (EC, 2002).

Some work done TEQ values of dioxin-like chemicals have recorded such concentrations as in the range of 0.009 to 0.678 pg WHO_{98} TEQ/m^3 from Latin America and much lower levels of 0.001 to 0.87 pg WHO_{98} TEQ/m^3 from the Pacific Islands (Bogdal *et al.*, 2012). Levels in Mexico were higher with a mean value of 0.022 pg WHO_{98} TEQ/m^3 (Bogdal *et al.,* 2012). Concentration from the Manizales city in Colombia were between 0.007 and 0.011 pg WHO_{2005} TEQ/m^3 (Cortes *et al.,* 2014).

2.3.2 New/emerging persistent organic pollutants

The current technological society born from the industrial revolution has caused a continuous production and emission of new toxic substances in the world. As such there is global circulation of new or emerging persistent organic pollutants (POPs) which are causing gradual and widely diffuse adverse effects to the global environmental quality. These new POPs are from different chemical families such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalenes (PCNs), polybrominated diphenyl ethers (PBDEs) and the perfluorinated compounds (PFCs) (Castro-Jiménez *et al.*, 2008).

The New or Emerging POPs as listed by the Stockholm Convention are as follows: alpha and beta hexachlorocyclohexane; chlordecone; hexabromobiphenyl; hexabromodiphenyl and heptabromodiphenyl ethers; lindane; pentachlorobenzene;

perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride; and tetrabromodiphenyl and pentabromodiphenyl ethers (UNEP, 2009b). Currently other chemicals are being considered for inclusion by the persistent organic pollutants review committee (POPRC) and these include endosulphan, hexabromocyclododecane, and short-chained chlorinated parafins (SCCPs) (UNEP, 2009b).

2.3.2.1 Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers (PBDEs) are a group of additive flame-retardants that have been widely used in commercial and domestic products (de Wit, 2002). Polybrominated diphenyl ethers (PBDEs) have a backbone structure of a brominated diphenyl ether molecule (Figure 2-11) that may have from 1 to 10 bromine atoms attached. Depending on the location and number of bromine atoms, there are 209 possible configurations or congeners and each has been assigned a unique brominated diphenyl ether (BDE) number as polychlorinated biphenyls (PCBs) (La Guardia *et al.*, 2006; McDonald, 2002). The chemical properties of PBDEs are listed Appendix vi.

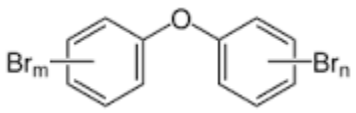


Figure 2-11: Polybrominated diphenyl ethers

PBDEs came into wide use beginning in the 1970s (Schecter *et al.*, 2010) have been marketed for use in commercial products as three technical mixtures: decabrominated diphenyl ether (Deca-BDE), octabrominated diphenyl ethers (Octa-BDEs), and pentabrominated diphenyl ethers (Penta-BDEs). Each of these mixtures is named according to the average number of bromine atoms contained in most molecules of the

mixture (Schecter *et al*., 2005). The commercial penta-BDE consists primarily of BDEs 47 and 99 (37% each), alongside smaller amounts of other tetra-, penta-, and hexa-BDEs; the octa-BDE contains a mixture of hexa (10-12%), hepta- (44-46%), octa- (33-35%), and nona- (10-11%). The deca formulation is basically 98% decabromodiphenyl ether, BDE 209 and 2% various nona-BDEs (Harrad and Hunter 2006). The uses for these commercial formulations are myriad: the penta product was employed principally to flame-retard polyurethane foams in carpet underlay, furniture, and bedding but has also been used in computer circuit boards and textiles; the octa formulation was used to flame-retard thermoplastics such as high-impact polystyrene, and the deca product is used principally in plastic housings for electrical goods such as TVs and computers, as well as in textiles (de Wit, 2002; Harrad and Hunter, 2006).

Worldwide, PBDE production is dominated by the deca- commercial formulation. An estimated global demand for PBDEs in 1992 was 40,000 metric tonnes of which 10% was penta-, 15% was octa- and 75% was decaBDE and in 1999, the global demand was estimated to be close to 70,000 metric tonnes (13%, 6% and 81% were produced as penta-, octa- and decaBDE, respectively) (Sjodin *et al*., 2003). In 2001, the global demand for the deca- formulation was estimated at 56,100 tonnes and that for the penta- product was 7,500 tonnes (Harrad and Hunter, 2006).

PBDEs are chemically and toxicologically similar to polychlorinated biphenyls (PCBs) (Syed *et al*., 2010; Birnbaum and Staskal, 2004). They were officially classified as persistent organic pollutant (POPs) and globally included in Annex A (elimination of production and use of all intentionally produced POPs) under the Stockholm Convention on POPs in 2009 (UNEP, 2009a). The deca BDE is not considered to be a classical POP, studies have shown that it can degrade to lower brominated PBDEs upon exposure to sunlight (Björklund, 2011). The usage of deca

BDE has been banned by some states in the U.S and is expected to have phased out in 2013 (Möller *et al*., 2011) whiles its use in the EU has been banned since 1 July 2008 according to the European Court of Justice ruling (de Wit *et al*., 2010).

Polybrominated diphenyl ethers (PBDEs) can enter into the environment during their production, use, disposal and recycling processes as well as from volatilization and/or leaching (Chen *et al*., 2007) and these are easily distributed and transport by air. Due to their physical and chemical properties, 20% of BDE-47, 60-90% of penta-hepta BDEs and almost 100% of BDE-209 are expected to partition to particles at room temperature, when released to air which means, 80% of BDE-47 and 10-40% of the airborne penta-hepta BDEs are expected to be present in the gas phase at room temperature (Shoeib *et al*., 2004; Björklund, 2011). Work done by Li *et al*. (2012) at the Great Wall station at King George Island, Antarctica, China, revealed that the air concentrations of Σ_{14} PBDEs ranged between 0.67 and 2.98 pgm^{-3}, with an average value of 1.52 pg /m^3. Ghana as a developing Country, has no data on PBDE levels in air though in 2009, measurements of PBDEs in human breast milk was done and levels recorded was 18 ng/g as mean concentration (Asante *et al*., 2011).

2.3.2.2 Hexabromocyclododecanes

Hexabromocyclododecanes (HBCDs) are brominated aliphatic cyclic hydrocarbons used as flame retardants in thermal insulation building materials, upholstery textiles, and electronics. They are a group of additive brominated flame retardants (BFRs) that are widely used in expandable polystyrene (EPS), extruded polystyrene (XPS), high impact polystyrene (HIPS) (electric and electronic appliances), and polymer dispersion for textiles (Miyake *et al*., 2009).

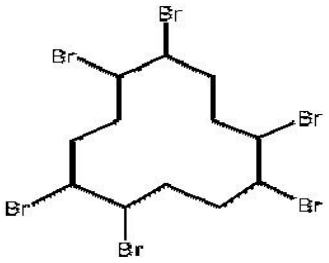


Figure 2-12a: Hexabromocyclododecanes

Hexabromocyclododecane (HBCD) is a colourless solid with a molecular formula of $C_{12}H_{18}Br_6$ and its structure consists of a ring of 12 carbon atoms to which 18 hydrogen and 6 bromine atoms are bound (Figure 2-12a) (USEPA, 2010). The technical (commercial) grade HBCD mixtures are obtained via bromination of cyclododeca 1, 5, 9-triene isomers. Six stereogenic centers at positions 1, 2, 5, 6, 9 and 10 are formed, which theoretically leads to 16 stereoisomers of 1, 2, 5, 6, 9, 10-hexabromocyclododecane. HBCD is a lipophilic compound with a relatively high octanol-water partitioning coefficient (log Kow) of 5.6.

In 2001, hexabromocyclododecanes had a world market demand of 16,700 metric tons (Morose, 2006). The commercial mixtures mainly consist of γ-HBCD (75-89%), while α-HBCD and β-HBCD are present in lower amounts (10-13% and 1-12%, respectively). Furthermore, at least two additional stereoisomers, named δ- and ε-HBCD are present at minor concentrations. HBCDs are subject to thermal rearrangement at temperatures above 160 °C, which results in a specific mixture of stereoisomers (78% α-HBCD, 13% β-HBCD, and 9% γ-HBCD) (Barotini *et al*., 2001). Such conditions can occur during the production or processing of materials containing HBCDs (e.g., extruded polystyrene) and therefore the relative abundance of the various HBCD stereoisomers may differ from that of the technical HBCD mixtures (Covaci *et al*., 2006).

Hexabromocyclododecane is used in foams and expanded polystyrene (insulation of foundation, walls and ceilings). In textile application (which is a smaller scale use), HBCD is used in back-coatings in protective clothing, tents, upholstery and other interior textiles: carpets, curtains, including automotive applications upholstered furniture (automobile interior textiles, car cushions). The high impact polystyrenes (HIPS) are used in housings of electronic products and wiring parts (UNEP, 2011). So the end products include insulation blocks in trucks and caravans as well as in building materials such as house walls, cellars, roofs, ground deck and parking decks, against frost heaving in roads and railway embankments, packaging material, video cassette recorder housing and electric equipment (de Wit, 2002).

Hexabromocyclododecanes (HBCD) are considered bioavailable and bioaccumulative based on studies of fish and fish eating animals (USEPA, 2010; Morose, 2006). As a result of their widespread use and their physical and chemical properties, HBCDs are now ubiquitous contaminants in the environment and humans. HBCDs enter the environment by a number of different pathways, such as emission during production of brominated flame retardants, or the manufacture of flame-retarded products, by leaching from consumer products, or following disposal.

HBCDs have been detected in air from different countries (Fromme *et al.,* 2014; Miyake *et al.,* 2009; Covaci *et al*., 2006). In Ghana however data exists only for human breast milk (0.54 to 3.2ng/g) (Asante *et al.,* 2011).

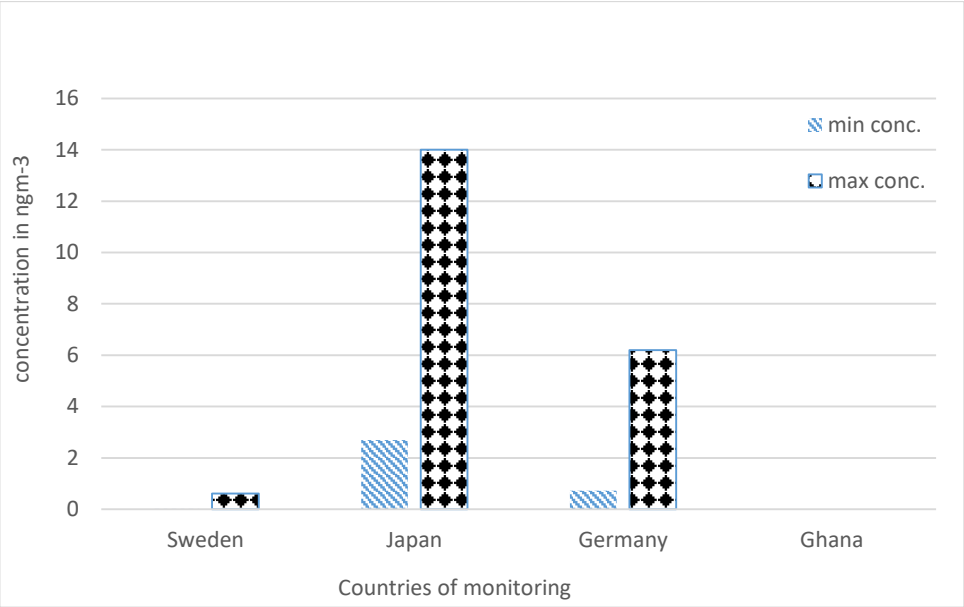


Figure 2-12b: Atmospheric HBCD concentrations (ngm^{-3}) from some countries

2.3.2.3 Polybrominated Biphenyls

Polybrominated biphenyls (PBBs) are aromatic hydrocarbons produced and used as flame retardants, basically due to their ability to meet flame resistance performance requirements and also for economic feasibility. PBBs are chemicals added to plastics or polymers used in a variety of consumer products such as computer monitors, televisions, paint, plastic foams and textiles (particularly in office buildings), in cars and aircrafts to prevent them from catching fire (ATSDR, 2004; de Boer *et al*., 2000).

Polybrominated biphenyls are the bromine analogues of polychlorinated biphenyls (PCBs) and so the systematic numbering system developed by Ballschmiter *et al*. (1992) for PCBs has been adopted for the corresponding PBB congeners. PBB thus theoretically, also have 209 possible congeners of which only a few occur in commercial chemical formulations. They consist mainly of hexa-, octa-, nona- and deca-bromobiphenyls (de Boer *et al*., 2000).

PBBs are solids or waxy substances at room temperature with a low vapour pressure. They show an unusual chemical stability and resistance to acids, bases, heat, reduction and oxidation (de Boer *et al*., 2000). They are virtually insoluble in water and highly resistant to degradation (UNEP, 2005). PBBs are soluble in various organic solvents and most have a log Kow > 7. They are therefore regarded as superlipophilic compounds (de Boer *et al*., 2000).

Commercial PBBs were manufactured in the early 1970s under different trade names. They were sold as Adine 0102 (Decabromobiphenyl), Bromkal 80-9D (Octanonabromobiphenyl) and FireMaster (Hexabromobiphenyl) which was the first PBB compound produced commercially (up to 80% hexa- and up to 25% hepta-bromobiphenyl). In 1974, FireMaster came to the attention of the public, having discovered that about 1000 pounds of PBB had been accidentally substituted for magnesium oxide as an additive to cattle feed in Michigan. The production of PBB was strongly reduced after the accident. (UNEP, 2005; de Boer *et al*., 2000; IPCS, 1994).

The acute toxicity of Polybrominated biphenyls (PBB) is relatively low (de Boer *et al*., 2000). The planar PBBs are most toxic because they bind to the aryl hydrogen receptor (AhR). The mono-ortho congeners are intermediate in toxicity and di-ortho congeners, least toxic. The 3,3’,4,4’,5,5’-hexabromobiphenyl was found to be the most toxic PBB congener in several systems, but this congener is present in low concentrations in technical PBB mixtures (Darnerud, 2003; IPCS, 1994). Such adverse effects of PBB on reproduction as resorptions and decrease viability of offspring have been observed in many species (Darnerud, 2003) including balance of endocrine systems of animals and humans (de Boer *et al*., 2000).

Very few data on atmospheric concentration of total PBB is available. Mean concentrations recorded in Taiwan was 0.0265 pg/m^3 over the oceanic air and 0.144 pg/m^3 on land (Chao *et al.,* 2014). Wang *et al.* (2010) recorded total PBB with concentrations from 0.149 to 0.556 pg/Nm^3 from a rural area.

2.3.2.4 Polyfluorinated compounds

Polyfluorinated compounds represent a large group of chemicals which are characterized by a partially or fully fluorinated carbon chain attached to various hydrophilic heads. Where all the hydrogen atoms in the hydrocarbon backbones have been substituted with fluorine atoms, it is known as a perfluorinated compound (PFCs) (Huber *et al*., 2011). Perfluorinated compounds, depending on the nature of the functional group, can be divided into:

(1) perfluorinated sulfonic acids (PFSAs) or perfluoroalkyl sulfonates
(2) perfluorinated carboxylic acids (PFCAs) or perfluoroalkyl carboxylates
(3) fluorotelomer alcohols
(4) high-molecular weight fluoropolymers and
(5) low-molecular weight perfluoro alkanamides

Perfluorinated alkylated acids (PFAA) such as perfluorooctane sulfonate (PFOS) (Figure 2:15a) and perfluorooctanoic acid (PFOA) (Figure 2:15b) are examples of fully fluorinated organic chemicals with a sulfonic or a carboxylic head group. These are anionic in nature. They are often referred to as key substances or reference for the first two groups mentioned (Stahl *et al*., 2011; Björklund, 2011).

[A] [B]

Figure 2-13: Structure of Perfluorooctane sulfonic acid [A], Perfluorooctanoic acid [B]

Perfluorinated compounds (PFCs) have been produced since the 1950s (Cornelis *et al*., 2012). The perfluoroalkyl acids (PFAAs) have been used as surfactants and surface protectors in many consumer products and industrial applications such as textiles, leather and fire-fighting foams due to the hydrophobic properties of the tail and the hydrophilic nature of the head (Kissa, 2001). The fluorine-carbon bonds are extremely stable giving these substances a very high thermal and chemical stability (Cornelis *et al*., 2012; Björklund, 2011).

The perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs) exhibit persistence to environmental and biological degradation with some analogues demonstrating bioaccumulative and toxic properties as well as global distribution (Huber *et al*., 2011; Ahrens *et al*., 2010). Persistent ionic compounds like perfluorooctane sulfonate (PFOS) and perfluoro carboxylates (PFCAs) reach remote regions far from production and emission areas by indirect long range atmospheric transport (LRAT) via neutral, volatile precursors such as fluorotelomer alcohols (FTOHs) as a possible transport pathway. Atmospheric oxidative transformation might then eventually degrade airborne fluorotelomer alcohols (FTOHs) to perfluoro carboxylates (PFCAs) and lead to their precipitation (Jahnke *et al*., 2009).

In 2009, perfluorooctane sulfonate (PFOS) was added to the Stockholm Convention on persistent organic pollutants (UNEP, 2009b). Zhao *et al*. (2012) as well as other authors reviewed measurements of PFOS in air in Japan and the highest mean concentration of 7.3 pg/m^3 was detected (Harada *et al*., 2006; Harada *et al*., 2005). In Canada samples analysed for ionic PFCs gave values as high as 28 pg/m^3 and total fluorotelomer alcohols (FTOHs) air concentration ranged from 890 to 47,000 pg/m^3 for the neutral PFCs (Shoeib *et al*., 2011). Measurement in China gave mean concentrations of 205 ng/g perfluorooctanoate (PFOA), 14.0 ng/g perfluoroheptanoate (PFHpA) and 4.86 ng/g perfluorooctane sulfonate (PFOS) (Zhang *et al.,* 2010). No data exists for Ghana in air.

2.3.2.5 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous pollutants that can be found as trace contaminants in air, and other environmental compartments (Pigini *et al.*, 2006). They are basically a group of over 100 different chemicals formed during the incomplete combustion of coal or other organic substances like tobacco, charbroiled meat or fossil fuels (Palm, 2009; EFSA, 2005). PAHs are also associated with automobile exhaust (Safo *et al.,* 2014b), accidental spilling and or seepage of hydrocarbons, coal liquefaction and gasification processes and from natural processes such as during volcanic eruptions, forest fires and surface run-offs from fire as well as geological processes (Juhasz, 1997). PAHs are also reported as belonging to a large chemical family comprising many different compounds with important biological activity in mutagenic and carcinogenic processes (RASFF, 2007).

PAHs have been grouped into low (152 to l78 g/mol), medium (202 g/mol) and high (228 to 278 g/mol) molecular weights. PAHs may exist in vapour or particle phase. The species with a molecular weight below that of pyrene (202 g/mol) exist to a large extent in the gas phase (Palm, 2009 cited Hoff *et al.,* 1987; Palm, 2009 cited Lee *et al.*, 1976). It is estimated that an average of 47% of the total PAHs have been reported in gas phase (particle-free PAHs). Three-ring PAHs are predominantly gaseous, six-ring PAHs primarily particulate and the five-ring PAHs are a mixture of both phases (Sheu *et al.*, 1977). Other physical and chemical properties are discussed in Appendix viii.

They are more stable, persistent and toxic than the light ones and they present a high lipophilic character. Molecular stability and hydrophobicity are two primary factors that contribute to such persistence (Wenzl *et al.*, 2006; Harvey, 1997; ATSDR, 1995). When adsorbed on particulate matter, PAHs can undergo photo-decomposition when exposed to ultraviolet light from solar radiation (ATSDR, 1995).

Most PAHs have no known use except for research purposes (HSDB, 1994; Hawley, 1987). A few are used in medicines, and to make dyes, plastics, and pesticides. In particular, naphthalene (also known as mothballs) is used in making dyes, explosives, plastics, lubricants, and moth repellent (Aronstein *et al*., 1993). Anthracene is used as intermediate in dye production, in the manufacture of synthetic fibers, and as a diluent for wood preservatives. It is also used in smoke screens as scintillation counter crystals and in organic semiconductor research (Hawley, 1987). Anthracene is used to synthesize the chemotherapeutic agent, Amsacrine. Acenaphthene is used as a dye intermediate in the manufacture of pharmaceuticals and plastics, and as an insecticide and fungicide (HSDB, 1994; Windholz, 1983). Fluorene is used as a chemical

intermediate in many chemical processes in the formation of poly-radicals for resins, and in the manufacture of dyestuffs). Phenanthrene is used in the manufacture of dye stuffs and explosives and in biological research (HSDB, 1994; Hawley, 1987). Fluoranthene is used as a lining material to protect the interior of steel and ductile-iron drinking water pipes and storage tanks (National Research Council, 1983).

The biological activity of PAHs depends upon their molecular structure. Thus, different isomers show diverse carcinogenic activity. Apendix iv shows names and carcinogenic activities of PAHs as stated by the US Environmental Protection Agency (EPA), (Fern´andez-S´anchez *et al.*, 2004).

Some PAHs have been identified as markers for various sources in urban atmospheres. These include phenanthrene, fluorathene and pyrene which are produced from coal combustion. Dominance of chrysene and benzo(k)fluoranthene have also been were suggested for their origin from coal combustion (Ravindra *et al.*, 2008, 2007; Smith & Harrison, 1998; Khalili *et al.*, 1995). Anthracene, phenenthrene, benzo(a)pyrene come from coke production. Pyrene, fluoranthene, and phenanthrene show reasonably high levels in emission from incineration (Ravindra *et al.*, 2006; Smith & Harrison, 1998). Additionally, wood combustion has been identified as a source which produces benzo(a)pyrene and fluoranthene. Industrial oil burning as a source is identified using the markers, fluoranthene, pyrene and chrysene. Oil combustion was reported to be associated with the high concentration of the more volatile PAHs such as fluorene, fluoranthene and pyrene, along with moderate levels of the higher molecular weight compounds, i.e. benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene (Ravindra *et al.*, 2006; Harrison *et al.*, 1996).

Significantly higher levels of benzo(ghi)pyrene, indeno(123-cd)pyrene, coronene, and phenanthrene are proposed as having petrol powered vehicles/ motor vehicle emissions as source (Ravindra *et al.,* 2006a; Smith & Harrison, 1998). Marr *et al.* (1999) and Miguel *et al.* (1998) found that heavy duty vehicles (diesel trucks) are the major source of lighter PAHs (i.e., 3-benzene ring PAHs and such others as fluoranthene and pyrene) whereas light-duty gasoline vehicles are dominant sources of higher molecular weight PAHs (4- and 5-benzene rings) such as B(a)P and dibenz(a,h) anthracene. Fluoranthene, pyrene and higher ratios of benzo(b) flouranthene, benzo(k)fluoranthene and thiophene compounds have marked diesel powered vehicles. Most polycyclic aromatic hydrocarbons can be generated from multiple sources (Cortazar *et al.,* 2008; Colombo *et al.,* 2006; Soclo *et al.,* 2000).

Benz(a)anthracene is found in flue gases, tobacco smoke and its condensate, automobile exhaust, creosote, coaltar, petroleum asphalt, roasted coffee and in charcoal broiled, barbecued or smoked meats. It is also found in variety of foods, including vegetable oils and baker's yeast. It is an atmospheric contaminant near power plants and busy highways, and tends to bind to particulate matter in the atmosphere with its primary removal mechanism from the atmosphere being thought to be ozonolysis reactions, where the expected half-life is less than 1day to several weeks depending on the nature of the particulate matter to which it is adsorbed (USEPA, 1994; Sittig, 1985). Pyrene is also known as benzo(d,e,f)phenanthrene. Pyrene consists, four fused benzene rings resulting in a flat aromatic system. Pyrene is a colourless solid and is the smallest peri-fused polycyclic aromatic hydrocarbon with the rings fused through more than one face. As a peri-fused PAH, pyrene is much more resonance stabilized than its isomer fluoranthene which is composed of both benzenoid and five-carbon-membered rings. Pyrene is forms during incomplete

combustion of organic compounds and was first isolated from coal tar where it occurs up to 2% by weight (Withey, 1992). Benzo(k)fluoranthene is however found in fossil fuels and occurs ubiquitously in products of incomplete combustion. It has been detected in mainstream cigarette smoke, gasoline engine exhaust, emissions from burning coal and from oil-fired heating, lubricating oils, used motor oils, crude oils (IARC,1983) in soils and ground water at hazardous waste sites (ATSDR, 1990).

Measurement of PAHs in air has seen increase due to its being ubiquitous. In Stockholm, Sweden, the sum of 14 different PAHs studied was 100—200ng/m^3 at the street-level site, the most abundant being phenanthrene with benzo(a)pyrene concentration varied between 1—2 ng/m^3 (Carl-Elis *et al.,* 2002). Lee *et al.* (1995) also in analysed PAH in air in Taiwan from a traffic source and the individual PAH concentrations ranged from 88.3 ngm^{-3} acenaphthylene to 3040 ng/m^3 naphthalene. In Ghana, Safo-adu *et al*. (2014b) measured PAH by a highway with concentrations of sum of 20 PAHs (Σ_{20} PAH) giving 809.80 ng/m^3 with pyrene being most abundant (171.40 ng/m^3). Atmospheric polychlorinated naphthalenes (PCNs), also gave concentrations of an average of 49 ± 5.4 pg/m^3 (Hogarh *et al.,* 2012). Average inhalation exposure to PAHs has been estimated to be 10ng/day (assuming an air intake rate of 20m^3/day) (EPA, 1989).

2.3.3 Inorganic pollutants: heavy metals

Heavy metals are intrinsic, natural constituents of our environment. Apart from the natural sources, several anthropogenic ones contribute to metal concentrations in the environment. Recently, industrial activities have raised natural concentrations of heavy metals causing serious environmental problems (Hawkes, 1997).

2.3.3.1 Manganese

Manganese (Mn) is the twelfth most abundant element in the earth's crust and the fourth most widely used metal in the world. There inorganic form of Mn compounds is the most common in the environment. It is one of the most abundant metals in soils, where it occurs as oxides and hydroxides. Manganese occurs principally as pyrolusite (MnO_2) and to a lesser extent as rhodochrosite ($MnCO_3$) Studies in animals have shown that very high levels of manganese in food or water can cause changes in the brain and may also injure the testes. A common effect in men who are exposed to high levels of manganese dust in air is impotence. High exposures to manganese in the environment might increases the risk of birth defects, but other factors besides manganese might have been responsible. A study on animals showed that exposure of pregnant females to high levels of manganese in air can lead to changes in behaviour of the offspring (Emsley, 2001).

2.3.3.2 Lead

Lead is causing concern in particular due to the possible impacts on the nervous systems of children, including learning and behavioural disabilities. Lead can severely affect the central nervous system. Overt signs of acute intoxication include dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, hallucinations, and loss of memory (Naja and Volesky, 2009).

Lead is a soft metal that resists corrosion. It is the most common of the heavy elements with average molecular weight of 207.2. Lead exists with several stable isotopes in nature and has a low melting point (327°C). Lead is more widely distributed in the general environment through atmospheric emissions - particularly from car exhausts

and lead poisoning is generally ranked as the most common environmental health hazard (Goyer, 1991; Sireli *et al*., 2006; Naja and Volesky, 2009).

2.3.3.3 Cadmium

Cadmium is a substance of particular concern due to the accumulation in agricultural soils, which may increase human intake by foodstuffs. It is of great concern because of its harmful effects on plants, animal and man. It is known to cause "itai-itai" disease; which is known to damage the joints, causing bones to soften and the body to shrink while the affected person dies a painful death (Ekpo *et al*., 2008). It is observed that fish exposed to high concentration of cadmium quickly develops lack of calcium and low blood haemoglobin (El-Naga *et al*., 2005).

Cadmium (Cd) is found in natural deposits as ores containing other elements. It is a silvery-white, lustrous, but tarnishable metal; it is soft and ductile and has a relatively high vapour pressure. Pure Cd compounds are rarely found in nature, although occurrences of greenockite (CdS) and otavite ($CdCO_3$) are known. The main sources of Cd are sulfide ores of lead, zinc, and copper. Cd is recovered as a by-product when these ores are processed (Shammas, 2009). Cadmium is chiefly used for electroplating, paint pigments, plastics, silver–cadmium batteries, and coating operations, including transportation equipment, machinery and baking enamels, photography, and television phosphors. Chemically, cadmium closely resembles zinc and occurs in almost all zinc ores by isomorphous replacement. Industrial and municipal wastes are the main sources of cadmium pollution (Naja and Volesky, 2009; Shammas, 2009).

2.3.3.4 Chromium

Chromium is a lustrous, silver-grey metal. It is one of the less common elements in the earth's crust, and occurs only in compounds. The chief commercial source of

Chromium is the mineral chromite, $FeCr_2O_4$. Chromium is mined as a primary product and is not recovered as a by-product of any other mining operation. There are no chromite-ore reserves, nor any primary production of chromite in the United States (Shammas, 2009). Chromium steel alloys provide high corrosion resistance and good hardenability. Chromium is used in many industrial applications ranging from tanning agents, paint pigments, and catalysts to impregnation solution for wood or photography. Clinically, acute irritative dermatitis or allergic eczematous dermatitis, bronchial asthma and cancer in the respiratory organs have been reported due to chromate dust or chromic acid fumes. Chromium concentrations in air is subject to large variations. In air the concentrations range from 0.3 ngm^{-3} in remote sites to 50 ngm^{-3} in urban areas (Naja and Volesky, 2009).

2.3.3.5 Nickel

Nickel is a hard, silvery-white metal that is malleable and ductile which is naturally present in various mineral ores such as garnierite, millerite, niccolite, pentlandite, and pyrrhotite (Argonne National Laboratory, 2005). Most of the world's supply of nickel is mined in Canada; others include Cuba, China, and Australia. Nickel is used in various coins and as a component of several alloys, including nichrome and permalloy, and in some stainless steels. Nickel alloy steels are used in heavy machinery, manufacturing, armaments, tools, and high-temperature equipment, including gas turbines and environmental devices used to control emissions such as scrubbers. Nickel is also used as a protective and ornamental coating for metals susceptible to corrosion, particularly iron and steel. In electrical appliances, wire goods, steel furniture and in the field of electronics (Argonne National Laboratory, 2005; Naja and Volesky, 2009). Nickel can be taken into the body by eating food, drinking water, or breathing air. It can be absorbed into the skin where it may stay, instead of being

absorbed into the blood (Argonne National Laboratory, 2005). Generally, people are exposed to low levels of nickel in ambient air, water, and food and also some exposure occurs from smoking. Typical average daily intakes of nickel from drinking water and inhalation of air are approximately 8 and 0.04 µg, respectively (ATSDR, 2005).

2.3.3.6 Copper

Copper is a chemical element. It is ductile and malleable. It is used as a conductor of heat and electricity. Copper is found mainly in the liver, muscle and bones of humans. Copper compounds are used as bacteriostatic substances, fungicides, and wood preservatives (Sarojam, 2009). Copper as an essential trace element for living organisms, is required for maintaining cellular function and acting as a cofactor for a number of key metabolic enzymes for their normal physiological activities (Monteiro *et al*., 2009). A high concentration of copper had been correlated with liver damage and zinc may produce adverse nutrient interactions with copper (Sarojam, 2009). Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomach aches, dizziness, vomiting and diarrhoea. High uptake of copper may cause liver and kidney damage and even death. Chronic copper poisoning results in Wilson's disease, accompanied by a hepatic cirrhosis, neurological degeneration, demyelization, renal disease and copper deposition in the cornea (WHO, 1988).

The varied toxicological effects of heavy metals on human and the environment has made their measurements in most environmental media common in Ghana except for the atmospheric medium. Inspite of limited air sampling equipment, some work has still been done in Ghana (Aboh, 2014; Ofosu *et al.,* 2012; Asante *et al.,* 2012; Thomas & Morawska, 2002).

Others such as Boamponsem *et al.* (2010), Affum *et al.* (2010) and Ofosu *et al.* (2013) have worked with somw passive samplers and other type of active samplers. Boamponsem *et al.* (2010) have used lichens to assess atmospheric heavy metal deposition in the Tarkwa gold mining district of Ghana using neutron activation analysis. They found concentrations of tin from a control site to be of 0.16 ppm wt and those from the exposed site to be in the range of 0.78 and 10.35 ppm wt. Others were with concentrations of aluminium, arsenic, cadmium, copper, cobalt, mercury, manganese, thorium and vanadium in of 8.38–69.55 ppm wt., 0.25–8.00 ppm wt., 0.38–1.41 ppm wt., 0.26–370 ppm wt., 0.87–6.13 ppm wt., 0.16– 1.24 ppm wt., 37.1–1097 ppm wt., 0.01– 0.21 ppm wt. and 1.53 – 27.24 ppm wt., respectively. Affum *et al.* (2010) also used lichens to assess the concentration of Manganese on the Madina-Tetteh Quarshie Road in the Greater Accra Region of Ghana. They found the average manganese concentration in the area to be 540.032 ± 19.896 mg/kg. Heavy metal concentration in Navrongo was assessed by Ofosu *et al.* (2013). They recorded the following and many more, Lead 31 ± 6 ng/m^3, Manganese 44 ± 26 ng/m^3, Chromium 19 ± 6 ng/m^3, and Nickel 57 ± 18 ng/m^3. Figure 2-16 also shows some measurements done in air in Australia (Lim *et al.*, 2005).

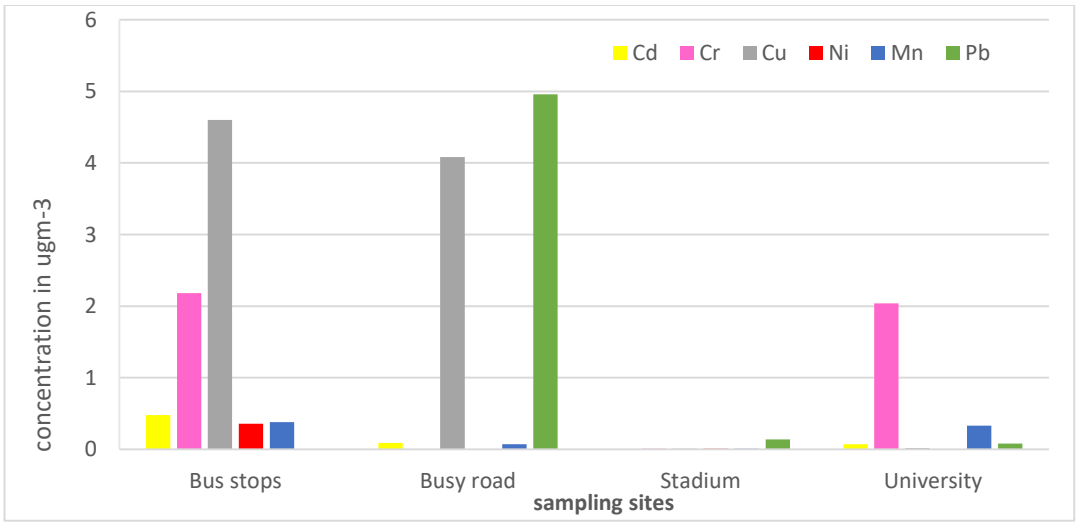


Figure 2-16: Levels (ng/m^3) of heavy metals from selected sites in Australia

2.5 Passive sampling

Passive air samplers (PAS) are seen as an alternative to the active volume samplers. PAS works by uptaking compounds by the principle of passive mass transfer, based on the free flow of compounds or analytes from the air to an accumulation matrix (Harner *et al.,* 2006). Passive samplers are cheaper in assessing and easier to manipulate and use and also of easier in maintenance than the active samplers (Levy, 2008).

Different types of adsorption matrix in passive air samplers have been developed and used. These include semi-permeable membrane devices (SPMDs), coated stir bars (CSBs) and polyurethane foams (PUFs) (Levy 2008; Ockenden *et al.,* 1998). SPMDs are integrative passive samplers. Both SPMD and PUFs are able to accumulate compounds during the sampling time until reaching an equilibrium stage. Their uptake is based on the contaminant concentration difference between the air and the semi-permeable device or the PUF. For SPMDs, only small compounds are able to penetrate through the membrane (Levy, 2008). The coated stir bar is a device whose design is a rod covered with a coating of a polymeric material, able to retain analytes or compounds through dissolution or partitioning (sorption). This type of passive sampler has only a single phase of a coating material (Levy, 2008). Other coated samplers used are polymer coated glass (POG) (Farrar *et al.,* 2006).

The PUF adsorbent has the advantage of adsorbing a wide range of organic pollutants based on its extensive exploration in air pollution monitoring. The PUF-based passive air sampling has been deployed by research groups throughout the world (Lee *et al.,* 2007; Klanova *et al.,* 2006; Pozo *et al.,* 2006; Harner *et al.,* 2004; Jaward *et al.,* 2004). Work done by Pozo *et al.* (2011) used PUF to sample various pesticides and

polychlorinated biphenyls (PCBs) in India. Harner *et al.* (2006a, b, 2004) applied it in their study to sample various analytes in different environments- remote areas, background/ rural areas, urban sites and the artic. Klanova *et al.* (2009, 2008, 2006) used passive air samplers for different air pollution studies, for polycyclic aromatic hydrocarbons in Czech Republic, for different organochlorine chemicals and to study spatial and seasonal trends across various countries.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter details the sampling area and sampling methodology used in the study. It highlights the prevailing conditions in the laboratory during the analyses of persistent organic pollutants (POPs) and heavy metals. Additionally in this chapter a method modification, where passive air sampling dome chambers were locally fabricated and assembled in accordance with Kohoutek *et al*. (2006) has been described. The preparation of polyurethane foams (PUFs) used as sampling adsorption matrix or filters in this work are also detailed. Finally in this chapter is outlined the various statistical tools applied to the results obtained.

3.2 Study area

The study samples were taken from Abetifi in the Eastern region of Ghana, Abetifi is located on latitude 000.45^{o} W and longitude 6.41^{o} N. It is a semi-urban agrarian setting with an altitude of 594.7m above sea level. It is one of the high altitude points in Ghana. Abetifi is also a forest area.

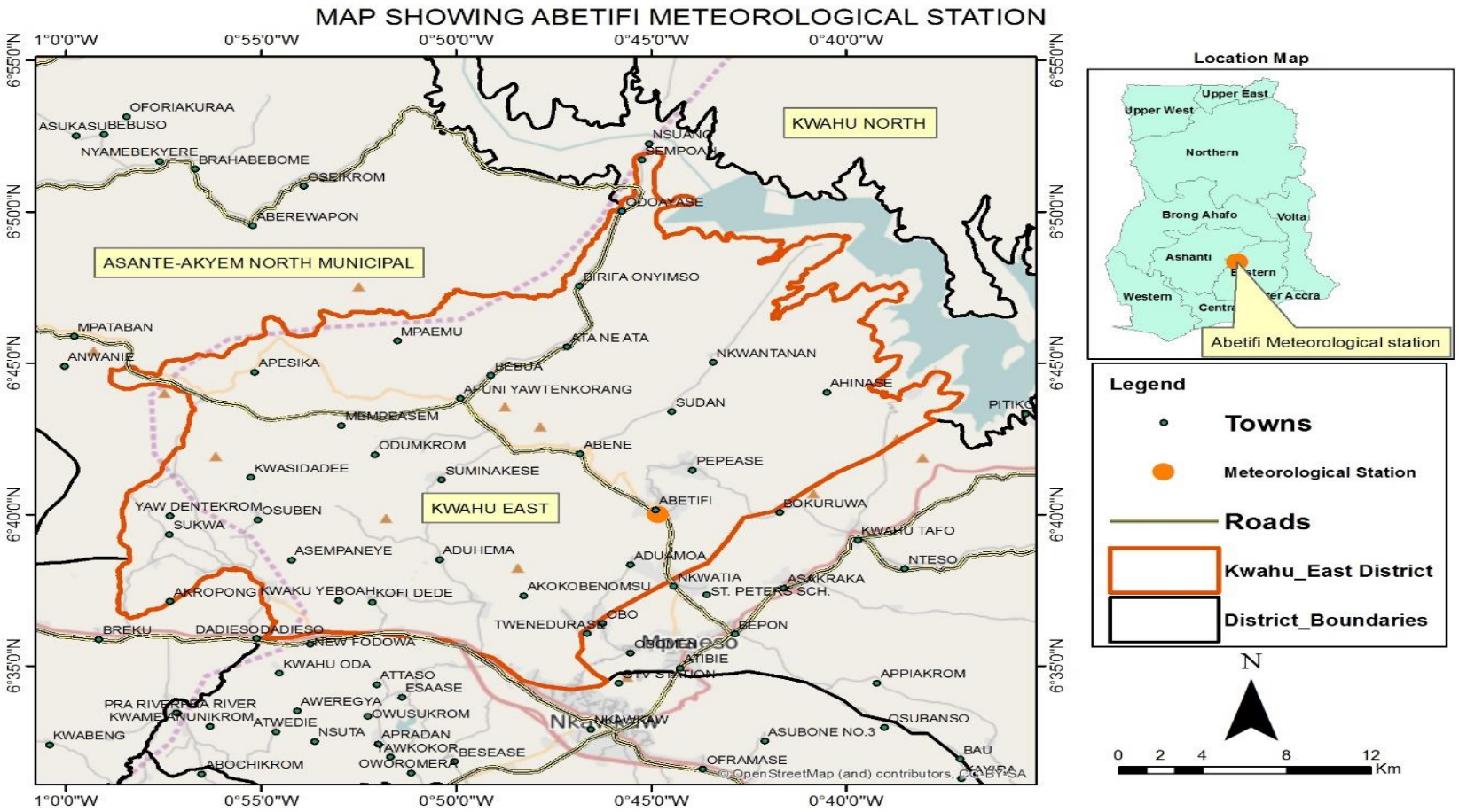


Figure 3-1: Map of meteorological station/synoptic stations in the Eastern Region where sampling was done.

3.3 Sampling technique

3.3.1 Passive air sampling technique

In this study, polyurethane foam-disk (PUF-disk) was used for sample collection. The sampling protocol employed in this study is according to Kohoutek *et al*. (2006). The PUF disk is a type of air filter, an adsorbing medium with a high retention capacity for the target analytes (Kohoutek *et al*., 2006). The PUF-disks used in this study is a low density PUF with the following specifications: a 15 cm diameter with a thickness of 1.0 cm and a density of 0.020 g/cm^3 from Ashfoam Ghana-Limited alongside the one used by Klanova *et al*., 2006. This is an N 3038 type, 15 cm diameter, 1.5 cm thickness and density of 0.030 g/cm^3 from the Gumotex Breclav in Czech Republic. The PUF disks were confined in stainless steel domed chambers, (locally-fabricated) designed to protect the disks from coarse particle deposition, precipitation and sunlight (Kohoutek *et al*., 2006). Based on work done by Shoeib and harner (2002), the sampling rate was estimated to be between 3 – 4 m^3/day. This rate was also used by Klanova *et al.* (2006) in work done in Africa including Ghana. This average rate of 3.5 m^3/day, roughly corresponds to 100 m^3 of the air sampled during four weeks of deployment of the PUF in the passive sampling dome chamber.

3.3.2 Local fabrication and assembling of sampling dome chambers

As part of the sampling method, passive air sampler (PAS) was fabricated in Ghana (using tools sold on the Ghanaian market) to collect/sample the atmospheric pollutants under study. The choice of using locally acquired tools was based on availability and accessibility for use in a developing-country setting/situation. The following were obtained and fabricated into a passive air sampling dome chamber.

1. Two sizes (big and small) of stainless steel bowls - Big bowl had the dimensions of the mouth being 27 and 24.6 cm for outer rim (or wider mouth) and inner diameters (wide mouth) respectively and the small bowl had 21.7 and 20.2 cm for outer and inner diameter respectively.
2. metal screws (9 mm in diameter)
3. rough metal rods (9 mm diameter, 16cm long)
4. pad (washer- 11mm in diameter)
5. long metal pipe (11mm in diameter, 9cm in length)
6. short metal pipe (11mm in diameter, 6.7 cm in length)
7. thin metals for hook and
8. a very short metal pipe used as metal insert in the PUF. This holds the PUF onto the rough metal rod.

In the fabrication, one small hole (11mm diameter) is perforated at the bottom of the big bowl each and five of such perforations are done for the small bowl each. The perforation in the middle of the big bowl is for fixing metal rods on which the two bowls are fixed (hinged). The four other perforations (aside the middle one) under the small bowl is to allow for the inflow of air into the sampler. The pads (washers) and nuts were used to fix and fasten the bowls together well. A complete passive air sampler set included one big & one small stainless steel bowl, five metal screws, one rough metal rod, four washers, one long & one short metal pipe and one hook. Figures 3-1a,b depict the fabricated dome chambers and its accessories, ready for assembling.

Figure 3-1a: A set of accessories for assembling one passive sampling dome chamber complete

Figure 3-1b: Accessories for assembling a passive sampling dome chamber

Figure 3-1c: Assembled fabricated sampling dome chamber

3.4.1 Assembling, mounting and removing of passive air sampler

Assembling of passive air sampler (PAS) was according to Kohoutek *et al*. (2006). A set of big and small stainless steel bowls, three metal screws and two safety nuts all 9 mm in diameter. The metal srews and safety nuts are sometimes used interchangeably since there is no difference between them. Both are metal screws. The bigger bowl used as the upper bowl is turned upside down when assembling, this is to protect the filter (PUF) from rain and solar radiation and also stabilize a stream of air around the filter. It also included one rough stainless steel rod which is 9 mm diameter and 16cm long, one long and short distance tubes with 9 cm and 6.7 cm length respectively (both 11 mm in diameter) and four pads/washers (11 mm in diameter). In addition were a thin metal for hook and a very short metal pipe used as metal insert in the PUF. This holds the PUF onto the rough metal rod. The pads (washer) and safety nuts are used to fix and fasten the bowls together well. Figure 3-1c shows the assembled passive air samplers.

1. The stainless steel rod was initially inserted and fixed to the big bowl with safety nuts and pad. A metal srew is placed onto the steel rod and used to fasten the upper bowl, preventing it from shifting. The long distance tube was inserted on the stainless steel rod followed by another metal srew/ nut to fasten and hold the tube.

2. A fresh PUF filter (made ready for sampling) with the metal insert (which holds the PUF onto the metal holder) was then placed onto a pad on the stainless steel rod and another pad and safety nut added and fastened well.

3. The short distance tube was then inserted onto the rod and a pad added. This was followed by inserting the small bowl and another pad including two safety nuts to fix and fasten the small bowl well.

Prior to replacing an already exposed PUF with a new one, the following steps are followed:

1. The whole sampling set was first detached from the hinge followed by the removal of the safety hook, safety nut and pad starting from the top.

2. The small bowl was carefully removed without contacting the PUF followed by the pad and safety nut fixing the distance tubes.

3. Cautiously the short distance tube and the pad next to the PUF were also removed, making sure there is no contact with the PUF.

Then with a fresh hand gloves on, the exposed PUF was gently removed including the stainless steel inserts placed in the centre and were wrapped in a pre-treated double-layered aluminium foil. The foil was labelled appropriately, placed into zip-lock polyethylene bags and placed immediately on ice cubes in a thermos insulated flask for onward transportation to the laboratory, where they were kept in a freezer at -18^{o}C until analysis.

3.4 Sample collection

Six passive air samplers each containing a polyurethane foam-disk (PUF-disk) were deployed at the same time at the sampling site and labelled under the following groups: A, B, C, D, E and F respectively. The PUF contained in sampler A was exposed for the analyses of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDTs), hexachlorocyclohexane (HCHs) and hexachlorobenzene (HCBs). That of sampler B was for the analyses of DRINS (aldrin, dieldrin, endrin) and sampler C for dioxins, furans, dioxin-like PCBs and polybrominated diphenyl ethers (PBDEs).

Sampler D was for the analyses of perfluorinated compound such as perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs). Sampler E for hexabromocyclododecane (HBCD) and polybrominated biphenyls (PBB) and sampler F for polycyclic aromatic hydrocarbons (PAHs). Sampling spanned two years; 2010 to 2011 with sampling duration of every 84 days for all other analytes. PAHs however was sample every 28 days in year one to help in method validation. The passive air samplers were hanged vertically, about 1.5-2.0 m above ground.

3.5 Materials and reagents

The reagents used in the analyses were as follows: Dichloromethane, n-hexane, cyclohexane, diethyl ether, toluene, acetone and acetonitrile, all of high performance liquid chromatographic (HPLC) grade; silica gel, florisil, hydrochloric acid and sodium sulphate, all from Sigma Aldrich, Germany.

The individual reference standards used for the quantification and identification of the organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), PCDDs (dioxins) and PCDFs (furans) were obtained from Cambridge Isotope Laboratories Incorporated, USA.

The individual reference standards for the organochlorine pesticides included alpha-hexachlorocyclohexane (α-HCH), beta-hexachlorocyclohexane (β-HCH), gamma-hexachlorocyclohexane (γ-HCH) and delta-hexachlorocyclohexane (δ-HCH). It also included 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene (p,p´-DDE), 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (p,p-DDD), 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane

(p,p-DDT), o,p-DDE, o,p- DDD, o,p-DDE, hexachlorobenzene (HCB), and pentachlorobenzene (PeCB).

Those for the PCB standards included PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138 and PCB 180 and that for dioxin and furan standards including the dioxin-like PCBs were isotopically labelled ^{13}C PCDDs/Fs (according to EN 1948), ^{13}C dl-PCBs (77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167 and 189) and for PBDEs, the standards included ^{13}C BDEs (28, 47, 66, 100, 99, 85, 154, 153, 183, 209), all of which were the standards used to spiked the samples. All standards were of 98.0 % to 99.5 % purity. The standard reference material (SRM) used in this work was urban dust 1649a obtained from the National Institute of Standards and Technology (NIST), USA.

3.6 Local PUF preparation and method validation

In this session, a method (Kohoutek *et al*., 2006) was modified where there was the local laboratory treatment (preparation) of polyurethane foams (PUFs) for use as sampling adsorption matrix or filters to be fixed in passive air sampling dome chambers which were also locally fabricated in Ghana.

3.6.1 Preparation of polyurethane foams locally for sampling

Yards of low density polyurethane foam (PUFs), thickness of 1 cm were obtained from Ashfoam Ghana-Limited (Figure 3-2). The foam is cut into circular shapes with the specification as 15 cm in diameter (density of 0.02 g/cm^3) and were treated according to Kohoutek *et al*. (2006). The PUFs were Soxhlet extracted for eight (8) hours in each solvent: first with acetone and then with dichloromethane (Klanova *et al.*, 2006). This helps to minimize possible contaminations. The PUFs were wrapped in a double-

layered aluminium foil and dried in an oven at 100^{o}C for 6 hours. They are then removed and stored in a cool dry place ready for use.

Figure 3-2: Sample polyurethane foam (PUFs) from factory

3.6.2 Polycyclic aromatic hydrocarbon sampling for testing the effectiveness and suitability of local PUF.

Two passive air samplers (PAS) fabricated in Ghana were deployed at Abetifi for air sampling. Each was fixed with a different specification of polyurethane foam. One was fixed with an N 3038 type PUF (density - 0.030 g/cm^3, 15 cm diameter, 1.5 cm thickness) acquired from the Gumotex Breclav in Czech Republic, usually used by MONET. The other was fixed with the locally prepared one with specification 0.020 g/cm^3, 15 cm diameter and 1.0 cm thickness. Both samplers were mounted as is illustrated in section 3.4. The deployment and removal of the PUFs were done every 28 days from January 2010 to January 2011. The PUFs were exposed for PAH analysis to access the effectiveness and suitability of the locally prepared PUFs used. The exposed PUFs were collected, transported on dry ice, stored in freezer. Samples were later taken through sample preparation processes which are described in detail in section 3.7.1 and made ready for instrumental analysis.

An urban dust 1649a, a standard reference material for polycyclic aromatic hydrocarbons in air sample was used to validate the method. This was taken through same process (section 3.7.1) as the sample and made ready for analysis as the exposed air filters (PUFs). The sample was run in triplicates. The result shows of the standard reference material is tabulated in Appendix viiib.

3.7 Sample preparation and analysis

All exposed polyurethane foams (PUFs) that were stored in the freezer were removed and allowed to assume room temperature. The PUFs were cut into small pieces with a clean pair of scissors onto a pre-treated aluminium foil and transferred straight into the Soxhlet apparatus where they extracted. The extraction and clean up protocols used in this work were according to EN 1948 and UNEP extraction protocols of POPs. The various groups went through different extraction, clean-up and fractionation methods. The various groups of analytes had different instrumental analyses. The basic process flow is in Figure 3-3.

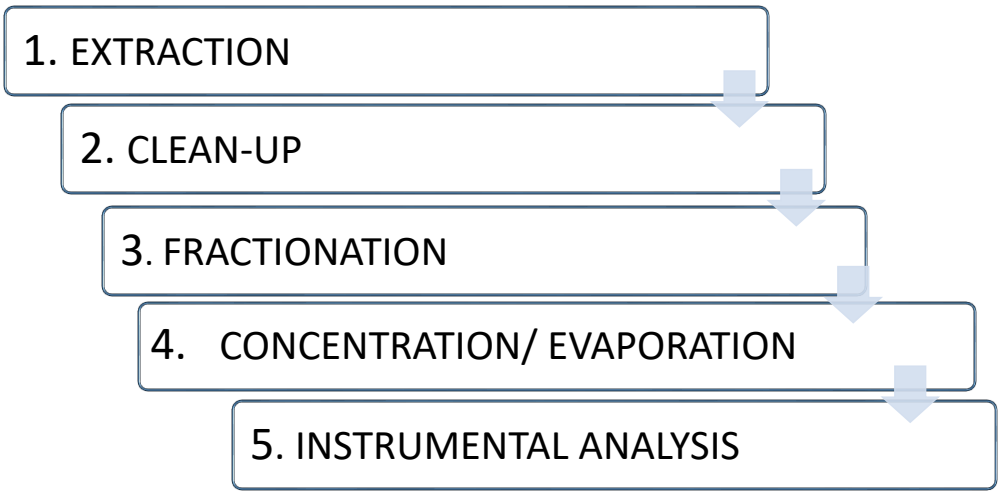


Figure 3-3: Flow chart for basic sample preparation and analytical procedure

3.7.1 Analysis of polycyclic aromatic hydrocarbons

3.7.1.1 Extraction- PAHs

This first group of filters analysed were those sampled for polycyclic aromatic hydrocarbons (PAHs). These were used to test for the efficiency and suitability of locally prepared polyurethane foam (PUFs) for sampling of organic pollutants. A total of 26 exposed PUFs, thirteen from each group of PUF specification [Ghana (0.020 g/cm^3, 15 cm diameter, 1.0 cm thickness) and MONET (0.030 g/cm^3, 15 cm diameter, 1.5 cm thickness)] were processed and analysed at RECETOX laboratory, Czech Republic.

The extraction done using a Buchi System B-811 automatic extractor. Extraction was in hot mode (40 °C) using 100 mL dichloromethane (DCM) for 4 hours (Klanova *et al.*, 2009). Field blanks were also analysed together with the samples. Prior to extraction, 10 µL of d_8-naphthalene, d_{10}-phenanthrene and d_{12}-perylene were used as surrogate standards to spike the samples and these were used to determine the method recoveries. Samples were then made ready for clean up.

3.7.1.2 Clean up–PAH

Cleaned up achieved on a silica gel column. A 0.5 g anhydrous sodium sulfate (Na_2SO_4) was added to 1.0 g of activated silica gel (60 - 100 mm mesh) on an 8 mL column, plugged with glass wool. The column was then filled with 5 mL DCM-n-hexane for conditioning. The stopcock on the set up was opened to allow the DCM-n-hexane run out until DCM-n-hexane just reached the top of the sodium sulfate into a receiving vessel whilst taping gently the top of the column till the silica gel settled well in the column. The air extract was then transferred onto the silica column with a disposable Pasteur pipette from an evaporating flask. Each evaporating flask was

immediately rinsed twice with 1 mL portions of DCM-n-hexane and added to the column by the use of the Pasteur pipette. The analytes were then eluted from column using 40 mL of DCM-*n*-hexane mixture (1:1 volume) and collected in a Turbo Vap II bottle. The eluate was concentrated using Turbo Vap II concentrator unit. This unit comprises a heated bath where the tubes are placed, and nozzles blowing nitrogen. This apparatus allows for the concentration of six (6) samples at a time. The set up is equipped with a sensor that checks the solvent level after concentration (~ 0.7 mL) and stops the nitrogen flow so that the samples are not evaporated to complete dryness. The sample was then transferred into a 20 mL vial and further reduced in volume to approximately 200 µL and made ready for instrumentation.

3.7.1.3 Instrumentation-PAHs

Instrumental analysis was done using GC-MS instrument (HP 6890-HP 5973) supplied with a J&W Scientific fused silica column DB-5MS (30 m x 0.25 mm id., 0.25 µm film thickness). Limit of quantification, 0.02 ng/sample PUF (~ 0.003 ng/g). Terphenyl was used as internal standard. A volume of 10 µL was injected. The oven temperature programme was as follows: Initial temperature was set at 80 ^{o}C for 5 min and ramped at 15 ^{o}C/min to 180 ^{o}C followed by a 5^{o} C/min ramping to 310 ^{o}C and held for 5 minutes. Helium was used as the carrier gas with a flow of 1.5mL/min. MS with an electron impact ionisation (EI) was operated at 70 eV in selected ion monitoring mode (SIM). The transfer line temperature was held at 280 ^{o}C, ion source temperature at 230 ^{o}C and quadrupole temperature at 150 ^{o}C.

3.7.2 Analysis of Cyclodien Pesticides /DRINS

3.7.2.1 Extraction - DRINS

Eight exposed polyurethane foam (PUFs), each representing one quarter of the year of sampling period (Jan - Mar, April - Jun, July - Sept, Oct - Dec. for 2010 and 2011). This set of PUFs were for group B analytes i.e. aldrin, dieldrin, endrin. The PUFs were each treated in a Soxhlet System, a Büchi (B-811) automatic extractor in hot extraction mode (40 °C) for 4 hours using 100 mL dichloromethane (Chu *et al*., 2003). One laboratory blank (solvent without sample) and one reference material each was analyzed alongside the PUFs. The air filters (PUFs) were spiked with the isotopically labeled standards. The extracts from the PUFs were concentrated to 5 mL under a gentle nitrogen stream at ambient temperature and made ready for cleaned up.

3.7.2.2 Clean-up - DRINS

The concentrated extracts (5 mL) were cleaned-up on a florisil column. A mass of 0.5 g anhydrous Na_2SO_4 was added to 1.8 g florisil (60 – 200 micron mesh size) on a 72 mL column plugged with glass wool and then filled with 10 mL of 20% of DCM in hexane for conditioning. The analytes were eluted using 20 mL of 20% of DCM/n-hexane first and followed by 50 mL DCM. The sample volume was reduced at ambient temperature under a gentle nitrogen stream and transferred into a 1 mL Gas Chromatograph (GC) vial in iso-octane, ready for instrumental analysis.

3.7.3.3 Instrumental analysis – DRINS

The instrumentation aspect of the analysis was achieved using a GC-MS/MS (Quattro Micro GC – Watters) supplied with a J&W Scientific fused silica column DB-5 MS (30 m x 0.25 mm id., 0.25 µm film thickness). The inlet temperature was 250 °C with a splitless mode injection of 1 µL. Helium was used as carrier gas and the purge flow

was 30 mL/min at 0.75 min. Oven temperature program was set initially to 70 °C for 1 min, ramped at 50 °C/min to 150 °C (0 min) and ramped again at 6 °C/min to 200 °C (0 min). This was followed by a final ramping at 16 °C/min to 280 °C and held for 5.5 minutes. The mass spectrometer is operated is operate in positive electron impact (EI+) MS/MS mode at 70 eV. The limit of quantification for cyclodiene pesticides was 0.05 ng per sample (~ 0.0071 ng/g).

3.7.3 Analysis of PCBs and organochlorine pesticides

3.7.3.1 Extraction- PCBs/OCPs

For the polychlorinated biphenyls and organochlorine pesticides (for group A analytes i.e. PCBs, DDTs, HCHs and HCBs), the PUFs were each treated in a Soxhlet System, a Büchi (B-811) automatic extractor in hot extraction mode (40 °C) for 4 hr using 100 mL dichloromethane (Chu *et al*., 2003). A laboratory blank and a reference material each was analyzed along with the PUF samples. The extracts were concentrated under a gentle nitrogen stream and cleaned up on a sulphuric acid modified silica gel column.

3.7.3.2 Clean-up - PCBs/OCPs

The sample extracts were cleaned up using the following protocol. A mass of 0.5 g anhydrous sodium sulphate (Na_2SO_4) was added to 1.8 g silica gel (60 – 200 micron mesh size) on a 72 mL column plugged with glass wool. This was acidified with 30% w/w sulphuric acid and conditioned with 10 mL n-hexane. Then 14 mL of n-hexane in portions of 1:1:1:11 was added stepwise to the extract and transferred onto the column with a disposable Pasteur pipette.

3.7.3.3 Fractionation - PCBs/OCPs

Fractionation of PCB and OCP analytes in the air filter samples (PUFs) was achieved by the following procedure. A 5 mL volume of the PUF eluate from the silica column (step above) is taken for the analysis of PCBs. After this, 10 mL of new eluent (hexane-diethyl ether mixture, 85:15 v/v) was added to the evaporating flask containing the remaining PUF eluate. This was swirled and transferred onto the same silica column by the help of disposable Pasteur pipette to wash all the OCPs (DDTs, HCHs and HCBs) off the column into another evaporating flask. This second fraction is the organochlorine pesticides portion of the PUF air extract.

3.7.3.4 Instrumentation - PCBs/OCPs

The two fractions (PCBs & OCPs) were then evaporated to near dryness under a gentle nitrogen stream at ambient temperature. Finally the concentrates were each dissolved in 1 mL iso-octane into a GC vial and made ready for analysis. A Gas Chromatograph with an electron capture detector (GC-ECD) (HP 5890) supplied with a quadrex fused silica column 5% phenyl methyl polysiloxane (UNEP, 2009) was used. A volume of 10 µL was injected. The oven temperature programme was as follows: Initial temperature was set at 90 ^{o}C for 3 min and ramped at 30 ^{o}C/min to 200 ^{o}C for 15 min and then to 265 ^{o}C at a rate of 5^{o} C/min for 5min then to 275 ^{o}C at the rate of 3 ^{o}C/min and allowed to stay for 15 min giving a total run time of 58 min. The injector setting is a pulsed spitless mode with a temperature of 250 ^{o}C at a pressure of 1.441 bar. Pulsed pressure was 4.5 bar, pulsed time 1.5 min, purge flow of 55.4 mL/min with a purge time of 1.4 min. The detector temperature was 300 °C in “constant makeup flow” mode (30 mL/min of Nitrogen gas).

The recovery results of the reference material for chlorinated compounds varied from 88 to 103 % for all samples for PCBs and from 75 to 98 % for the organochlorine pesticides (OCPs). The limit of quantification (LOQ) for PCBs was 0.01 ng per sample (~ 0.001 ng/g) and that of the organochlorine pesticides was 0.02 ng per sample (~ 0.003 ng/g).

3.7.4 Analysis of PCDD/F, Dioxin-like PCB and PBDE

3.7.4.1 Extraction - PCDDs/Fs, dioxin-like PCBs and PBDEs

All exposed PUFs (for group C analytes i.e. PCDDs, PCDFs, dl-PCBs & PBDEs) were treated according to Kukucka *et al.* (2010) with slight modification. All samples were extracted with 100 mL toluene in a Soxhlet extractor, 60 minutes warm Soxhlet (100 °C) followed by 30 minutes of solvent rinsing with toluene in a B-811 extraction unit (Büchi, Switzerland). The samples were spiked with 10 µL of ^{13}C PCDDs/Fs (according to EN, 1948), ^{13}C dl-PCBs (77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167 and 189) and ^{13}C BDEs (28, 47, 66, 100, 99, 85, 154, 153, 183, 209).

3.7.4.2 Clean-up - PCDDs/Fs, Dioxin-like PCBs & PBDEs

The PUFs extracts were concentrated to 5 mL volume under a gentle nitrogen stream at ambient temperature. Extracts were cleaned-up on a 30% w/w sulphuric acid modified silica gel (addition of 2 mL H_2SO_4 to silica gel column). Extracts were then eluted with 40 mL of dichloromethane/n-hexane mixture (1:1 v/v) into an evaporating flask.

3.7.4.3 Fractionation - PCDDs/Fs, Dioxin-like PCBs & PBDEs

The fractionation of the various analytes (PCDDs, PCDFs, dl-PCBs & PBDEs) was into two major fractions. This was achieved in a micro column of 6 mm internal diameter, containing from bottom to top: 50 mg silica gel, 70 mg charcoal/silica gel (1:40) and 50 mg of silica gel.

The PBDE and mono-ortho dl-PCB fractions were collected first. In eluting the PBDE and the mono-ortho dl-PCB fractions, the packed column was conditioned (prewashed) with 5 mL of toluene and followed by 5 mL of DCM/cyclohexane mixture (30%). The PUF extract was then applied and eluted with 9 mL DCM/cyclohexane mixture (30%).

The dioxins, furans and the dioxin-like PCBs (non-ortho dl-PCBs) fractions were labelled as fraction 2 and for this, a volume of 40 mL toluene was used as the eluent. Each fraction was concentrated using stream of nitrogen in a TurboVap II (Caliper Life Sciences, USA) concentrator unit and transferred into an insert in a vial. The syringe standards (^{13}C PCDDs, ^{13}C PCBs 70, 111, 138 and 170, ^{13}C BDEs 77 and 138) were added to all samples making a final volume of 50 µL in toluene, ready for instrumentation.

3.7.4.4 Instrumentation: PCDDs/Fs, Dioxin-like PCBs & PBDEs

A High Resolution Gas Chromatograph coupled with a High Resolution Mass Spectrometry (HRGC/HRMS) was used for this analysis. This was done by means of an Agilent Technologies (7890 J&W, USA) gas chromatograph system on a DB5-MS column (60 m long × 0.25 mm i.d. × 0.25 µm film thickness), column coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ (Electron ionisation) mode at the resolution of >10 000. The polybrominated biphenyl

ethers (BDEs) were analysed for on the same system using 15 m x 0.25 mm x 0.10 μm DB5 column (Agilent J&W, USA). For BDE 209, the MS resolution was set to >5000.

3.7.4.5 G.C. temperature programming: PCDDs/Fs & Dioxin-like PCBs

The GC operation conditions for PCDDs/Fs were as follows: Inlet temperature was 280 ^{o}C with a splitless mode injection of 1uL. Helium was used as carrier gas at a constant flow rate of 1.9 mL/min. The oven temperature was set initially at 135 °C (1 min hold), increased to 220 °C at 15 °C/min. At 220 °C, temperature increased at a rate of 1 ^{o}C/min to 240 ^{o}C and then to 260 ^{o}C at a rate of 3.5 ^{o}C/min and finally to 310 ^{o}C at 6 ^{o}C/min (6.5 min hold). Total run time was 47.21 min. The transfer line temperature was held at 280 ^{o}C for both the PCDDs/PCDFs and the dl-PCBs.

The GC operation conditions for dl-PCBs were also as follows: Inlet temperature was 280 ^{o}C with a splitless mode injection of 1μL. Helium was used as carrier gas at a constant flow rate of 1.7 mL/min. The oven temperature was set initially at 130 °C (1 min hold), increased to 190 °C at 40 °C/min, followed by an increased at a rate of 1.5 ^{o}C/min to 240 ^{o}C and finally to 310 ^{o}C at 6 ^{o}C/min with a 6.5 min hold giving a total run time was 49.58 min.

In this study, the recoveries of the isotopically labeled standards for the dioxins and furans were 55 - 90% while that for the dl-PCBs, ranged between 60 and 90% and the brominated flame retardants (BDEs) had recoveries ranging between 60 and 110%. The percentate recoveries were calculated from the concentration recorded by instrument per the original concentration before the spiking. The limit of quantification for the dioxins, furans and the dl-PCBs were all 0.15 pg per sample (~ 0.021 pg/g)

while the polybrominated flame retardants (PBDEs) gave the lowest value of 0.01 pg per sample (~ 0.0014 pg/g).

3.7.5 Analysis HBCD and PBB

3.7.5.1 Extraction – HBCDs and PBBs

All samples for hexabromocyclododecane (HBCD) and polybrominated biphenyl (PBB) analyses were extracted using dichloromethane (100 mL) in a Büchi System B-811 automatic extractor according to protocol by MONET (2013) and Miyake *et al.* (2009) method with slight modification. Samples were extracted in a hot Soxhlet mode (40 °C) for 60 minutes. The sample extract volumes were reduced to 5 mL after extraction under a gentle nitrogen stream at ambient temperature. Sample was then made ready for clean-up process.

3.7.5.2 Clean-up and fractionation- HBCD /PBB

The concentrated extracts were cleaned-up on a sulphuric acid modified silica gel (30% w/w) and eluted with 40 mL dichloromethane/n-hexane mixture (1:1). Fractionation was achieved by taking 5 mL volume of eluate from the silica column (from the clean-up stage) for the analysis of HBCDs. An isotopically labelled γ-HBCD ($^{13}C_{12}H_{18}Br_6$) was then added into the sample before HBCD analysis was done. A volume of 20 mL of new eluent (n-hexane) was added to the evaporating flask containing the remaining PUF eluate. This fraction of the eluate is for the analysis of PBBs. The samples were all concentrated under a gentle stream of nitrogen and picked in acetone: acetonitrile solvent mixture (50 μL) into a GC vial, ready for instrumental analysis.

3.7.5.3 Instrumentation- HBCD

For the analysis of the hexabromocyclododecanes, high performance liquid chromatography coupled with a double mass Spectrometry (HPLC-MS/MS) instrumental analysis was performed. This was on an Agilent 1100 series (Agilent Technologies, Waldbronn, Germany) equipped with a Phenomenex LUNA C-18 endcapped (3 μm) column (100 x 2 mm), with a pre-column Phenomenex Secure Guard C18 (Phenomenex, Torrance, CA, USA) and a mass spectrometer, AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) which used electrospray ionization. The ions were detected in the negative mode. The limit of quantification for HBCD was 0.01 ng per sample (~ 0.0014 ng/g).

3.7.5.4 Instrumentation- PBB

A High Resolution Gas Chromatograph coupled with a Mass Spectrometry (HRGC/MS) was used to analyse the PBBs. This was done by means of an Agilent Technologies (7890 J&W, USA) gas chromatograph system on a DB5- MS column (60 m long × 0.25 mm i.d. × 0.25 μm film thickness) column coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The MS was operated in EI+ (Electron ionisation) mode at the resolution of 10 000. Detection mode was SIM. The GC operation conditions for PBBs were as follows: Inlet temperature was 270 ^{o}C with a splitless mode injection of 1μL. Helium was used as carrier gas at a constant flow rate of 1.2 mL/min. The oven temperature was set initially at 100 °C (4 min hold), increased to 160 °C at 30 °C/min, followed by an increased at a rate of 30 ^{o}C/min to 160 ^{o}C and finally to 315 ^{o}C at 10 ^{o}C/min with a 2 min hold giving a total run time was 25 min. The limit of quantification for PBB was 0.1 ng per sample (~ 0.014 ng/g).

3.7.6 Analysis of perfluorinated compounds

3.7.6.1 Extraction- PFOA/PFOS

For the analyses of the perfluorinated compunds, extraction protocol protocol by MONET (2013) was followed. The samples were extracted with 100 mL methanol with the addition of ammonium acetate (5mM) in a Soxhlet extractor (60 minutes warm Soxhlet followed by 30 minutes of solvent rinsing) in a B-811 extraction unit (Büchi, Switzerland) after being spiked with the isotopically labelled standards (^{13}C MeFOSA and ^{13}C MeFOSE). Extracts were then made ready for clean-up.

3.7.6.2 Clean-up -PFOA/PFOS

The samples were cleaned up by first reducing the volume to 5 mL under a gentle stream of nitrogen. The concentrated extracts were cleaned-up using a syringe filter with a nylon membrane (13 mm diameter and 0.45 μm pore size specification). The eluate filtrate was concentrated to 50 μL using stream of nitrogen in a TurboVap II (Caliper Life Sciences, USA) concentrator unit and transferred into a mini vial. The syringe standards (^{13}C PFOA, ^{13}C PFOS) (Wellington Laboratoriess) were added to all samples and the final volume was 500 μL, made ready for analysis.

3.7.6.3 Instrumentation - PFOA/PFOS

An HPLC-MS/MS instrumental analysis was performed using an 1100 HPLC (Agilent, USA) equipped with a SYNERGI 4u Vision RP 80A 50 mm x 2 mm column (Phenomenex, USA) coupled to an QTRAP 5500 (ABSciex, CA, USA). The MS was operated in negative ion spray ionization (EI-) mode using two MRM transition for each compound. The recovery calculated for the perfluorinated compounds (PFOS and PFOA) was in the range of 100 and 105% and a limit of quantification of 0.002 ng per sample (~ 0.0003 ng/g).

3.8 Quality assurance and quality control

Laboratory quality control procedures were followed during the analysis of each set of samples. These measures included the use of HPLC grade reagents in the preparation of solutions and in the extraction process. Solvent blanks which were made up of only solvents used to dilute the standards were run to ascertain the signals produced by the solvent or any impurities. Laboratory blanks were also prepared for each set of samples during the sample extraction and analysis. The concentrations found were all below the quantification limits for all the compounds. In ensuring quality results, a recovery process for each set of analyte was undertaken where spiking of the air filters with appropriate surrogate standards was done prior to extraction.

A standard reference material, urban dust 1649a from NIST was used to validate the method for the analysis of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (to represent all the organochlorine chemicals). The urban dust was taken through same process as the sample described above and made ready for analysis. Appendix viii a and b show the results of the standard reference material for PCBs and PAHs.

3.9 Feasibility studies of using polyurethane foams to sample heavy metal analysis

As part of this study, the feasibility of using polyurethane foams (PUFs) to sample and analyse heavy metals was tested. Here also, two samplers were mounted as is described in section 3.4.1 above. However, the PUF filters were changed every 28-days for six months in the year 2011 at Abetifi according to the protocol used by

Kohoutek *et al*. (2006) method. Analysis was done at the Nuclear Chemistry and Environmental Research Centre, Ghana Atomic Energy Commisssion. Polyurethane foam used for this part of the work has was obtained with specifications as described in section 3.6.1 and its preparation before deployment is as accordance as detailed in same section (section 3.6.1).

3.9.1 Preparation of exposed polyurethane foams for heavy metal analysis

3.9.1.1 Sample treatment for heavy metal analyses

3.9.1.1.1 Digestion of air filters (PUFs)

The exposed filters/polyurethane foams were cut into pieces to allow for homogeneity using a pair of clean scissors. A 0.5 g weight of each exposed (piece of) foam was weighed into a thoroughly clean glass beaker. A volume of 4.0 mL of 65% Conc. HNO_3 was added to the weighed samples in a fume chamber followed by 1.0 mL of 98% Conc. H_2SO_4 and allowed to homogenize. The beakers were placed on a hot plate at a temperature of 100 ^oC for 4 hours to allow for thorough digestion. A volume of 6 mL of same 65% Conc. HNO_3 was poured into an empty glass beaker and used as a reagent blank for Atomic Absorption Spectrometer (AAS) (VARIAN AA 240 FS) reading. A blank sample was also prepared with an unexposed filter treated in the same way as the exposed filters. Each digested sample was diluted and made up to 20 mL with distilled water and made ready for AAS readings.

3.9.1.2 Quality control and method validation for metal analyses

For quality control purposes, standards solutions were run after every five runs. Sample runs were repeated and mean value recorded by the equipment. A sample

blank, which is an unexposed PUF was analysed. This was to check for the contribution of metals from the PUF before exposure/ deployment. A laboratory method blank was also prepared following the same method as the sample expcept that it was without a sample. This was to check for any contaminat contribution from the method. A quality control standard solution of various elements with known concentrations were also run and checked for recovery. The recovery was calculated by finding the percentage of the measured or recorded concentration per the original or the expected concentration of metal in standard solution. The percentage recoveries were in the range as indicated in Table 3-1.

Table 3-1: Recovery range for AAS quality control standard solution (%)

Element	Concentration before anlysis (mg/L)	Concentration after anlysis 1 (mg/L)	Concentration after anlysis 2 (mg/L)	% Recovery range
Ni	5.00	5.001	4.629	92.59 - 100.02
Cd	2.00	2.002	2.195	100.1 – 109.75
Mn	2.00	1.997	1.932	96.60 - 99.85
Pb	5.00	5.001	4.587	91.74 - 100.02
Cu	5.00	4.996	5.401	99.92 - 108.02
Cr	5.00	2.002	4.762	40.04 - 95.24

In addition, an air particulate on filter, a standard reference material; air particulate on filter- NIST 2783 was used to validate the method. This was taken through same process as the sample and made ready for analysis as a test sample. The result of the standard reference material; air particulate on filter- NIST 2783 is found in Appendix ix.

3.10 Method for exposure & risk assessment of dioxin-like chemicals

3.10.1 Toxic Equivalence Factor (TEF)/ Toxicity Equivalency (TEQ)

The concept of toxicity equivalency (TEQs) and toxic equivalence factor (TEF) systems which allows these compounds (dioxins/furans, dioxin-like PCBs) to be considered together in exposure calculations and risk assessments was applied in this study. For the assessment of exposure and risk in chemicals that exist in environmental and biological samples as complex mixtures of congeners, such as dioxin-like chemicals, the WHO established concept (TSD, 2010) was applied.

In the TEF scheme, the toxicity of tetrachloro dibenzo-p-dioxin (TCDD) is set at 1 and the toxicity of the other dioxins and furans is expressed as fraction (TEF) of the TCDD toxicity. The analytical data from a given sample can thus be converted to provide a TCDD toxic equivalency (TEQ) which is usually used for risk assessment and management purposes. In calculating for the TEQ, in the scheme, the concentration of each monitored dioxin (PCDD) and furan (PCDF) congener is multiplied by its respective TEF value assigned by WHO. All the products are then summed to give 2,3,7,8-TCDD equivalent concentration (TEQ) (TSD, 2010). The following equations were employed in the exposure calculation and risk assessment in this study.

$$\text{Total Toxicity Equivalence } (TEQ) = \sum_{n=1}^{k} (TEFn \ x \ Cn) \quad \text{.....Eqn. (1)}$$

TEF_n = toxic equivalency factor of individual congener
Cn = concentration of the individual congener in the complex mixture
k = total number of congeners

In order to be able to correlate the relative contribution of dioxin-like PCBs and dioxins to the total TEQ based toxicity, the “TEQ-ratio” is introduced.

$$TEQ\ ratio = \frac{dlPCB-TEQ}{PCDD/F-TEQ}$$ .....Eqn. (2)

Consequently, if the TEQ ratio is “1”, the TEQ contribution from dioxin-like PCBs is equal to that from dioxins. If the TEQ ratio is bigger than one, the contribution from dl-PCBs is higher than that from dioxins (EC, 2002).

3.11 Data analysis

To help identify the distributionf of air contaminant in this study, Microsoft Excel 2010 SPSS (version 21) and UNMIX were used. The statistical tools used in the work are descriptive statistics, Pearson‘s correlations and ANOVA. In the work, column graphs are used for individual concentrations and line graphs are used to describe time trends. ANOVA was used to find the difference in means of the various analytes within the same group and from the two types of PUF used. UNMIX model was used to identify polycyclic aromatic hydrocarbons pollution sources. Principal Ccomponent Aanlysis (PCA) was also used to group the various analytes to help identify their source groupings.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter describes the results obtained in a two-year atmospheric monitoring for contaminants such as persistent organic pollutants in Abetifi, Ghana. They are summarized in tables and figures subsequently. It also includes analysis of heavy metals in air using polyurethane foam (PUF). All graphs and tables presented show data analysed per quarter (84 days). January – March 2010, coded Ab-1, April – June 2010 as Ab-2, July – September 2010 as Ab-3 and October – December 2010 as Ab-4. It continues with January – March 2011 coded as Ab-5, April – June 2011 as Ab-6, July – September 2011 as Ab-7 and October – December 2011 as Ab-8. The first part of this chapter shows the validation results of using locally prepared PUF for samling polycyclic aromatic hydrocarbons as test analytes deployed every 28 days.

4.2 Concentrations of PAH for validation of method

Table 4-1 shows concentrations of the various sampling periods (28-days each) beginning January 2010 to January 2011. These are labelled ABm-1 to ABm-13 as results from MONET PUFs and ABg-1 to ABg-13 as those from Ghana PUF. The table also shows the mean concentration in ng/m^3, standard error and ANOVA at 95% confidence limit of 16 individual polycyclic aromatic hydrocarbons (PAHs) in air sampled from Abetifi. This result is grouped into low & medium weight PAHs and that of high molecular weight PAHs.

From Table 4-1, PAH concentrations for the ABms, varied between a minimum of 10.673 ng/m^3 (ABm-9) and a maximum of 25.635 ng/m^3 (ABm-1) for the low and

medium molecular weight PAHs. The high molecular weight (HMW) PAHs were in the range of 0.535 ng/m^3 (ABm-1) minimum and 1.307 ng/m^3 (ABm-7) maximum. Those from the ABg labels were between a minimum of 10.54 ng/m^3 (ABg-11) and a maximum of 25.143 ng/m^3 (ABg-6) for the low to medium molecular weight PAHs whiles the high molecular weight PAHs ranged from below the limit of quantification to 2.221 ng/m^3 (ABg-4).

Table 4-1: Mean concentration (ng/m^3) standard error and ANOVA of polycyclic aromatic hydrocarbons in air filters from Abetifi.

MONET														ANOVA @95% Cl	
PAH	Conc/ID	ABm-1	ABm-2	ABm-3	ABm-4	ABm-5	ABm-6	ABm-7	ABm-8	ABm-9	ABm-10	ABm-11	ABm-12	ABm-13	p-value	f
L/MMW	Mean/ngm-^{3}	25.635	23.831	12.058	18.554	22.971	19.511	21.041	11.982	10.673	18.119	16.799	11.748	12.192	0.836	0.605
	±Std Error	8.69	7.59	2.78	5.11	8.27	6.13	6.10	2.74	2.17	5.48	4.64	2.52	2.54		
	n	14	14	14	14	14	14	14	14	14	14	14	14	12		
HMW	Mean/ngm-^{3}	0.535	1.154	1.292	1.241	1.241	1.212	1.307	0.959	1.042	0.917	1.02	1.031	0.766	0.904	0.511
	±Std Error	0.15	0.33	0.40	0.35	0.31	0.32	0.37	0.27	0.28	0.25	0.28	0.30	0.23		
	n	10	10	14	10	10	10	10	10	10	10	10	10	10		

Ghana																
PAH	Conc/ID	ABg-1	ABg-2	ABg-3	ABg-4	ABg-5	ABg-6	ABg-7	ABg-8	ABg-9	ABg-10	ABg-11	ABg-12	ABg-13	p-value	f
L/MMW	Mean/ngm-^{3}	18.291	20.191	15.713	13.77	16.85	25.143	11.752	15.842	13.994	10.668	10.54	12.501	11.323	0.771	0.681
	±Std Error	5.23	6.19	3.54	2.16	3.984	9.83	2.82	3.52	3.17	2.20	2.16	3.41	2.46		
	n	14	14	16	14	12	12	16	12	14	12	12	14	14		
HMW	Mean/ngm-^{3}	-	0.894	1.082	2.221	1.422	0.812	1.407	0.805	1.022	1.017	0.702	-	1.023	0.878	0.574
	±Std Error	-	0.12	0.22	0.31	0.30	0.10	0.31	0.18	0.28	0.25	0.18	-	0.24		
	n		10	10	10	10	10	10	10	10	10	10		10		

4.2.1 PAH trend and correlation

4.2.1.1 Concentration and correlation of medium molecular weight PAHs

The concentration trend is compared for the medium molecular weight (MMW) PAHs. The MMW- PAHs contain basically four-rings and are those with molecular weight of 202 g/mol and formular of $C_{16}H_{10}$. They include fluoranthene (FLT) and pyrene (PYR) (Seitz *et al.*, 2012).

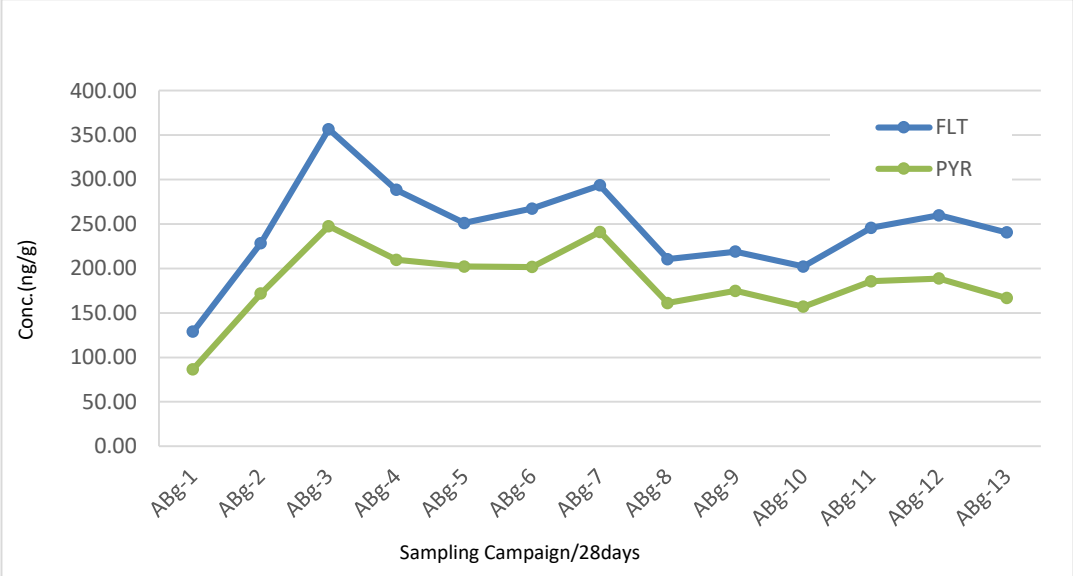


Figure 4-1a: Concentration trend of medium molecular weight PAHs in air

The concentration trend for fluoranthene and pyrene was plotted (Figure 4-1a), giving rise to a rhyming contour trend; they both rise and fall, rise again and fall though fluoranthene consistently was higher in concentration than pyrene. The correlation between the MMW PAHs gave a positive Pearson correlation of 0.961. The concentration of fluoranthene ranged from a minimum of 0.184 ng/m^3 to a maximum of 0.509 ng/m^3 and that of pyrene, from 0.124 to 0.354 ng/m^3. A possible reason for the same trend is that fluoranthene and pyrene are isomers (Seitz *et al.*, 2012) and as such their emission may be from the same sources throughout the year of sample

collection. Overton *et al.* (1981) identified high levels fluoranthene and pyrene isomers as contamination profiles of pyrogenic products of fire.

4.2.1.2 Trend and correlation of high molecular weight PAHs

Figure 4-1b shows the concentration trend for some of the high molecular weight PAHs analysed. These included benzo(a)anthracene (BaA), chrysene (CHRY) and benzo(b)fluoranthene (BbF).

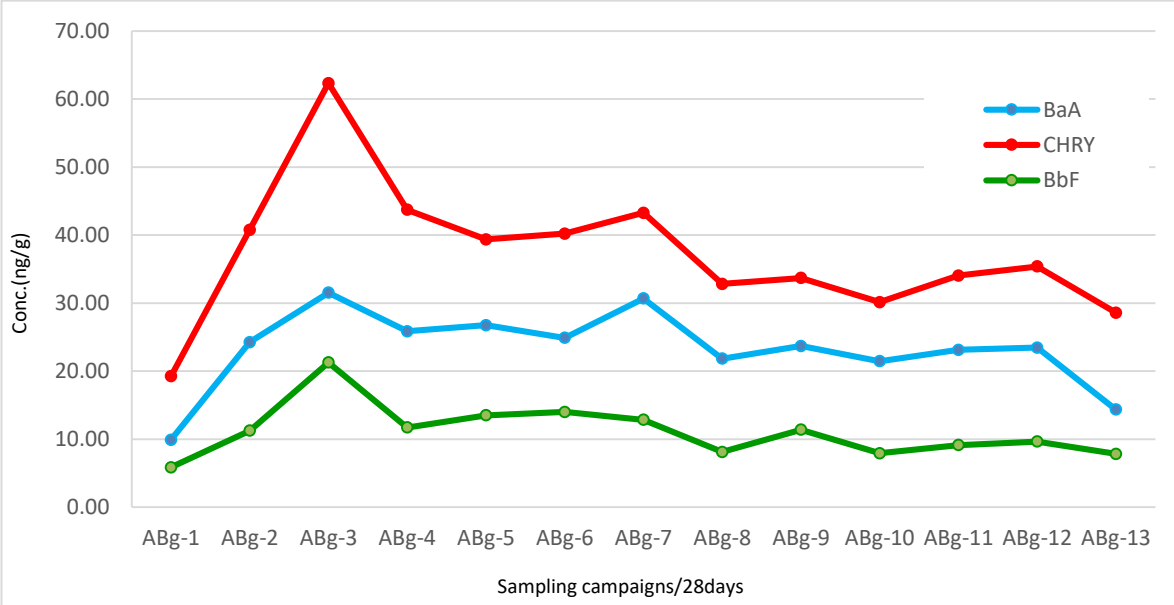


Figure 4-1b: Concentration trend of high molecular weight PAHs in air.

The trend revealed in Figure 4-1b is similar for all three HMW PAHs, throughout the sampling year, they all show some level of increase at the same time and then when there is a decrease in one, there is a marginal decrease in the others too. This kind of trend is indicative of same emission source and probably a point source though concentrations varied. The Pearson correlation between these three pairs of HMW

PAHs was 0.874 for BaA/CHRY and 0.805 for BaA/BbF, as well as 0.947 CHRY/BbF.

Benz (a)anthracene (BaA) is known as an atmospheric contaminant with a wide variety source. It is found near busy highways, in automobile exhaust, creosote, coal tar and petroleum asphalt. Inaddition, it is also found in flue gases, tobacco smoke and its condensate (USEPA, 1994; Sittig, 1985).

The study site is a forest mountainous area. It is however close to a very busy highway Nsawam-Nkawkaw-Kumasi highway, where road works were being done during the year of sampling. This busy road can be the major contributor of BaA in terms of automobile exhaust, coal tar and petroleum asphalt. Since the trend in concentrations are similar for all three HMW PAHs under consideration, there is likelihood of same source emission as such same atmospheric contamination source.

4.2.1.4 PAH pollution souce identification in Abetifi

4.2.1.4.1 Diagnostic PAH ratio source identification

Some polycyclic aromatic hydrocarbons have been identified as markers for various sources in atmospheres. These known as diagnostic isomer ratios are indices that have associated different isomer ratios of PAHs to possible sources such as petrogenic, fuel combustion, wood and coal combustion or mixed origin (Yunker *et al.*, 2002; Dickhut *et al.*, 2000; Soclo *et al.*, 2000). Diagnostic or isomer ratios are widely used to determine the origins of PAHs present in environmental samples. The individual compound ratios are known to provide accurate and reliable estimation of the emission sources of PAHs (Okedeyi *et al*., 2012). Table 4-2 shows six of the characteristic PAH diagnostic ratios obtained in this study.

Table 4-2: Characteristic PAH diagnostic ratios

PAHs Sam.season	Phe/Ant	Ant/ (Ant+Phe)	Flu/ (Flu+Pyr)	BaA/ (BaA+CHRY)	BaA/CHRY	BbF/BkF
ABg-1	18.34	0.052	0.60	0.34	0.51	2.52
ABg-2	12.38	0.075	0.57	0.37	0.59	3.30
ABg-3	19.14	0.050	0.59	0.34	0.51	3.37
ABg-4	10.43	0.087	0.58	0.37	0.59	2.85
ABg-5	8.90	0.101	0.55	0.40	0.68	2.60
ABg-6	9.56	0.095	0.57	0.38	0.62	3.43
ABg-7	8.68	0.103	0.55	0.41	0.71	3.62
ABg-8	9.16	0.098	0.57	0.40	0.67	2.51
ABg-9	8.66	0.104	0.56	0.41	0.70	3.98
ABg-10	7.99	0.111	0.56	0.42	0.71	2.72
ABg-11	9.24	0.098	0.57	0.40	0.68	2.07
ABg-12	11.55	0.080	0.58	0.40	0.66	2.88
ABg-13	0.00	0.000	0.59	0.33	0.50	2.82

Considering the ratio Phe/Ant, a “>15” is indicative of a petrogenic source and a “<10” is signature of a pyrolytic source (Okedeyi *et al.*, 2012; Guo *et al.*, 2011). The results from this study (Table 4-2), 15.4% of the ratios were greater than 15 and 61.5% less than 10. Hencce the major source is pyrolyic. The ratios obtained here were slightly higher than that obtained by Zhang *et al.* (2008) (7.07 – 8.41) in China from a vehicular road and Okedeyi *et al.* (2012) in South Africa from a power plant site (1.1 -1.9).

According to Zhang *et al.* (2006), the isomer ratio Ant/(Ant + Phe) with values less than 0.1 (<0.1) is indicative of a petrogenic source and a greater than 0.1 (>0.1) is signature of a pyrolytic pollution source. From the result, 30.77% gave values above 0.1 (0.103 - 0.111) and 69.23% gave values below 0.1 (0.00 – 0.098). This result therefore shows a more of petrogenic pollution signature. Other works have shown higher ratios such as work done in India (0.27 -0.42) (Khillare *et al.*, 2014) and in South Africa, (0.38 -0.45) (Okedeyi *et al.*, 2012) and Spain recording ratio of 2 (Callen *et al.*, 2011).

Ravindra *et al.* (2008) stated that a Flu/(Flu+Pyr) ratio of a less than 0.5 (< 0.5) gives an inferred source of gasoline and a greater than 0.5 (> 0.5), indicates a diesel source. From this study, the Flu/(Flu+Pyr) ratio gave a range of 0.55 to 0.60 (which are all greater than 0.5) as such indicating a diesel pollution source (100%). This result is higher than that obtained by Ravindra *et al.* (2008) (0.06 – 0.32).

When the ratio of BaA/CHRY is employed as a diagnostic tool, a range of 0.47 – 0.59 shows a petrogenic source (Teixeira *et al.,* 2013) and a range of 0.6 – 0.92 is indicative of pyrolytic signature, specifically wood combustion (Dickhut *et al.,* 2000). With reference to Table 4-2, 38.5% of the source contribution was due to a petrogenic source (0.50 – 0.59) and 61.5% falls within the range of contribution from wood combustion (pyrolytic source). The values in this study were lower than that of wood combustion. It can be inferred from the ratios that, the pollution source at Abetifi is one of a pyrogenic source. Values obtained in this work are within the ratios obtained by Callen *et al.* (2011) (0.4 – 1.5) but far lower than that obtained by Muendo *et al.* (2006) (0.87 – 1.06) and Lin *et al.* (2008) (1.08 -1.31).

Per BaA/(BaA+Chry) diagnostic ratio for source allotment, an unburned petrol source should give a "< 0.2" value and when the petrol is combusted, the source should give values in the range of 0.20 - 0.35 (Tobiszewski *et al.,* 2012). Other combustion sources as per the same diagnostic ratio (BaA/(BaA+Chry), should give a " > 0.35" value (Yunker *et al.,* 2002) with specifics of 0.45 being diesel combustion and 0.48 being wood combustion (Teixeira *et al.,* 2013). From this study values determined using the isomer ratios for BaA/(BaA+Chry) were in the range of 0.33 to 0.42. The ratios obtained from Abetifi are lower than what obtained by Muendo *et al.* (2006) (0.46 – 0.51). However, the result obtained by Khillare *et al.* (2014) (0.4) is within the range of what was obtained in this work. The source proportions of petrol combustion

in this study was 38.5% and that of other combustions gave 61.5% (> 0.35). It is hence obvious that other sources aside petrol combustion are basically contributing to the atmospheric PAH pollution at Abetifi.

From literature, if the ratio BbF/BkF is > 0.5, the pollution source is one from diesel according to Ravindra *et al.* (2008). No data was given for a less than 0.5 indication. According to Tobiszewski *et al.* (2012), ratios in the range of 2.3 -2.9 are indicative of aluminium smelter emissions. From this study, the ratio (BbF/BkF) gave values which are all greater than 0.5 (i.e. 2.07 to 3.98) hence contamination can be said to be one of a diesel source with about 53.8% showing signatures of alumimium smelting.

It is worth noting that the ratios Phe/Ant, BaA/(BaA+Chry) and BaA/Chry gave same percentage of pollution source distribution of 61.5% at Abetifi, a signature of a pyrolytic source. However the Flu/(Flu+Pyr) and (BbF/BkF) ratios showed a 100% diesel source pollution.

More ratios showed a pyrolytic source than petrogenic which probably is assumed to be vehicular. But with the vehicular source, diesel signature is more prominent than that of petrol. Conclusively from the above discussion, the diagnostic ratios revealed a mixed source pollution at Abetifi.

4.2.1.4.2 Source identification using UNMIX

From the model, 10 species were identified and there were 17 observations which produced two distinct sources. The signal to noise ratio in the data was 5.50 and a minimum square root (Min. Rsq) of 0.94. The source compositions are presented in Table 4-3 and the sources plotted in Figure 4-2.

Table 4-3: UNMIX source composition

Species	Source 1	Source 2
ACEN	7.19	0.258
FLU	37.6	9.84
PHE	217	125
ANT	24.5	5.71
FLT	134	125
PYR	104	91.3
BaA	13.9	9.59
CHRY	18.9	22.8
BbF	5.86	5.88
BaP	1.87	0.291

The Table 4-3 shows two sources contributing to the polycyclic aromatic hydrocarbon pollution in the Abetifi environment. The major contributors to the source separation are basically the same type of polycyclic aromatic hydrocarbon; Phenanthrene (Phe), Fluoranthene (Flt) and pyrene (Pyr). In source one, their contribution were as Phe = 217, Flt = 134 and Pyr = 104. The highest contributor here is phenanthrene. Phenanthrene is a three-memberd ring PAH. By finger-printing, pyrene, fluoranthene, and phenanthrene together show reasonably high levels in emission from burning (Smith & Harrison, 1998; Ravindra *et al.*, 2006a). This therefore means both sources of pollution are from burning.

Their contribution however distinguishes source one. According to Marr *et al.* (1999) it is found that heavy duty vehicles (diesel trucks) are the major source of lighter PAHs (i.e., 3-benzene ring PAHs and such others as fluoranthene and pyrene). In this study, the 3-ring PAHs, phenanthrene contributed about a double, the contribution of pyrene and fluoranthene.

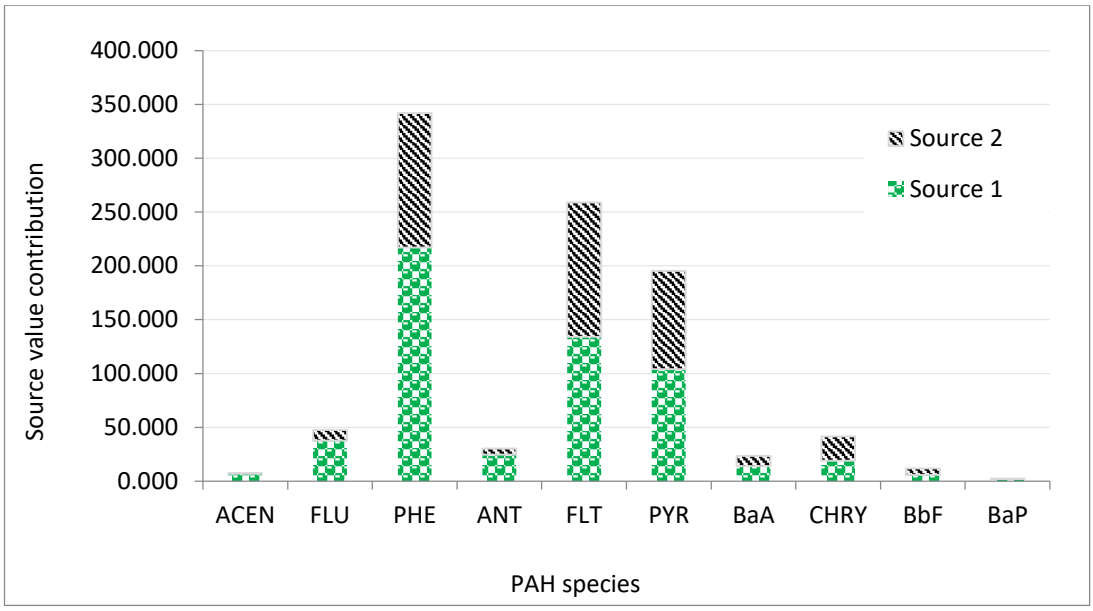


Figure 4-2: Major sources of polycyclic aromatic hydrocarbon pollution

This is an indication that the burning is from diesel. Source one (1) therefore is diesel pollution and source two (2), a burning which is likely to be biomass. The UNMIX model confirms what was discussed earlier when the diagnostic ratios were used revealing two major sources of wood/biomass burning and diesel combustion.

4. 2 Persistent organic pollutants in air

The target contaminants quantified from the study are summarized as:

(1) sum of DRINS (Σ DRINs) which are concentrations of aldrin, dieldrin and endrin,

(2) sum of DDT (Σ DDTs) as that including p,p-DDT, o,p-DDT, p,p-DDE, o,p-DDE, p,p-DDD, and o,p-DDD concentrations,

(3) sum of HCB (Σ HCBs) as concentration of hexachlorobenzene and pentachlorobenzene,

(4) sum of HCHs (Σ HCHs) as the total concentrations of alpha, beta, gamma and delta-hexachlorocyclohexanes. All the four groups above; Σ DRINs, Σ DDTs, Σ HCBs and Σ HCHs are pesticides.

The other group is under industrial products and are grouped as the sum of indicator polychlorinated biphenyls (Σ In-PCBs) and dioxin-like polychlorinated biphenyls (Σ Dl-PCBs). These include PCB 28, 52, 101, 118, 138, 153 180 and PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189 respectively.

The figure below (Figure 4-3) shows the analytes detected and quantified from the study are grouped as in.

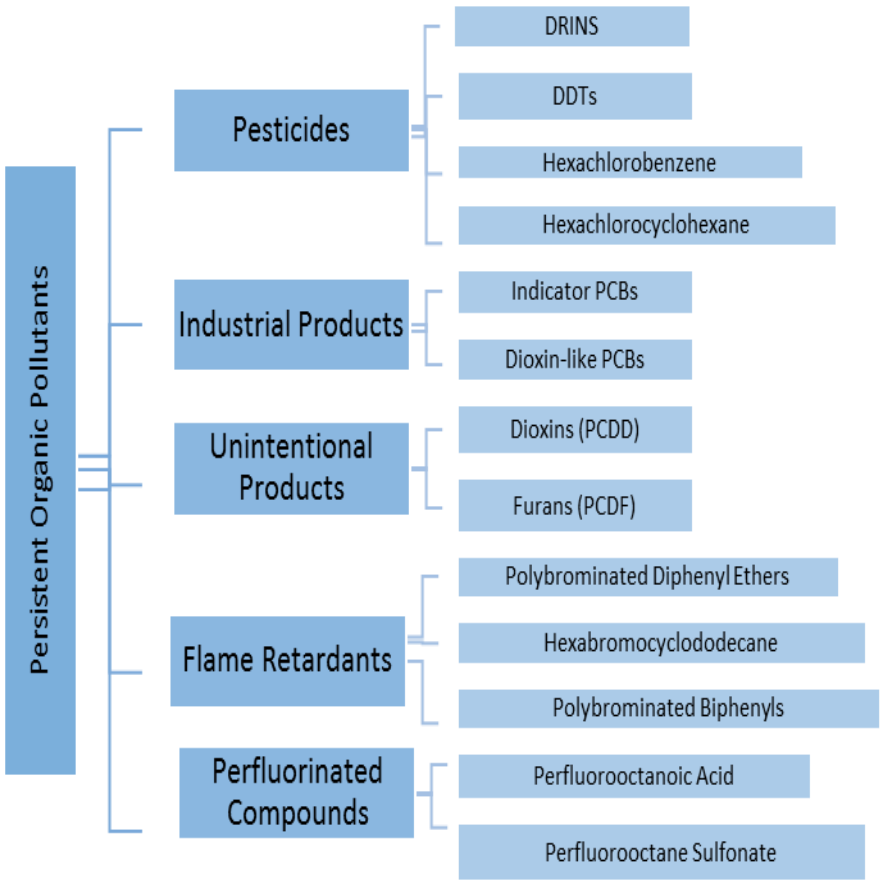


Figure 4-3: Hierarchy of persistent organic pollutants as presented in this section

The next group of analytes considered belong to the unintentionally produced pollutants. These are dioxins (PCDD) and fruans (PCDF) and are grouped as

(1) sum of PCDD (ΣPCDDs) which includes 1,2,3,7,8- pentachlorodibenzo-p-dioxin, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin, 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin, 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin and

(2) sum of PCDF (ΣPCDFs) representing 1,2,3,7,8-pentachlorodibenzofuran, 2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzofuran, 1,2,3,6,7,8-hexachlorodibenzofuran, 2,3,4,6,7,8-hexachlorodibenzofuran, 1,2,3,7,8,9-hexachlorodibenzofuran, 1,2,3,4,6,7,8-heptachlorodibenzofuran, 1,2,3,4,7,8,9-heptachlorodibenzofuran and octachlorodibenzofuran.

Flame retardants as a group are discussed following the unintentional products. These are polybrominated diphenyl ethers (PBDEs), hexanbromocyclododecanes (HBCDs) and polybrominated biphenyls (PBBs). They are described as

(1) sum of PBDE (Σ PBDEs), consisting PBDE 28, 47, 66, 85,100, 99, 153, 154, 183 and 209;

(2) sum of HBCD (Σ HBCDs) representing the total of alpha, beta, gamma and delta-HBCDs;

(3) sum of PBB (Σ PBBs) which consists of moBB 3, diBB 15, triBB 18, teBB 52, peBB 101, hxBB 153, hpBB 180, ocBB 194, noBB 206 and deBB 209.

Additionally, the perfluorinated compounds are discussed. This group consists of perfluorooctane sulfonates (PFOS) and perfluorooctanoic acids (PFOA).

Table 4-4 a & b present the mean concentrations in pg/m^3 and ng/m^3 of the various groups of contaminants, their standard errors and ANOVA at 95% confidence level including f and n (number of counts) values.

The various groups of contaminants tabulated are pesticides, indicator polychlorinated biphenyls (In-PCB), flame retardants such as hexabromocyclododecanes (HBCD) and polybrominated biphenyls (PBB) and such perfluorinated compounds as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). It also includes dioxin-like PCBs (Dl-PCB), dioxins (PCDD), furans (PCDF) and polybrominated diphenyl ethers (PBDE). The target analytes were sampled every 84 days (quarterly) from Abetifi in 2010 and 2011.

With reference to Table 4.4a, annualized mean calculation showed that the sum of furans (Σ PCDF) had the least concentration (0.0092 pg/m^3) and the sum of polybrominated biphenyls (Σ PBB), the highest (0.0069 ng/m^3). When summed up, the annualized mean concentration of analytes were in the decreasing order of PBB > DRINs > DDT > HCHs > HCB > PFOS > HBCD > In-PCB > PBDE > dl-PCB > PCDD > PCDF. However when the quarterly means were compared, both dioxin and furan group recorded least concentrations of 0.0056 pg/m^3 at different times; first quarter of year 2010 (Ab-1) and last quarter of year 2010 (Ab-4) respectively (Table 4.4a). The pesticides group recorded the highest concentrations when summed up. This sumation comprises the DRINS, DDTs and HCHs. These were during the second and third quarters of year 2011 (i.e. Ab-6 = 0.0228 ng/m^3 and Ab-7 = 0.0211 ng/m^3). The obsevations did not follow any particular trend.

Table 4-4a: Mean concentration of target analytes (pesticides, industrial products) of air samples in Abetifi, Ghana

		Pesticides (ng/m^3)				Industrial Products (ng/m^3)		Unintentional Chemicals (pg/m^3)	
Sample ID	Analytes →	DRINS (n-6)	DDT (n-12)	HCB (n-4)	HCH (n-8)	In-PCB (n-14)	Dl-PCB (n-24)	PCDD (n-10)	PCDF (n-10)
Ab-1	Mean	0.0099	0.0020	0.0020	0.0025	0.0009	0.1738	0.0107	0.0056
	± *Std. Error*	*0.0013*	*0.0004*	*0.0008*	*0.0008*	*0.00*	*0.0047*	*0.0003*	*0.0014*
Ab-2	Mean	0.0055	0.0056	0.0029	0.0033	0.0009	0.1771	0.0097	0.0067
	± *Std. Error*	*0.0003*	*0.0001*	*0.0001*	*0.0001*	*0.00*	*0.0068*	*0.0004*	*0.0016*
Ab-3	Mean	0.0052	0.0047	0.0025	0.0032	0.0007	0.1248	0.0077	0.0107
	± *Std. Error*	*0.0003*	*0.0009*	*0.0001*	*0.0001*	*0.00*	*0.0043*	*0.0003*	*0.0027*
Ab-4	Mean	0.0037	0.0061	0.003	0.0025	0.0047	1.9371	0.0056	0.0084
	± *Std. Error*	*0.0002*	*0.0001*	*0.0001*	*0.0008*	*0.0001*	*0.0819*	*0.0002*	*0.0018*
Ab-5	Mean	0.006	0.0045	0.0028	0.0035	0.0023	0.4183	0.0202	0.0142
	± *Std. Error*	*0.0003*	*0.0001*	*0.0001*	*0.0001*	*0.0001*	*0.0175*	*0.0083*	*0.0023*
Ab-6	Mean	0.0115	0.0053	0.0017	0.0044	0.0008	0.1228	0.0168	0.0086
	± *Std. Error*	*0.0039*	*0.0001*	*0.0003*	*0.0021*	*0.00*	*0.0443*	*0.0069*	*0.0015*
Ab-7	Mean	0.0075	0.005	0.0038	0.0049	0.0008	0.0885	0.0142	0.0097
	± *Std. Error*	*0.0003*	*0.0012*	*0.0019*	*0.002*	*0.00*	*0.03*	*0.0055*	*0.0019*
Ab-8	Mean	0.0036	0.0077	0.0031	0.0033	0.0011	0.1313	0.0074	0.0096
	± *Std. Error*	*0.0002*	*0.0002*	*0.0001*	*0.0001*	*0.00*	*0.0451*	*0.0041*	*0.0023*
Significance	*P-value*	*0.696*	*0.092*	*0.954*	*0.938*	*0*	*0*	*0.508*	*0.108*
	F	*0.67*	*1.83*	*0.28*	*0.33*	*9.97*	*4.42*	*0.9*	*1.76*

Table 4-4b: Mean concentration of target analytes (flame retatdanats & perfluorinated compounds) of air samples in Abetifi, Ghana

		Flame Retardants			Perfluorinated compounds	
		(pg/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Sample ID	Analytes →	PBDE(n-20)	HBCD(n-6)	PBB (n-8)	PFOA (n-15)	PFOS (n-6)
Ab-1	Mean	0.5885	0.0012	0.0047	nd	nd
	± *Std. Error*	*0.0283*	*0.0005*	*0.0002*	-	-
Ab-2	Mean	0.821	0.001	0.009	nd	nd
	± *Std. Error*	*0.0404*	*0.0002*	*0.0003*	-	-
Ab-3	Mean	0.535	0.0002	0.0062	nd	nd
	± *Std. Error*	*0.0210*	*0.00004*	*0.0005*	-	-
Ab-4	Mean	0.842	0.0003	0.0054	0.00018	nd
	± *Std. Error*	*0.0292*	*0.00*	*0.0005*	*0.00*	-
Ab-5	Mean	0.4444	0.0005	0.0048	0.00118	nd
	± *Std. Error*	*0.0126*	*0.00*	*0.0002*	*0.0007*	-
Ab-6	Mean	0.3063	0.0001	0.0046	0.00432	0.00023
	± *Std. Error*	*0.0101*	*0.00004*	*0.0002*	*0.0028*	*0.00*
Ab-7	Mean	0.8684	0.0005	0.0094	0.00061	0.00568
	± *Std. Error*	*0.0227*	*0.00*	*0.0003*	*0.0001*	*0.003*
Ab-8	Mean	0.3979	0.0002	0.0109	0.00238	0.00016
	± *Std. Error*	*0.0121*	*0.00*	*0.0031*	*0.0001*	*0.00*
Significance	P-value	*0.571*	*0.006*	*0.361*	*0.106*	*0.003*
	F	*0.82*	*3.4*	*1.12*	*1.75*	*3.3*

Nd-not detected

From the study, ANOVA analysis revealed four groups of contaminants or analytes as exhibiting significant differences in their concentrations ($p < 0.05$). These are indicator polychlorinated biphenyls (In-PCBs) and dioxin-like polychlorinated biphenyls (dl-PCBs) (Table 4.4a). The perfluorooctane sulfonate (PFOS) ($p = 0.007$) and hexabromocyclododecanes (HBCD) ($p = 0.006$). This significance where the p values were less than 0.05 ($p < 0.05$) thus means, there are some factors (probably quaterly difference in meteorological factors) contributing to the difference in the concentrations of those analyte groups. Nontheless, the remaining groups of analytes showed no such significance in the sampling times ($p > 0.05$). This suggests that the difference in their concentrations is essentially due to chance.

In the subsequent sections, concentrations of the individual analytes that contributed to the total concentration of the group is discussed using graphs and tables. Each group is described in detail.

4.2.1 Concentration of DRINs

Figure 4-4 is a graph showing the concentrations (ng/m^3) of aldrin, dieldrin and endrin collectively known as DRINs, measured in air. From the studies, aldrin and endrin were each detected only once during the whole sample collection period. The concentration of aldrin was 0.012 ng/m^3, recorded in Ab-1; the first quarter of the first year and endrin was 0.021 ng/m^3 recorded in Ab-6. The highest concentration (0.0224 ng/m^3) was recorded for dieldrin and this was in quarter Ab-7. Although dieldrin showed 100% detection throughout the sampling period, concentrations were comparable to that of aldrin and endrin which were detected only once. Dieldrin's the least concentration was detected in both Ab-4 and Ab-8 (0.011 ng/m^3), both last quarters of year 1 and year 2 respectively.

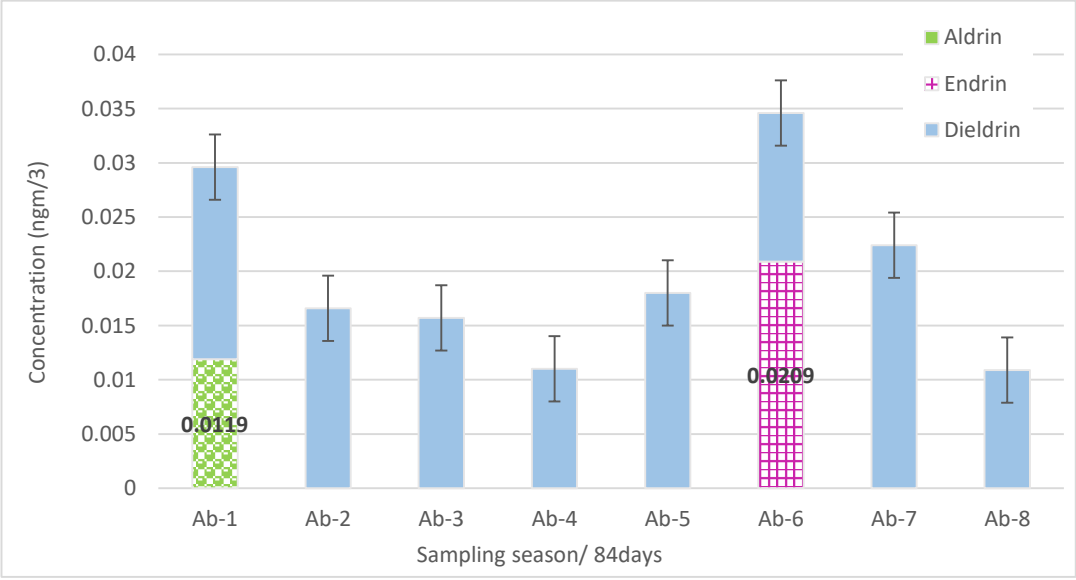


Figure 4-4: Concentration of aldrin, dieldrin & endrin in air

The trend for aldrin and dieldrin from this work is very much similar to that obtained by Alegria *et al*. (2006) in Tapachula and in Southern Mexico where aldrin was not detected at all sites investigated (concentration is assumed to be zero). On the contrary, dieldrin was detected in virtually all samples at all sites (Alegria *et al*., 2006; 2008) (0.0009 - 0.011 ng/m^3). Dieldrin levels from this results were lower than some results from Gioia *et al.* (2005) (0.0031—0.13 ng/m^3 in the years 1996—1998 and 0.0082 – 0.075 ng/m^3 in 2000) but conforms to some results by Harner *et al.* (2006) from some remote places; 0.006 ng/m^3 for Fox Lake site, 0.0101 ng/m^3 for Alert site and 0.063 ng/m^3 for Bermuda. Though dieldrin concentration from this result (0.0119 ng/m^3) could be described as low, they are about 10 times higher than values in Levy (2008) (0.0023 ng/m^3) where samples taken from a very remote mountainous environment and that of Harner *et al.* (2006) (0.0022 ng/m^3) also from the Whistle mountain, another remote environment.

Dieldrin is a highly persistent pesticide having a half-life of 3—4 years in soils and an atmospheric persistence estimated to be 4 to 40 hours (Gh EPA, 2007). Dieldrin has been banned in Ghana since 1985, could the level of concentration observed in this study be due to just the degradation (as a result of its half-life) or there could be other factors contributing to its consistent detection in air throughout the study period?

According to UNEP report, the current air concentrations of pesticides are largely governed by environmental cycling between soil, water and the atmosphere, and this cycle is dependent on climate change and climate variability (UNEP, 2009). Knowing that soil matrix serves as sink for most persistent organic toxicants, it is therefore likely to be the source of dieldrin concentration in the air (observed in this study) when the soil is disturbed by any anthropogenic activity. Additionally, the consistent detection of dieldrin could be due to it being a degradation product or metabolite of aldrin under

certain conditions (Levy, 2008). It is possible therefore that the levels of dieldrin detected in the air are partly the degradation products of aldrin and partly a cycling of dieldrin from soil or sediment sink.

The observation of aldrin and dieldrin being recorded only once in this study is confirming the UNEP COP report (2009). The report considered all the work done under th global monitoring programme and concluded that concentrations for aldrin and dieldrin in air have been decreasing over the past 10–15 years and are now levelling off (UNEP, 2009) probably due to their ban decades ago.

4.2.2 Concentration of DDT and its derivatives

The distribution of DDT (dichlorodiphenyltrichloroethane) and its derivatives in air samples analysed in this study are indicated in Figure 4-5a. The six individual analytes considered in this section are the para-para (p'p') and ortho-para (o'p') isomers of DDT and their derivatives or metabolites; DDE (dichlorodiphenyldichloroethylene) and DDD (dichlorodiphenyldichloroethane). They are presented as p'p'-DDT, o'p'-DDT, p'p'-DDE, o'p'-DDE, p'p'-DDD and o'p'-DDD.

From Figure 4-5a, the highest concentration (0.0459 ng/m^3) of the sum of all derivatives (Σ_6 DDT) (DDT family) was observed in Ab-8 (Oct ─Dec.2011) followed by 0.0361 ng/m^3 measured in Ab-4 (Oct ─ Dec. 2010). These were closely followed by Ab-2 (0.0335 ng/m^3) and Ab-6 (0.0318 ng/m^3); the second quarters (Apr ─Jun.) of both year 2010 and 2011 respectively. Concentrations observed for the sampling periods Ab-3, Ab-5 and Ab-7 were very close: 0.0280 ng/m^3, 0.0273 ng/m^3 and 0.0298 ng/m^3 respectively.

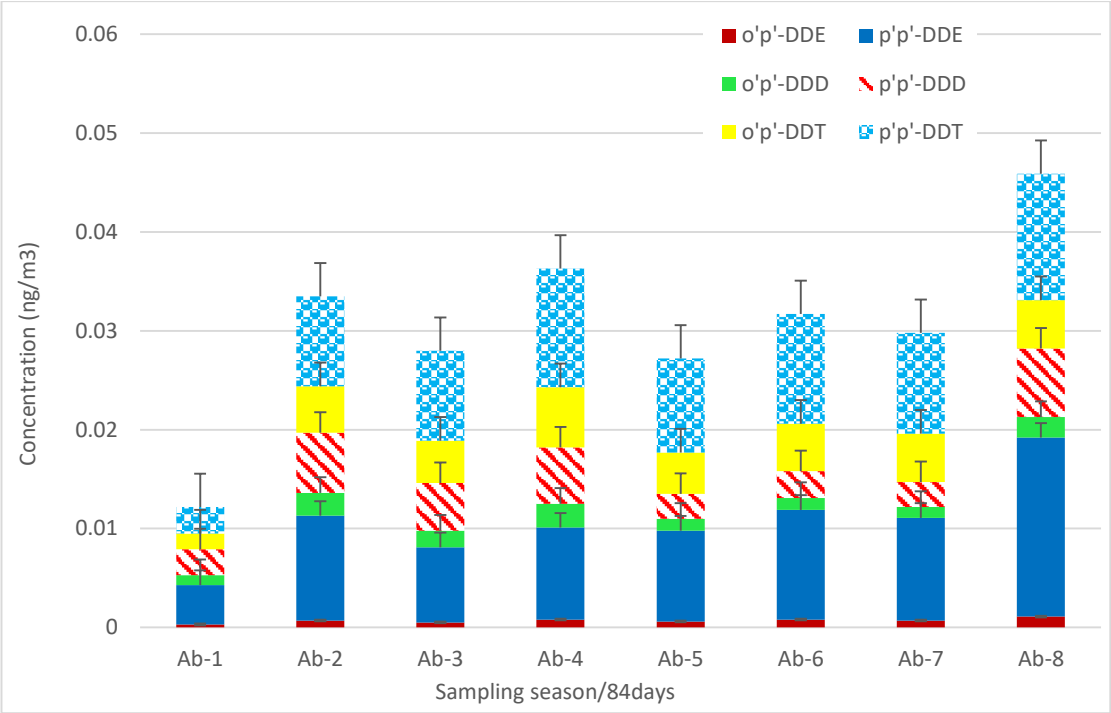


Figure 4-5a: Distribution of DDT and its derivatives (ng/m^3) in air

The concentration of the individual analytes varied from one sampling period to the other. The least in concentration throughout all study time was o'p'-DDE (dichlorodiphenyldichloroethylene) which ranged from 0.0003 ng/m^3 in Ab-1 to 0.0011 ng/m^3 in Ab-8. Its isomer p'p'-DDE on the other hand, recorded over 30% when the sum of all DDT and derivatives (Σ_6 DDT) were analysed. p'p'-DDE recorded percentages as follows: 32.79% for Ab-1, 31.64% for Ab-2, 34.90% for Ab-7 and 39.43% for Ab-8. At the Ab-6 sampling period, which is April— June 2011, p'p'-DDE recorded same percentage concentration of 35.02% as p'p'-DDT, its parent analyte. The remaining sampling periods, Ab-3, Ab-4 and Ab-5 was dominated by p'p'-DDT even though, the individual isomer with the highest concentration throughout the study was p'p'-DDE (0.0181 ng/m^3) recorded in the last quarter of the year 2011 (Ab-8). This observation of para-para (p'p'-) isomer concentrations higher than the ortho-para (o'p') is expected. This is because technical grade DDT is a

mixture of about 85% p'p'-DDT and 15% o'p'-DDT isomers (Pozo *et al.*, 2011; Gh EPA, 2007).

The detection of DDT and its derivatives in the air samples analysed, is an indication of either a past agricultural or health sector usage of DDT in the area. These concentrations are in accordance with concentrations recorded in 2008 in air at Kwabenya (0.010 – 0.014 ng/m^3) and East Legon (0.033 ─0.034 ng/m^3) by Adu-Kumi *et al.* (2010b; 2012).

4.2.2.1 Pollution source of DDT at Abetifi – DDT degradation ratio

Figures 4-5b & 4-5c show various degradation trends of dichlorodiphenyltrichloroethane (DDT) during the study period. These trends will help establish the actual DDT pollution source whether its presence is as a result of past or current use. The ratios of ortho-para and para-para dichlorodiphenyldichloroethane (DDD) to dichlorodiphenyl trichloroethane (DDT) i.e DDD/DDT are represented in Figure 4-5b. It can be observed that, the ortho-para ratio of DDD/DDT decreased gradually from Ab-1 to Ab-7 and then increased at Ab-8 whereas the para-para decreased sharply from Ab-1 to Ab-6 and then increased again to Ab-7 and Ab-8.

A decrease in trend of these ratios is an indication of a fresh input of parent analyte - DDT or recent exposure to the environment (Liu *et al*., 2009). Ghana banned the use of DDT pesticide since 1985 (Darko *et al.*, 2008) for both agricultural purposes and in the health sector.

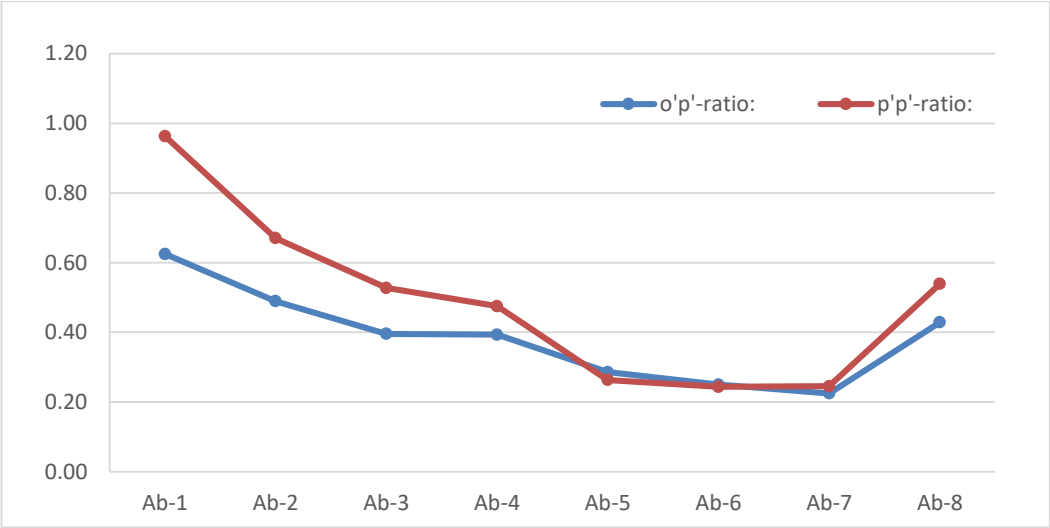


Figure 4-5b: Graph of o'p' and p'p' (DDD/DDT) ratios in study

This fresh input signature is not expected to be from current use or application of DDT in Ghana bue to the ban. This indication of a "fresh input" signature can be possibly attributed to a "weathered" DDT. A "weathered" DDT is where there is resurfacing of DDT from sinks through the process of re-volatilization which might be due to anthropogenic activities in the area. Sinks for past use of DDT could be the soil or sediment and sometimes water bodies. DDT has been reported in soil, sediment and from water bodies in Ghana (Kuranchie *et al.*, 2011; Darko *et al.*, 2008). In addition to the re-volatilization, the presence of DDT could also be attributed to the phenomenon of long range atmospheric transport (LRAT) through "grasshopper" effect, where the POPs (DDT in this case), are transported from places they were applied to the area of detection, where they were not originally applied (UNEP, 2009).

Figure 4-5b showed an increase in both ortho-para and para-para ratio of DDD/DDT towards the end of the graph (later part of the study period). An increase in this graph is an indication of the degradation of parent analyte– DDT into its metabolites but at a slow rate. According to Hitch and Day (1992) DDT degrades to DDD under anaerobic conditions. This fact is probably the reason for this observed trend in this study.

Figure 4-5c, gives another DDT degradation trend. It is a ratio of DDE/DDT under aerobic condition (Hitch and Day, 1992). From the graph, ortho-para DDE/DDT ratio showed a bit of a gentle fluctuating trend whereas the para-para DDE/DDT ratio decreased sharply from Ab-1 to Ab-4 (first sampling year; 2010) and then increased from Ab-5 to Ab-8 (second sampling year; 2011).

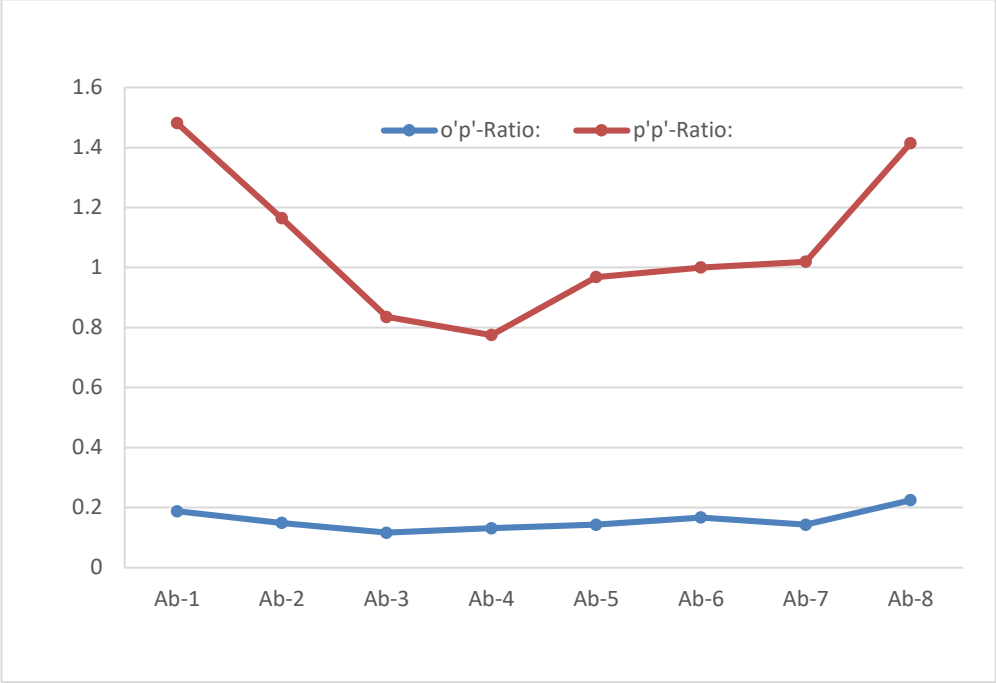


Figure 4-5c: Graph of o'p' and p'p' (DDE/DDT) ratios in study

The trend shows an increase in this ratio and this implies past exposure of DDT (Liu *et al.*, 2009) and which mainly is an origination from historical application. This trend conforms to what was observed at Lake Bosomtwi area by Adu-Kumi *et al.* (2012). The graph also reveals a degradation of DDT to DDE which depicts an aerobic condition degradation. The conclusion therefore by inference would be, in year 2010, there was a fresh input of DDT into the atmosphere from the possible effects of long range transports and from releases from old sinks and in year 2011 there was a degradation.

4.2.2 Concentration of pentachlorobenzene and hexachlorobenzene

Figure 4-6 shows a graph which compares pentachlorobenzene (PeCB) and hexachlorobenzene (HCB).

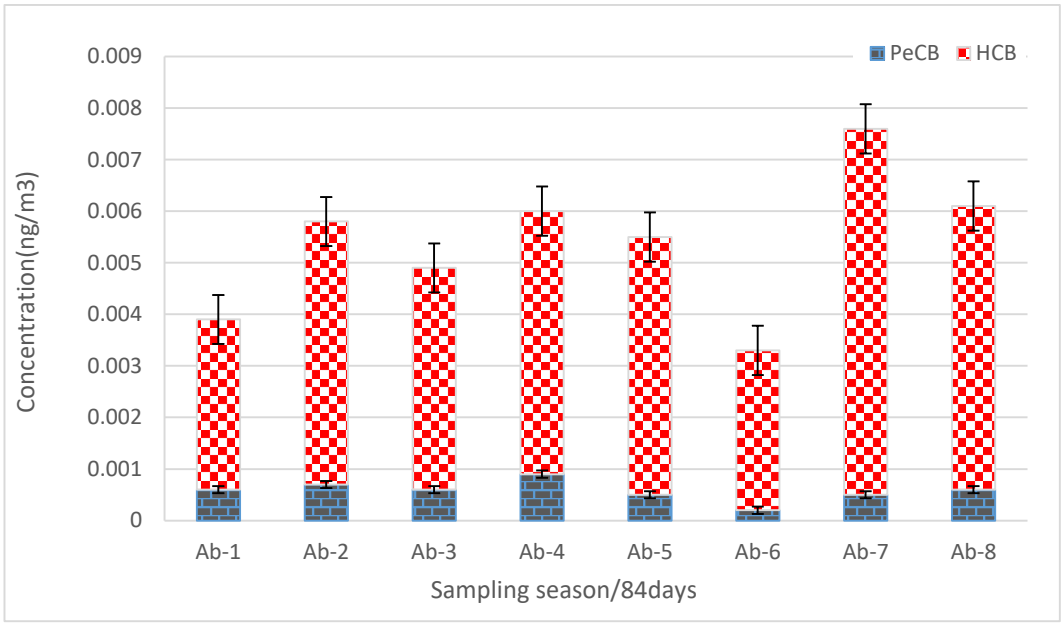


Figure 4-6: Comparison of atmospheric levels of PeCB & HCB ng/m^3

The contamination of the air by PeCB observed from this study was quite uniform for most sampling times. Most values by approximation were 0.001 ng/m^3. The least concentration however was recorded in Ab-6 (0.0002 ng/m^3). Pentachlorobenzene (PeCB) concentrations recorded in this work is far lower (0.0002 – 0.0009 ng/m^3) than the work done in 2008 in Ghana by Adu-Kumi *et al.* (2010) and Klanova *et al.* (2009) where the concentrations of PeCB was between 0.05 and 0.15 ng/m^3. The concentration of PeCB therefore can be said to have decreased drastically over two years. The concentration of HCB unlike PeCB varied throughout the study (Figure 4-6). Concentrations ranged from 0.0031 to 0.0071 ng/m^3. HCB is the only chemical, classified under the Stockholm Convention as belonging to three different groups: Pesticides, industrial compound and unintentional production (UNEP, 2002).

At present, HCB is no longer produced as a pesticide or an industrial chemical (UNEP, 2007). It is found in the environment as a by-product in the production of a large number of chlorinated compounds, solvents and several pesticides and has also found to be emitted from metallurgical industries (Gh EPA, 2007). The concentrations recorded in this study are likely to be of historical use or due to the presence and activities of some the industries mentioned. HCB has an estimated half-life in soils of 2.7-5.7 years and of 0.5-4.2 years in air (Pavlova, 2014; Gh EPA, 2007) and so takes a long time to break down. HCB concentrations found in this study are about 10 times lower compared to that obtained by Levy (2008) (0.0674 ng/m^3) from Bavarian forest in Central Europe and 100 times lower than what was recorded by Faraar *et al.* (2006) (0.410 ng/m^3). They recorded a range of 0.165 - 0.865 ng/m^3 samplers from remote areas like Ireland and Norway giving the lower values and other sites like Russia and Italy giving the higher values. This shows a decrease and a degradation of HCB in the atmosphere.

4.2.4 Concentration of hexachlorocyclohexane

The isomers of hexachlorocyclohexane (HCH) are discussed in this session: alpha-HCH (α), beta-HCH (β), gamma-HCH (γ) and delta-HCH (δ) whose atmospheric concentrations are shown in Figure 4-7. The concentrations of the sum of HCH (Σ HCH) ranged from 0.0101 ng/m^3 (Ab-1) to 0.0197 ng/m^3 (Ab-7). The beta-isomer recorded the least concentrations (0.0003 – 0.0009 ng/m^3) throughout the sample collection period.

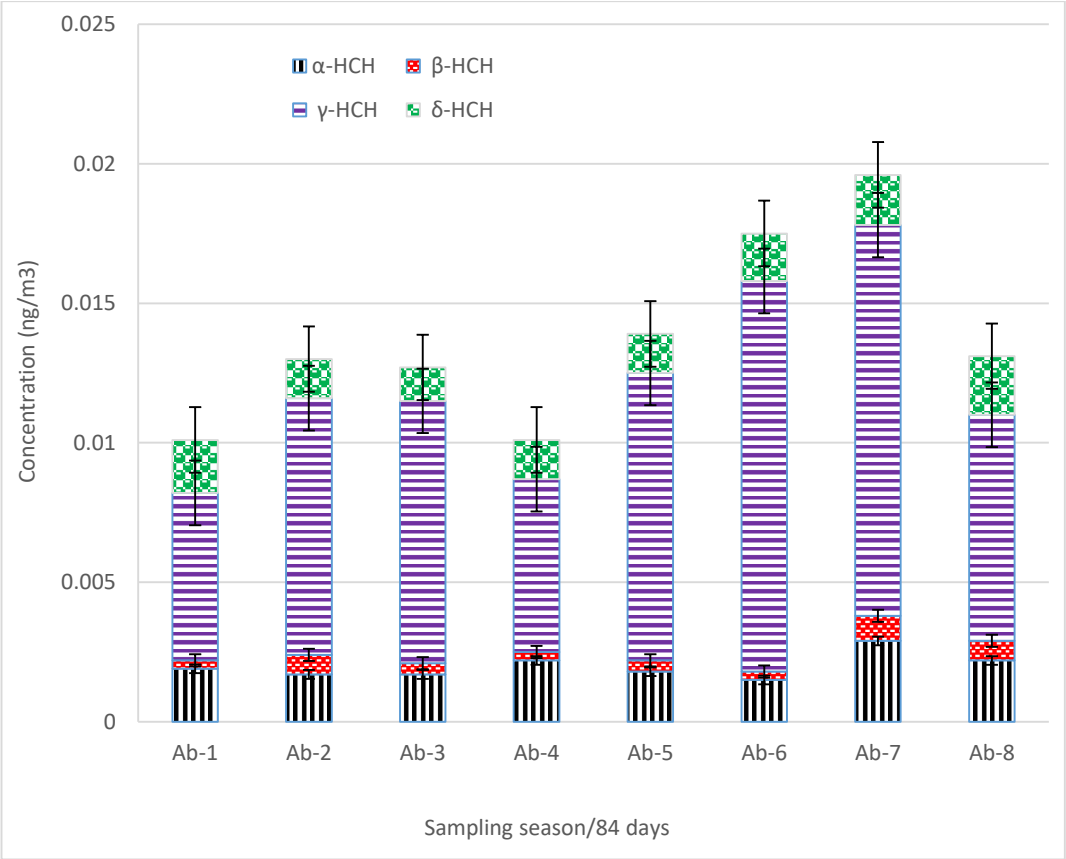


Figure 4-7: Concentrations of four HCH isomers (ng/m^3)

This is in conformity to the technical-grade HCH composition, which comprises α, β, γ and δ–HCH isomers with beta being least (7-10%) (Linderholm, 2010) and gamma, highest in composition (approx.99%) (HSDB, 2009). Figure 4.7 shows a distribution of the four isomers. Their quantitation revealed a trend suggestive of technical-HCH usage in the area. The levels found in the air may either be as result of present or historical usage or else a signature of long range atmospheric transport.

Gamma-HCH (γ-HCH) recorded highest concentration in all sampling seasons in this study, it ranged from a minimum of 0.006 ng/m^3 in season Ab-1 to a maximum of 0.014 ng/m^3 in seasons Ab-6 and Ab-5. This isomer was marketed and used in Ghana over years under the trade name lindane or gammalin 20. It was extensively used as an insecticide on cocoa, in consequence the potential for misapplication on other crops

and on soil. Though lindane has been banned over a decade ago, this practice (misapplication) might be contributing in part to the levels of γ-HCH detected in this study. Results for γ-HCH from this study conforms well with work done by Harner *et al.* (2006) with data from remote and mountainous places such as Bermuda - 0.00032 ng/m^3, Alert - 0.008 ng/m^3, Whistle mountain - 0.0061 ng/m^3 and Fox Lake - 0.018 ng/m^3. Some other research works which recorded higher data than the results obtained from this work are as follows: Levy (2008) recorded 0.0341 ng/m^3 from the Bavarian and Bohemian forest, Harner *et al.* (2004) recorded 0.0256 – 0.0522 ng/m^3 from George and Downsview respectively and Faraar *et al.* (2006) measured 1.776 ng/m^3 from Portugal and 1.07 ng/m^3 from the UK.

According to Akron (2009), technical-grade lindane is stable under normal temperature and pressure. The prevalence the gamma isomer in this study aside the fact that it was used extensively on farms in Ghana could also be its stability in the environment.

4.2.4.1 Pollution source of lindane at Abetifi

The isomer ratio of alpha- to gamma-HCH (α-/γ-HCH) used to apportion pollution sources of either fresh input of the chemical or an effect of a long-range transport was employed in this part of the study. The ratio α-/γ-HCH ranges from 3 to 7 if the presence of the contaminant is purely a technical grade HCH. The value is higher than the range given if the pollution source is one of a long range transport and lower, when there is continuous application of technical-grade lindane (99% γ–isomer) (Zhu *et al.*, 2014). In the present study, the ratio of α-/γ-HCH is shown in Table 4-5.

Table 4-5: Isomer ratio of alpha to gamma-HCH

HCHs/ Sampling ID	Ab-1	Ab-2	Ab-3	Ab-4	Ab-5	Ab-6	Ab-7	Ab-8
α-HCH	0.03	0.02	0.02	0.03	0.03	0.02	0.04	0.03
γ -HCH	0.09	0.13	0.13	0.09	0.15	0.20	0.20	0.12
α-HCH/γ-HCH	0.32	0.18	0.18	0.35	0.17	0.11	0.21	0.27

From the table (Table 4-5), ratios ranged from 0.11 to 0.35, a far lower ratio from that documented by Harner *et al*. (2004), (1.1—2.3) in the Great Lakes Basin and he concluded that these values (1.1—2.3) are typical of background air. However, with reference to Zhu *et al.* (2014), values below this range (3—7) is suggestive of a fresh application of technical lindane (99% γ–isomer) or gamalin 20 in the sampling area. In his work, Zhu *et al.* (2014) recorded ratios of 2.2—6.9 revealing a combined source influence by both technical HCHs and lindane (99% γ–isomer) in the sampling area. Conversely, this study result showed a signature of only fresh input of technical lindane (99% γ–isomer).

Abetifi is in the Eastern region of Ghana, one of the areas, where cocoa farming is a major activity. Since lindane is banned in Ghana, its presence could logically therefore be from re-suspension/re-volatilization from sinks. Sinks for past use of lindane could be the soil or sediment and sometimes water bodies. Lindane has been recorded to be in soil, sediment and from water bodies in Ghana. Adu-kumi *et al.* (2010a) recorded 0.72 ng/g in fish sampled from the Volta Lake. Likewise Kuranchie *et al*. (2011) reported 0.28 - 1.04 µg/kg from same lake. Kuranchie *et al*. (2011) further investigated sediment and water samples and reported concentrations of 0.40 - 0.80 µg/kg at Weija and 0.35—0.58 µg/kg at Nsawam and 0.02—0.08 µg/L for Weija and 0.04—0.07 µg/L

for Nsawam. That not withstanding, analytical investigations of a number of organochlorine pesticides in human organs, body fluids and other reported incidents suggest that some of these chemicals are still in use in illegally the country (Adu-kumi 2010a cited Ghana NIP, 2007) hence a likely reason for the fresh input signature observed in this study.

4.2.5 Levels of indicator polychlorinated biphenyls

The atmospheric concentrations of polychlorinated biphenyls (PCBs) studied in this work is detailed in tables and Figures below. The data distribution of seven PCBs analysed included PCBs: 28, 52, 101, 118, 138, 153 and 180, these are indicators of the presence of other PCB congeners in the environment. From the result of this study (Figure 4.8), all sampling time points/seasons in the two years recorded all the seven indicator PCB congeners under review. These indicator PCBs were consistently quantified with values ranging from a minimum individual PCB of 0.0002 ng/m^3 to a maximum of 0.014 ng/m^3. PCB 180 recorded the least value throughout the study. The highest level recorded by an individual PCB was in Ab-4 by PCB 118 which has inturn, affected the concentration of the total PCBs (Σ_7 PCB) as recorded in the that quarter of the year, Ab-4 (Oct–Dec 2010).

The sum of indicator PCBs (Σ_7 PCB) was in an increasing order of Ab-3 < (Ab-6 = Ab-7) < Ab-1 < Ab-2 < Ab-8< Ab-5< Ab-4. The values recorded in this study are far lower than those measured in Ghana in 2008 (0.069–0.203 ng/m^3) (Klanova *et al*., 2011; Adu-Kumi *et al*., 2010).

The fact that all indicator PCBs were detected at Abetifi; a semi-urban environment, assumed to be prestine, is an indication of the widespread nature of PCBs in Ghana as

these chemicals were expected more in the urban areas. Additionally, the presence of the indicator PCBs on an altitude as 594.7m, signals the "grass-hopper" effect of PCBs (being transported by air) as such ascertaining their long-range atmospheric transport (LRAT) property (Klanova *et al*., 2011).

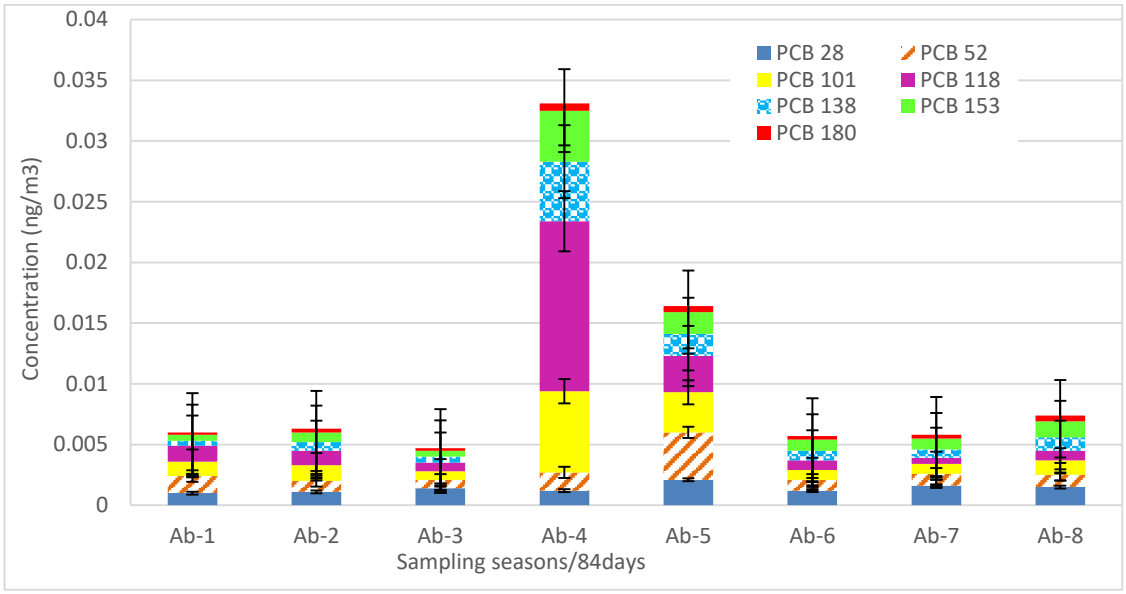


Figure 4-8: Atmospheric concentration (ng/m^3) of indicator PBCs from Abetifi

Polychlorinated biphenyl (PCB) 180 congener which recorded least concentration throughout the sampling period, had concentrations ranging from 0.0002 (Ab-1 & Ab-3) to 0.0006 ng/m^3 (Ab-4) (Figure 4-8). These levels are comparable to results obtained by Levy (2008) (PCB 180–0.0009 ng/m^3) also for a three month exposure duration but lower than Faraar *et al.* (2006) (0.01—0.015 ng/m^3). This low concentration could be due to the fact that PCB 180 (395.5 gmol^{-1}) is a high molecular weight PCB and for such highly chlorinated congeners, they partition more in the particulate-phase which are not easily volatilized (Klanova *et al*., 2008) and also equilibrium may still have not been reached (Levy, 2008). Additionally, the protective dome chamber of the sampler around the PUF-disk used in this study, limits the ability of particles to deposit on the filter (foam) (Pozo *et al.*, 2012) hence such low

concentrations recorded compared to the other congeners. Furthermore, it is estimated that the particle-phase sampling rate is approximately 10% of the gas-phase rate (Klanova *et al*., 2008), hence the observed result for PCB 180.

Passive air sampling (PAS) using polyurethane foams (PUFs), which is the technique employed in this study adsorbs best, gas-phase PCB congeners such as PCB 28 (257.5 g/mol) and PCB 52 (292 g/mol) (Klanova *et al*., 2008; Levy, 2008). It is striking however to see a record of a one-time high concentration of PCB 118 (326.5 g/mol) which was the highest individual PCB (Ab-4) measured during the whole sampling period. The dorminance of PCB 118 is characteristic signature of the Aroclor 1254 (A1254) commercial mixture (EAUK, 2007), as such PCB 118 fingerprint is major contribution from technical formulation (Chakraborty *et al.*, 2016).

4.2.5.1 Pollution source of polychlorinated biphenyl at Abetifi

The polychlorinated biphenyl (PCB) congener pattern in air can be used to explain potential emission sources. Fresh emission sources tend to have PCB patterns that resemble technical mixtures and are enriched in the higher homologue groups (Cl_6 to Cl_{10}) while those profiles that are enriched in lower molecular weight congeners (Cl_3 to Cl_5), are indicative of secondary source contributions (e.g re-emission from soil, sediment or water bodies) and also suggestive of a long-range transport or else, a global background signature (Pozo *et al*., 2012).

In this study, lower PCB congerners dorminated the atmospheric profile with 57.89% and the higher congeners, 42.1%. The PCB source of pollution is therefore from a mixed source dominated by secondary source contribution, a signature of long-range transport.

4.2.6 Concentration of dioxins, furans and dioxin-like polychlorinated biphenyls

Dioxins and furans are not intentionally produced pollutants. They are however ubiquitous in our environment. These chemicals are found in the environment as mixtures, have a total of 210 possible positional isomers (congeners) in the ratio of 75:135 for dioxins and furans respectively. In this study nine furan and five dioxin congeners were recorded.

4.2.6.1 Dioxins

Seven homologues of dioxins were analysed for in this study and the results revealed that the two congeners; 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (HxCDD) isomer and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) isomer (the most toxic form) were not detected. On the other hand, octachlorodibenzo-p-dioxin (OCDD) was detected throughout the study (Figure 4-9). Considering the first sampling year (year 2010) (i.e. Ab-1 to Ab-4) only octa- (OCDD) and hepta- (HpCDD) homologues were recorded. The total concentration of seven dioxin congeners (Σ_7 PCDD) ranged from 0.0281 to 0.1011 pg/m^3. This compares well with Kukucka *et al.* (2009) where dioxins were analysed from five remote sites in Czech Republic. They recorded for Σ_7 PCDD, 0.103 pg/m^3 for Nacetin, 0.261 pg/m^3 for Cervena and 0.669 pg/m^3 for Jedlova. The other sites such as Paseracky Chodnicet, Ivacena and Boubin recorded levels of 0.057 pg/m^3, 0.037 pg/m^3 and 0.086 pg/m^3 respectively. However, they were lower than the values measured by Meng *et al.* (2016) in China (0.2134 – 0.3435 pg/m^3).

From Figure 4-9, a trend is observed where the total dioxin concentrations decreased gradually from the first to last quarter in both years (Ab-1 to Ab-4 and Ab-5 to Ab-8) nonetheless, the total dioxin concentrations (Σ_7 PCDD) in air increased in the second year of sampling.

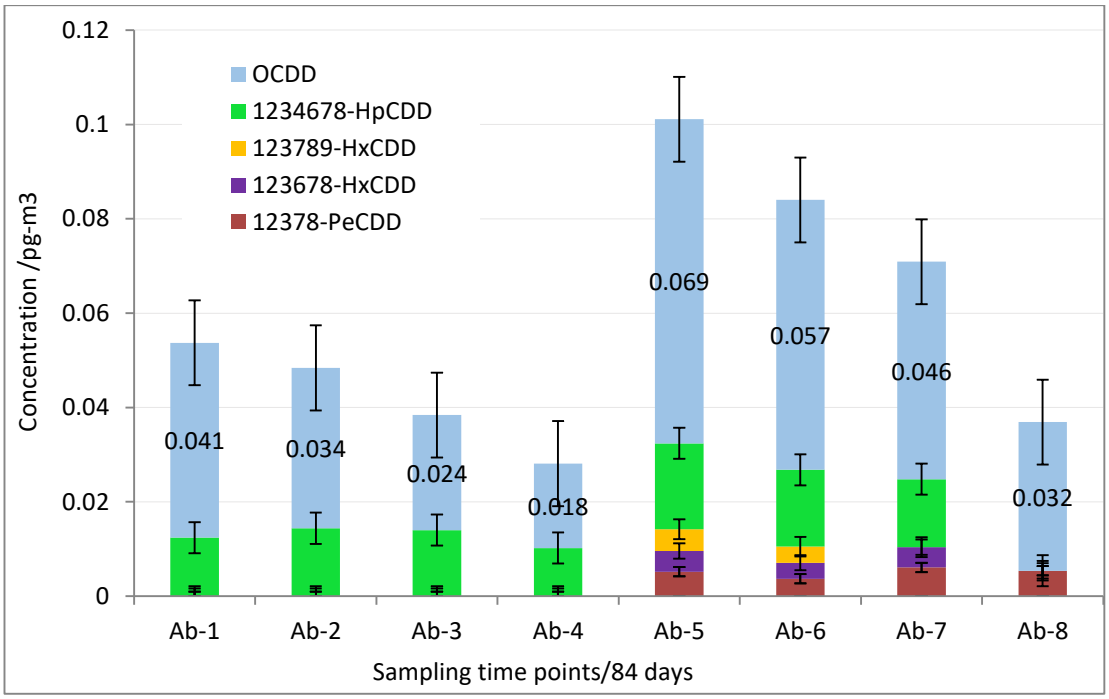


Figure 4-9: Atmospheric concentrations of dioxins (PCDD) from Abetifi

Octachlorodibenzo-p-dioxin (OCDD) recorded highest value from all the sampling periods, with concentration ranging from 0.018 to 0.069 pg/m^3. This range fairly compares with Meng *et al.* (2016) recorded in China (0.121–0.193 pg/m^3). Research has associated the dominance of OCDD in atmospheric pollution to combustion activities (Baker and Hites, 2000).

Running a Pearson's correlation for total dioxin (Σ_7 PCDD) for the two years, there was a strong positive value (r = 0.984) revealed but trend showed no significant difference (p = 0.725). This means the increased trend observed for the concentration of total dioxin (Σ_7 PCDD) in the year 2011 was basically due to chance. No specific factor is responsible for the increase. However, some influences of meteorological factors were observed. Correlation values for Σ_7 PCDD showed a 69% correlation with average precipitation (mm) (r = 0.69) and a 24% influence from the temperature (°C) prevailing at Abetifi during the time of sampling (r =0.235) but a negative correlation was observed for relative humidity (r = -0.775).

The atmospheric dioxins found in Abetifi could be from any of these possible sources; fuel exhausts, burning of industrial, municipal and household wastes. Ghana has no engineered landfill sites, rather designated dump sites; where burning times/periods are left to the discretion of those in charge.

In this study, the passive air samplers (PAS) were hanged vertically, about 1.5—2.0 m above the ground which is a breathing level/ height of the average man with an average sampling rate estimated as 3.5 m^3/day, corresponding to 100 m^3 of the air sampled during four weeks of deployment of the polyurethane foams (PUF) (Shoeib and harner (2002). In view of that, the least concentration of total dioxin measured when calculated for a-28 day sampling at Abetifi, gave 0.028 pg/m^3 and the highest volume concentration gave 0.101 pg/m^3 which means that within a month, the dioxin concentration in the air was between a minimum of 0.028 pg/m^3 and a maximum of 0.101 pg/m^3.

4.2.6.2 Furans

In this study, (Figure 4-10) nine (9) out of the ten (10) furan congeners known for their toxicity were detected. The concentrations measured ranged from less than the limit of quantification (LOQ) to 0.231 pg/g. Which translates to 0.0015 - 0.0231 pg/m^3. The congener with the highest concentration was 2,3,4,7,8 -PeCDF (0.0231 pg/m^3) which was recorded in the third quarter of the first year of sampling (Ab-3). Total furan concentrations (Σ_9 PCDF) recorded and calculated per 28 days were in the levels of 0.056 to 0.107 pg/m^3 in year 2010 and higher values in 2011 (0.086—0.142 pg/m^3).

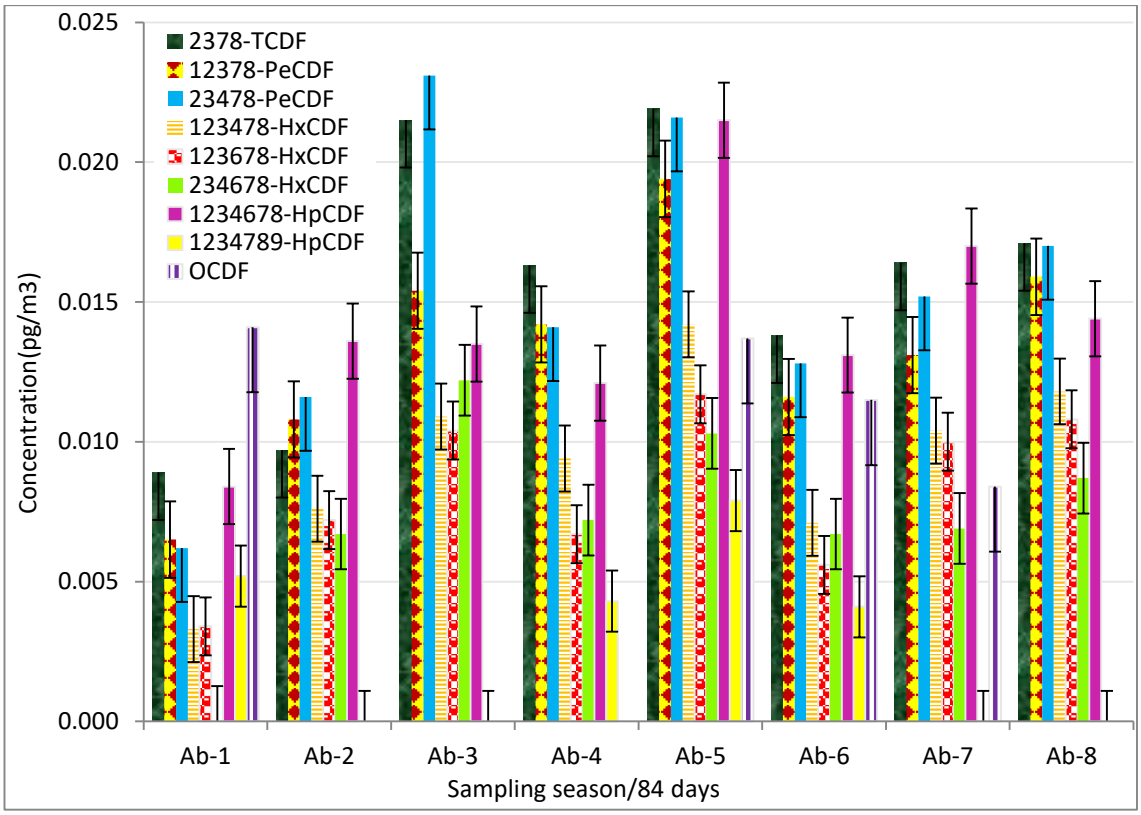


Figure 4-10: Atmospheric signature of furan in Abetifi measured in pg/m^3

The total furan concentrations (Σ_9 PCDF) measured at Abetifi were found to be in the range of 0.056 - 0.142 pg/m^3 which were higher than that documented by Kukucka *et al*. (2009) but far lower than what was measured in China (Σ_{10} PCDF) 0.682 and 0.777 pg/m^3 (Meng *et al.*, 2016). Kukucka *et al*. (2009) measured values for Σ_9 PCDF from varuios remote and mountainous sites and recorded 0.002 pg/m^3 for Nacetin, 0.003 pg/m^3 for Cervena and 0.148 pg/m^3 for Jedlova. He also reported 0.002 pg/m^3 and 0.032 pg/m^3 for site Ivacena and Boubin respectively.

Unlike the trend of concentration observed with the dioxins, the most toxic form of furan- 2,3,7,8-tetra chlorodibenzofuran (TCDF) was detected throughout the study (100% occurrence). This means TCDF is abundant in the air at Abetifi. Concentrations ranged between 0.009 and 0.022 pg/m^3 which is comparably lower than Meng *et al.* (2016) (0.0160–0.0295 pg/m^3). The hexa-congeners 123478-HxCDF, 123678-HxCDF

and 234678-HxCDF were all detected in concentrations ranging between 0.003─ 0.014 pg/m^3. One of the hepta-CDF congeners was detected with higher concentrations (0.022 pg/m^3) but octa-CDF levels were much lower. From literature, hepta- and octa-CDF signatures are known to be mainly caused by chemical manufacturing, especially polyvinylchloride (PVC) manufacturing processes (Isosaari *et al.,* 2000) and higher level of 123478-HxCDF and 1234678-HpCDF to be caused by refinery plant (USEPA, 2001).

4.2.6.3 Dioxin-like PCBs

The dioxin-like PCBs are such PCB congeners that have substitutions in the para-and at least two of the meta-positions. These include four (4) co-planar or non-ortho PCBs (PCBs No. 77, 81, 126, 169) and eight (8) mono-ortho congeners (PCBs No. 105, 114, 118, 123, 156, 157, 167, 189) (EC, 2002). The total concentration of dl-PCBs recorded during each sampling period in this study are (Σ_{12} dl-PCB) Ab-1= 2.09 pg/m^3, Ab-2= 2.12 pg/m^3, Ab-3= 1.50 pg/m^3 and Ab-4 is 23.25 pg/m^3. The second year also recorded values as 5.02 pg/m^3, 1.47 pg/m^3, 1.06 pg/m^3 and 1.58 pg/m^3 for Ab-4, Ab-5, Ab-7 and Ab-8 respectively. The concentration recorded in Ab-7 (1.06 pg/m^3) is similar to that obtained by Cortes *et al.* (2014) from Palogrande in Colombia (1.11 pg/m^3), the others such as that recorded for Ab-1- Ab-3 and Ab-2 are comparable to that from Liceo (2.23 pg/m^3) (Cortes *et al.,* 2014). Dioxin-like pollutants are influenced by seasonal sources and specific meteorological conditions which hinders pollutant dispersion (Cortes *et al.,* 2014). In this work, the monthly average precipitation (mm) was the main driver of the gas phase concentrations of dl-PCBs with a correlation gave a 0.744 (r = 0.744). However documentation from Cortes *et al.* (2014), concluded that concentrations recorded might be related to the semi-volatility property of dl-PCB, which depends on

ambient temperature as was observed in their work (temperature difference: 15–27 °C) in Colombia (Cortes *et al.*, 2014). Yet at Abetifi, the prevailing ambient temperature during the years of sampling ranged from 23.5–26.8 °C, a fairly constant temperature. At Abetifi, the correlation between dl-PCB levels and temperature was 0.017 (r = 0.017).

4.2.6.1 Dioxin-like co-planer PCB congeners

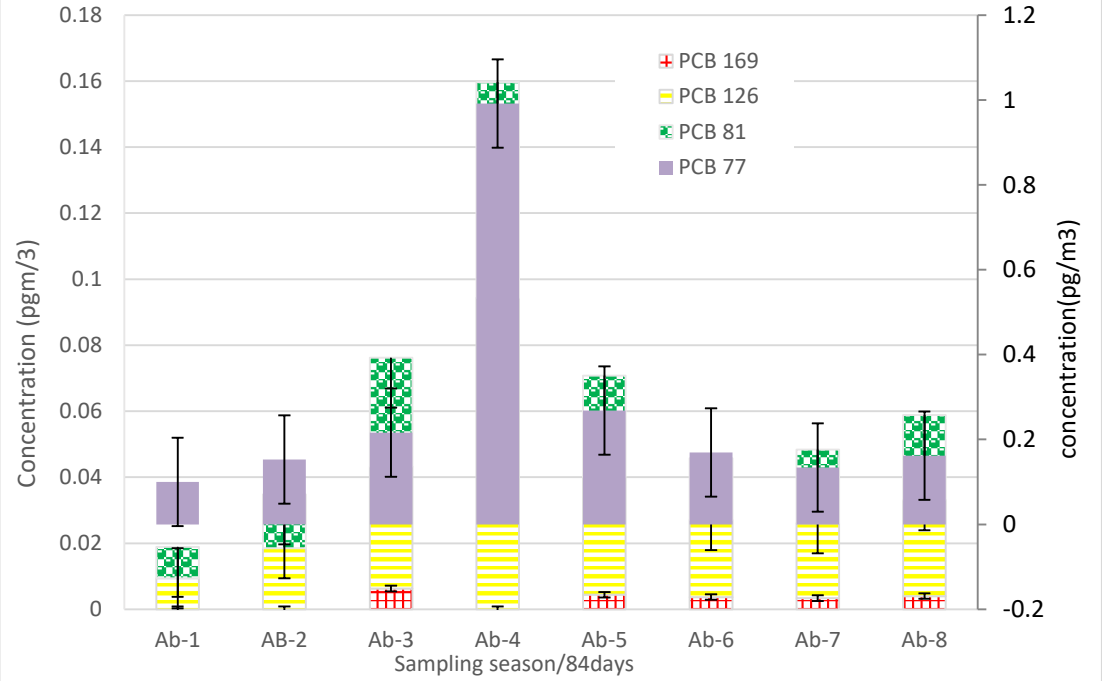


Figure 4-11a: Graph of co-planar/non-ortho PCB congeners analysed in air

Figure 4-11a is a graph of dioxin-like co-planar PCB congeners analysed in air from Abetifi. All the co-planar congeners were detected in the study. The concentration trend in this study was consistent in a decreasing order of PCB 77 > PCB 126 > PCB 81 > PCB 169 for all sampling time points. These co-planer PCBs are very significant in this study as they are the most toxic of the dioxin-like PCBs. They are very stable with no restrictions in twisting the phenyl rings along the plane, making them very lipophilic as such they can stay in the body of humans for a longer period of time. The

same trend (PCB 77 > PCB 126 > PCB 81 > PCB 169) was observed and Cortes *et al.* (2014) but different from by Levy (2008).

PCB 77 recorded the highest concentration in all the sampling time points. Concentration of PCB 77 ranged between 0.1003 and 0.9917 pg/m^3. The highest level was recorded in Ab-4 (last quarter of year 1). This concentration is about 20 times higher than what was recorded by Levy, (2008) (PCB 77 = 0.04 pg/m^3). For PCB 126, values ranged from 0.009 - 0.094 pg/m^3 whereas Levy (2008) recorded 0.001 pg/m^3 and PCB 81 was not detected. On the contrary, this congener was consistently quantified throughtout the sampling at Abetifi (0.065–0.010 pg/m^3).

4.2.6.3.2 Concentration of mono-ortho PCB congeners

Figure 4-11b shows the concentration of mono-ortho PCB congeners analysed in the air in this study. Results show the dominant mono-ortho congeners to be PCB 105, PCB 118 and PCB 156 in the order, PCB 118 > PCB 105 > PCB 156 in all the sampling campaigns. Congener 118 gave highest concentrations throughout the sampling period. Levels ranged between 0.5243 pg/m^3 (Ab-7) ─13.996 pg/m^3 (Ab-4). The same trend was documented by Cortes *et al.* (2014) and Levy (2008).

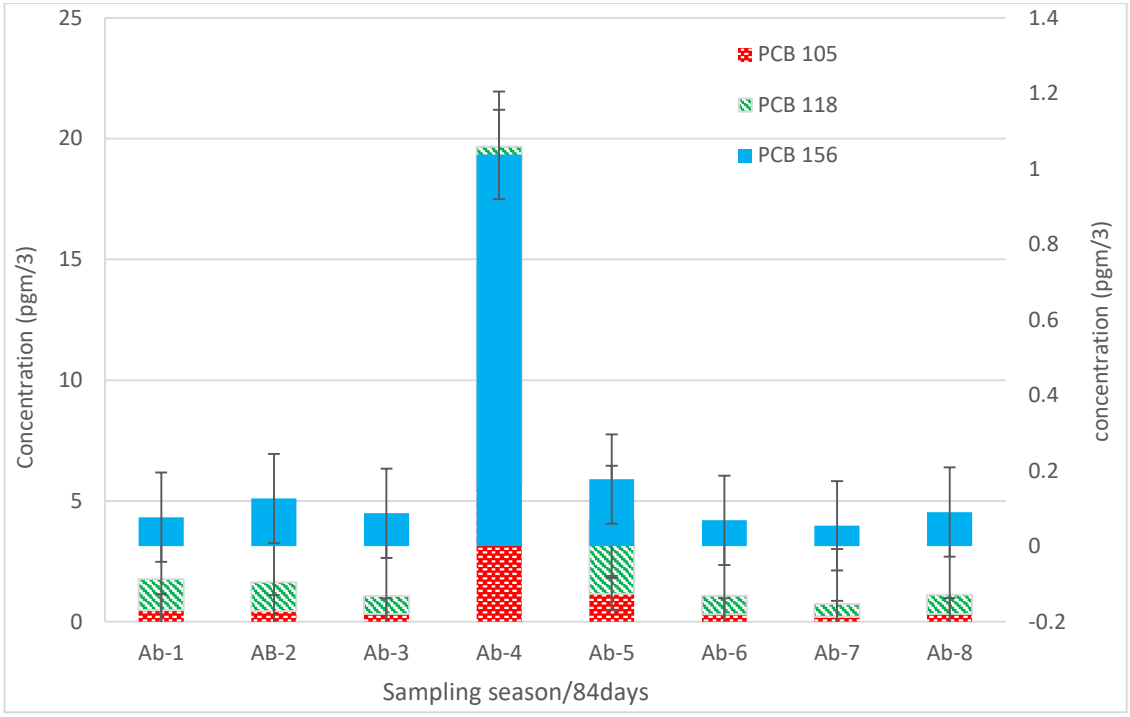


Figure 4-11b: Graph of concentrations of mono-ortho PCB congeners (pg/m^3)

Highly significant percentage (>50% of the total mono-ortho congeners) of PCB 118 concentrations were recorded in each sampling time. It recorded 65.34%, 61.57%, 61.94%, and 63.35% in the first, second, third and fourth quarter (sampling time points) of the first sampling year (year 2010). In the second year of sampling (year 2011), it was 64.56%, 61.01%, 59.60% and 58.19% in the order of first to fourth sampling time points. PCB 118 is the only dioxin-like PCB which is also an indicator PCB consequently its high level is of concern. This congener is a core proportion of a technical formulation (Chakraborty *et al.*, 2016). Consequently, its dorminance is typical signature of the Aroclor 1254 commercial mixture (EAUK, 2007). (Chakraborty *et al.*, 2016).

4.2.7 Trend of indicator and dioxin-like PCBs

The Figure 4-11c is a graph comparing the trend of concentrations (pg/g) recorded for the sum of indicator PCBs (Σ_7 PCB) and that of dioxin-like PCBs (Σ_{12} PCB). The graph reveals a strikingly interesting trend; where the sum of the twelve dioxin-like PCBs runs along side (pari pasu) the seven indicator PCBs. The trend was same for both groups over the sampling duration. The trend confirms the indicator PCBs as indicators.

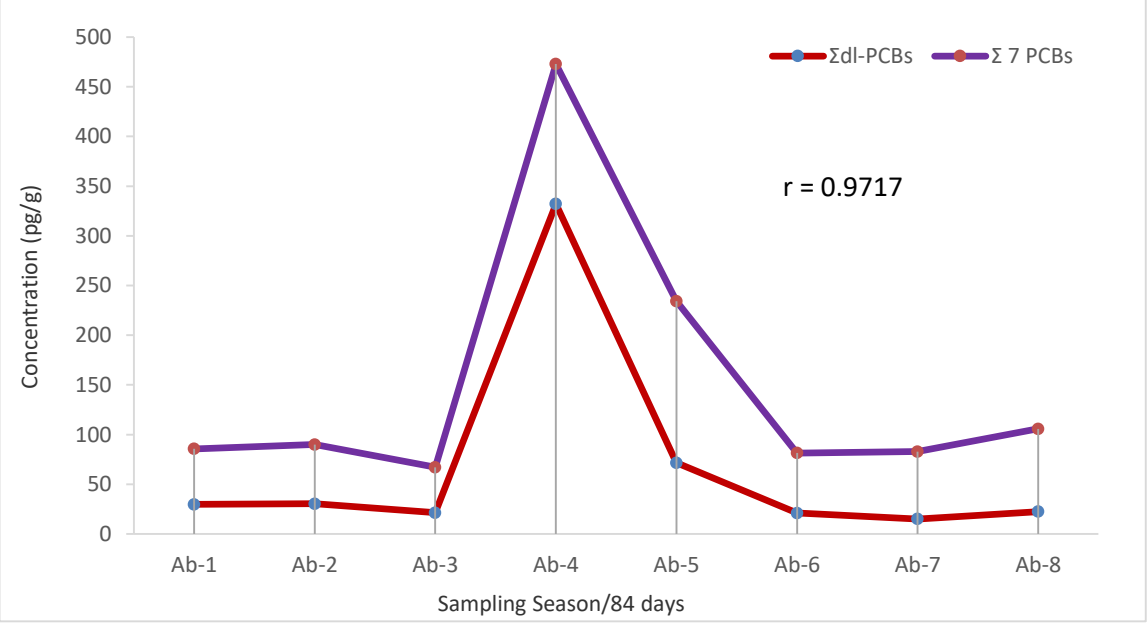


Figure 4-11c: Comparison of indicator PCB and dioxin-like PCB trend

The Pearson's correlation value r for the two groups (indicator PCBs and that of dioxin-like PCBs) was 0.9717, a very strong positive association with a 0.007 ($p < 0.05$) significance. The likely reason for this observation in trend would be same emission source, where probably all the PCBs were being produced from a particular source during all the sampling period and no diffuse source might have contributed to the levels of PCBs observed at Abetifi.

4.2.8 Toxicity equivalency and exposure assessment of dioxin and dioxin-like PCBs

The use of Toxicity Equivalence Factors (TEFs) and Toxicity Equivalency (TEQs) is a key component in risk assessment. So far, it is the best available approach to assess health risks from mixtures of dioxin-like chemicals (TSD, 2010). The current WHO data available for TEF calculation is the 2005 TEF (i.e. TEF $_{WHO-05}$). This was used in the calculation of the TEQ in this work. For the exposure assessment in this study, a 20 m^3 of air was used as the inhaled volume of air per day for an adult of an average weight of 70 kg (WHO, 2000b). Table 4-6 shows the toxicity equivalency (TEQs) values for dioxins and furans, summed as total dioxins, and the TEQ values for dioxin-like PCBs. It also comprises "TEQ ratio" which shows the contribution from dl-PCBs to the total dioxin-like chemicals present in the air. Furthermore, the table contains the exposure assessment calculated for total dioxins and for dioxin-like PCBs at Abetifi on a daily basis.

Table 4-6: TEQ & exposure assessment of dioxins and dioxin-like PCBs

Sampling	(pg TEQ m-3)			TEQ Ratio	(pg/kg bw per day)	
Time points	TEQ PCDD/F	TEQ dl-PCBs	Σ TEQ (PCDD/F+dlPCB)	dl-PCB / (PCDD/F)	PCDD/F Exposure	dl-PCB Exposure
Ab-1	0.0039	0.0010	0.0049	0.2600	0.0011	0.0003
Ab-2	0.0072	0.0019	0.0091	0.2673	0.0021	0.0006
Ab-3	0.0132	0.0039	0.0171	0.2996	0.0038	0.0011
Ab-4	0.0089	0.0102	0.0191	1.1490	0.0025	0.0029
Ab-5	0.0195	0.0039	0.0234	0.1992	0.0056	0.0011
Ab-6	0.0122	0.0025	0.0147	0.2043	0.0035	0.0007
Ab-7	0.0162	0.0024	0.0186	0.1494	0.0046	0.0007
Ab-8	0.0160	0.0031	0.0191	0.1938	0.0046	0.0009

The TEQ values for dioxins and furans together calculated for Abetifi, ranged from 0.004 pg WHO_{2005} TEQ/m^3 (Ab-1) to 0.020 pg WHO_{2005} TEQ/m^3 (Ab-5). These concentrations are within the range of what was measured by Bogdal *et al.* (2012) in Latin America (0.009—0.678 pg WHO_{98} TEQ/m^3) and the Pacific Islands (0.001–0.87 pg WHO_{98} TEQ/m^3) and comparable to that recorded in Mexico (0.022 pg WHO_{98} TEQ/m^3). The Abetifi concentration is however far lower than those recorded in other European countries (WHO, 2000b) Such as the measurements done in Brazil which gave a range of 0.037–0.167 pg WHO_{98} TEQ/m^3 (Bogdal *et al.*, 2012) and in Mexico in 2009 (< 0.001–0.410 pg WHO_{98} TEQ/m^3) Bogdal *et al.* (2012) cited Cardenas *et al.* (2011).

The dioxin-like PCB TEQ values in this study (Abetifi-Ghana), is in the range of 0.001 pg WHO_{2005} TEQ/m^3 (Ab-1) to 0.010 pg WHO_{2005} TEQ /m^3 (Ab-4) (Table 4-4). This range is comparable in magnitude to that recorded by Syed *et al.* (2013) (0.001–0.031 pg WHO_{2005} TEQ /m^3) but lower than what was measured over large areas by Bogdal *et al.* (2012): Africa (0.007–0.278 pg WHO_{98} TEQ/m^3), Latin America (0.001–0.248 pg WHO_{98} TEQ/m^3) and the Pacific Island (0.023 pg WHO_{98} TEQ/m^3).

The total dioxin-like chemicals (PCDD/F+dl-PCB) gave exposure values in the range of approximately 0.005–0.02 pg WHO_{2005} TEQ/m^3 in this work. This compares with various sites from the Manizales city as reported by Cortes *et al.* (2014). Sites from the Manizales city in Colombia as Liceo (0.011 pg WHO_{2005} TEQ/m^3), Palogrande (0.007 pg WHO_{2005} TEQ/m^3), Sena (0.001 pg WHO_{2005} TEQ/m^3) and Nubia (0.016 pg WHO_{2005} TEQ/m^3). It is worth noting that the dl-PCBs contribution (in ratio) to the total dioxin-like chemical toxicity in the air in this study was about 0.2 for all the sampling times except for Ab-4 where, the contribution was approximately 115% higher than that from total dioxins. This result is comparable to Heinzow *et al.* (2004).

In this work, Heinzow *et al.* (2004) had high contributions from dl-PCBs (0.89–0.94 in ratio) than the dioxins and furans. This contribution (1.15 fold) from DL-PCB from Abetifi is basically as a result of the high concentration of PCB 118 recorded in Ab-4. Cortes *et al.* (2014) cited Yeo *et al.*, 2004 as reporting PCB 118 as the predominant congener from rural areas of Kyonggi-do, Korea. PCBs with higher chlorination may increase human health risks because such PCBs are retained longer in fatty tissues (Dodoo *et al.*, 2013) and PCB 118 is penta-chlorinated hence it has a higher health risk potential.

4.2.9 Exposure assessment to dioxin and dioxin-like chemicals

Cancer risk which can be caused by dioxin-like chemicals are of importance in assessing how much of such chemicals humans are exposed to in the study area. Computations from this study reveal daily exposure to atmospheric dioxins at Abetifi to be in the range of 0.0011 to 0.0056 pg/kg bw per day (Table 4-4). The least exposure was recorded in the first quarter of the year 2010 and the highest exposure was observed in which occurred in the first quarter of the year 2011. The dioxin-like PCBs were lower in the range of 0.0003 to 0.0029 pg/kg bw per day. The total daily atmospheric exposure to all the dioxin-like chemicals analysed (i.e. dioxin, furans and dl-PCBs) from Abetifi will therefore be in the range 0.0014 to 0.0067 pg/kg bw per day.

4.2.10 Flame retardants

4.2.10.1 Concentration of polybrominated diphenyl ethers

Figure 4-12a shows a graph of commercial polybrominated diphenyl ether (PBDE) congeners analysed in air (pg/m^3) from Abetifi, Ghana. These include deca-BDE (PBDE 209), octa-BDE (PBDE 183) and penta-BDE (PBDE 47 & 99). The total PBDE in this study (Σ_{10} PBDE) was in the range of 0.438 pg/m^3 to 1.241 pg/m^3. These values were far lower than what was recorded in Faraar *et al.* (2006) (Σ_{10} PBDE - 8 pg/m^3) and extremely lower than what was documented by Yang *et al.* (2013) (Σ_{12} PBDE - 67 pg/m^3). However, it is higher than data by Zhu *et al.* (2014) with concentrations averaging 0.08 pg/m^3.

From the study, the dominant commercial PBDE homologues are penta- and deca-BDEs, same was recorded by Su *et al.* (2010) from Alert site in Canada. Octa-BDE was least in all the sampling seasons with concentrations in the range of 0.06 pg/m^3 in Ab-6 to 0.11 pg/m^3 in Ab-8. In the first year, the deca-BDE was the highest during all sampling time points and throughout the study, its concentrations ranged from 1.467 pg/m^3 (Ab-8) to 6.04 pg/m^3 (Ab-2). The maximum concentration of deca-BDE (BDE 209) recorded is comparable to work done by Hearn *et al.* (2012) where BDE 209 concentration gave 6.4 pg/m^3.

The concentration trend of PBDEs from the study (octa-BDE < penta-BDE < deca-BDE) reveals the global production trend and release of such flame retardants into the environment in 1999 (Sjodin *et al.*, 2003). In that year, the global demand was estimated to be close to 70,000 metric tonnes in which 13% of it were produced as penta-, 6% as octa- and 81% as deca-BDE, respectively (Sjodin *et al.*, 2003) and in

2001, the global demand for the deca- formulation was estimated at 56,100 tonnes and that for the penta- product was 7,500 tonnes (Harrad and Hunter 2006).

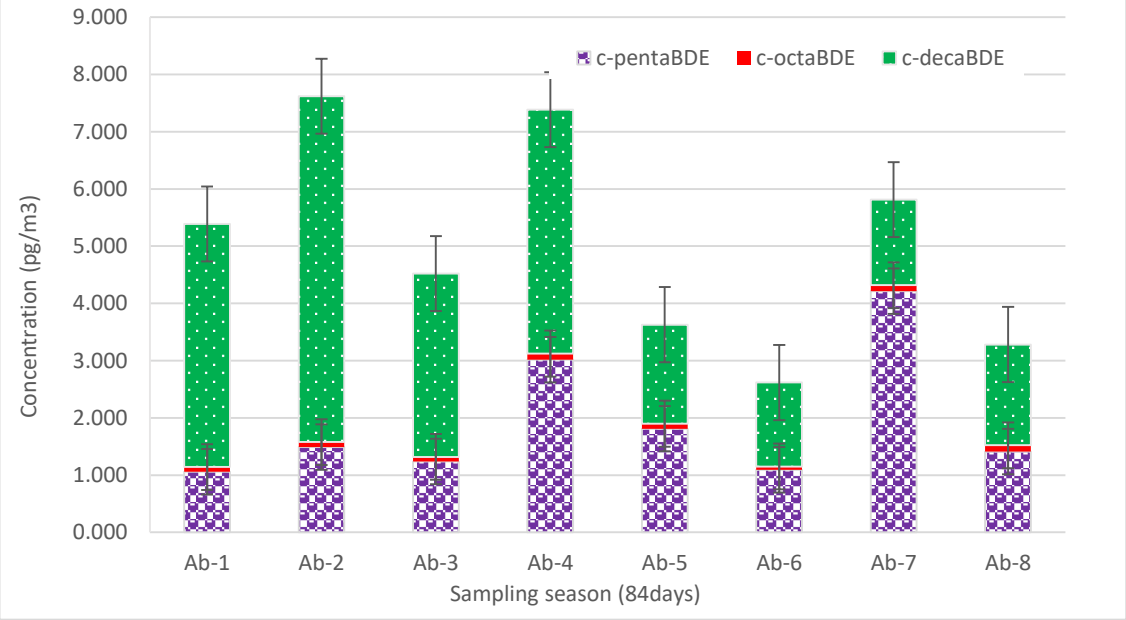


Figure 4-12a: Commercial PBDE congeners (pg/m^3) analysed in air.

Deca-BDE (BDE 209) has been used in plastic housings for electrical goods such as televisions and computers, as well as in textiles. The detection of high levels of BDE 209 could be a signature of its burning of such materials in the open. Open burning is very common in Ghana. Though deca-BDE is expected to partition into a particulate phase (Bossi *et al.*, 2015; de Wits *et al.*, 2010) than the gas phase, it was on the contrary, detected more in this study eventhough the method used (PUF) is expected to adsorb more gas-phase analytes.

The pentabromodiphenyl ether (PBDE 47 & 99) concentrations recorded in Abetifi were from 0.15 pg/m^3 (Ab-1) to 0.6 pg/m^3 (Ab-7). This range was far lower (lower in the order of 0.1) than what was recorded by Pozo *et al.* (2006). They measured 2.0 pg/m^3, 5.0 pg/m^3 and 5.8 pg/m^3 form Alert site in Canada, Barrow in Alaska and Nyalesund at Svalbera respectively. From the result of this study, 62.5% of the

concentrations were approximatly 0.2 pg/m^3, same as reported for Canada (Pozo *et al.*, 2006). Octabromodiphenyl ether (octa-BDE) recorded the least concentration in this study. This is probably a reflection of its global percentage release before their ban (i.e. 15% in 1992 and 6% in 1999) (Sjodin *et al.*, 2003).

4.2.10.2 Meteorological trends with concentration of deca- & penta-BDEs

From Figure 4-12b, the effect of rainfall, temperature and humidity patterns were observed pertaining to the trend in concentration of BDE 209 recorded in this study. The humidity-dependence concentration of BDE 209 gave a correlation of 0.609. This reveals a 61% influence on the concentration of BDE 209 as regards the humidity pattern. Rainfall pattern correlated weakly but positively with BDE 209 concentration to the extent, 18% (Pearson's correlation, r = 0.175).

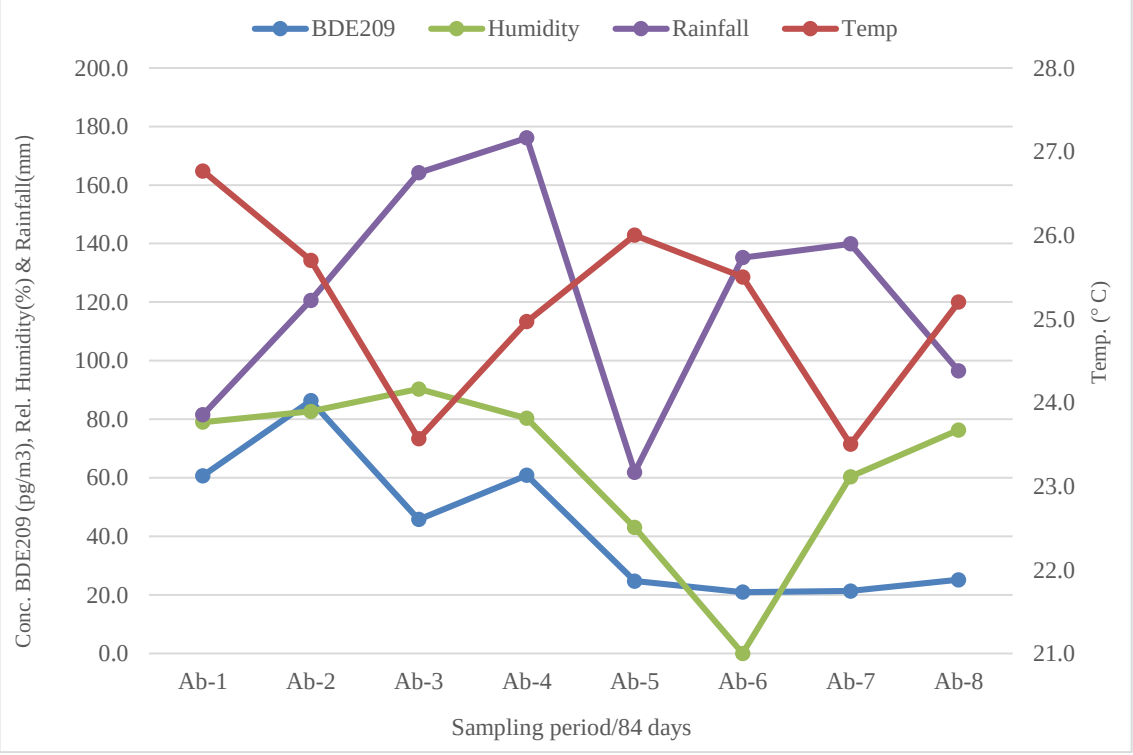


Figure 4-12b: Comparison of BDE209 (pg/m^3) with rainfall, temperature &humidity trends

Deca-BDE (BDE 209) is expected to partition into a particulate phase (Bossi *et al.*, 2015) subsequently, work done by Wang *et al.* (2012) in Southern China recorded mean value of 41 pg/m^3 with 4 pg/m^3 in the gas phase and 37 pg/m^3 in the particulate phase. Wang *et al.* (2012) assigned high temperature as one of the reasons for the high concentration of the total PBDEs (Σ_{14} PBDEs - 58 pg/m^3). The mean summer temperature prevailing at the time was of 26–28 °C. Comparatively in this study temperature range was slightly lower, a range of 23.5–26.8 °C. The temperature pattern in this work associated with the concentration of BDE 209 to a 29% extent.

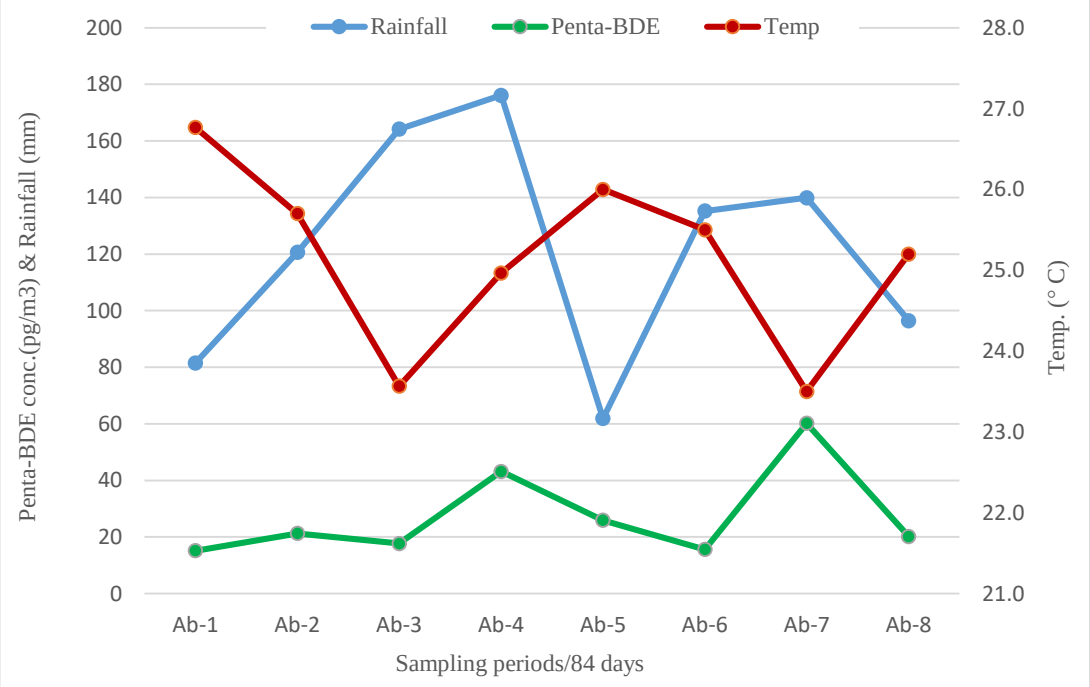


Figure 4-12c: Comparison of Penta-BDE (pg/m3) with rainfall and temperature patterns

Unlike the trend observed for deca-BDE (BDE 209) concentrations with reference to rainfall pattern (correlation, r = 0.175 i.e. 18%) (Figure 4-12b), the penta-BDE (BDE 47 & 99) showed a higher influence of rainfall pattern (37%) (a Pearson correlation value r = 0.369) (Figure 4-12c). According to the method used in this study, the PUFs

were shielded from both rainfall and sunshine by the sampler-type (i.e. bowls) deployed. Yet, from the results PBDE concentrations correlated positively with rainfall pattern.

In France, Castro-Jiménez *et al.* (2011) recorded high concentrations of gas-phase PBDEs in summer between May and August with prevailing temperatures of 19–22 °C and made the observation that, it was probably the time when there was high volatilization. Similarly with reference to de Wits *et al.* (2010), re-volatilization or re-emission of PBDEs from secondary sources such as sink is a process largely controlled by temperature changes. It is therefore expected that the atmospheric concentrations should correlate considerably with temperature (Bossi *et al.*, 2015) positively (de Wits *et al.*, 2010). Nonetheless the concentrations of the penta-BDEs recorded in this study are basically affected negatively by temperature (Figure 4-12c) with a Pearson correlation value r, being -0.554.

As postulated by Harner and Shoeib, (2002), at zero degrees Celcius (0° C), BDE 47 will have 88% association with particles and BDE 99 will have 97% association. Total penta-BDE in this work is basically BDE 47 & 99. Prevailing temperature in this work ranged from 23.5 to 26.8 °C. Hence the penta-BDEs might all be in the gas-phase. Particulate BDEs are subject to long range transport (de Wits *et al.*, 2010). It can therefore be concluded that, the source of penta-BDEs is not as a result of long range atmospheric transport but could be a local one. Open burning of household items in the area could be a possible contamination source of Penta-BDEs.

4.2.10.3 Concentration of hexabromocyclododecanes

From the study (Figure 4-13), all the technical isomers of hexabromocyclododecanes (HBCD) were detected during all the sampling seasons or time points. Percentage detection frequencies were 100% alpha (α), 87.5% beta (β) and 100% (γ) gamma. The total concentrations of Σ HBCD ranged from 0.0003 to 0.0037 ng/m^3. Beta HBCD was least concentrated during all the sampling period. This result is in conformity to the percentage of beta component (1—12%) found in technical mixtures of HBCD.

HBCDs were detected in this study and results were in the range of 0.6—3.7 pg/m^3 (Figure 4-13). The maximum value recorded in this study is just a little above the minimum value (2 pg/m^3) of the Swedish urban study Covaci *et al*. (2006). This could be due to the high lipophilicities and low vapour pressures of HBCDs which makes the majority of the airborne fraction sorbed to particulate matter as such, allowing only a minor fraction in the gas phase Covaci *et al*. (2006) for adsorption onto PUF and for detection.

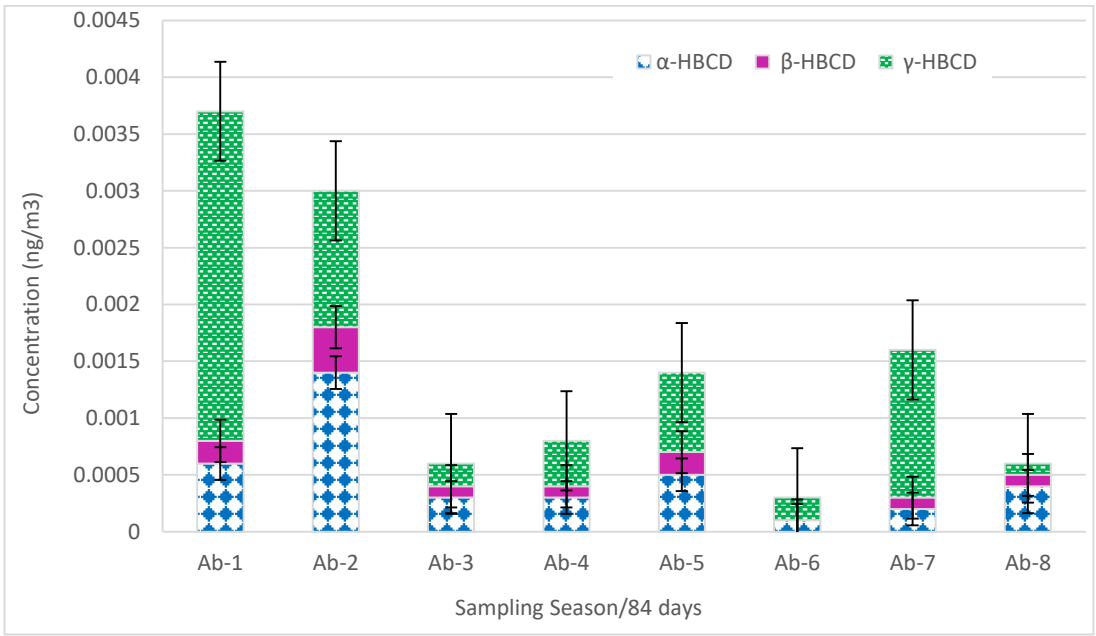


Figure 4-13: Technical (commercial) HBCD isomers analysed in air (ng/m^3)

4.2.10.4 Concentration of polybrominated biphenyls

Polybrominated biphenyls (PBBs) specifically hexabromobiphenyl was included in the chemicals listed for elimination under the Stockholm convention on POPs which was amended in 2009 (UNEP, 2009). In this study, ten (10) brominated biphenyl congeners were analysed for (Table 4-7). These included monobiphenyl (moBB 3), dibromobiphenyl (diBB 15), tribromobiphenyl (triBB 18), tetrabromobiphenyl (teBB 52), pentabromobiphenyl (peBB 101), hexabromobiphenyl (hxBB 153), heptabromobiphenyl (hpBB 180), octabromobiphenyl (ocBB 194), nonabromobiphenyl (noBB 206) and decabromobiphenyl (deBB 209).

Table 4-7: Concentration of PBBs (ng/m^3) in air

PBB/				Samplig	Periods			
(ng/m3)	Ab-1	Ab-2	Ab-3	Ab-4	Ab-5	Ab-6	Ab-7	Ab-8
moBB 3	0.0031	0.0054	0.0082	0.006	<0.001	<0.001	0.0183	0.0205
diBB 15	<0.001	<0.001	<0.001	<0.001	0.0121	0.015	0.0142	0.0047
triBB 18	0.0015	0.0046	0.0058	0.0043	0.005	0.0028	0.007	0.0076
teBB 52	<0.001	<0.001	<0.001	<0.001	0.002	0.0005	0.0041	0.0013
peBB 101	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0024
hxBB 153	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0035	<0.001
hpBB 180	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
ocBB 194	<0.001	<0.001	<0.001	0.0113	<0.001	<0.001	<0.001	<0.001
noBB 206	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
deBB 209	0.014	0.0258	0.0108	<0.001	<0.001	<0.001	<0.001	0.0289
Sum of PBBs	0.0186	0.0358	0.0248	0.0216	0.0191	0.0182	0.0471	0.0653

From the study (Table 4-7), hepta- and nona-bromobiphenyls (one of the commercial PBBs) were not detected at all during the sampling. The other eight had the following percentage occurrence during the study period; moBB 3 had 75% occurrence, diBB

15, teBB 52 and deBB 209 all recorded 50% occurrence and triBB 18 had 100% occurrence. This means the triBB 18 is the dorminant bromobiphenyl congener at Abetifi. Chao *et al.* (2014) had diBB15, a much lower weight PBB as their most prevalent congener when they measured PBBs in the air above the ocean. Wang *et al.* (2010) recorded a different congener, hexabromobiphenyl (hxBB153) as the dorminant PBB. This bromobiphenyl (hxBB 153) is the main congener under consideration, selected by the Stockholm Convention for monitoring. In this work, it was only recorded during sampling period Ab-7 with a comparably low concentration of 0.0035 ng/m^3.

The other PBBs (peBB 101, hxBB 153 and ocBB 194) measured in Abetifi, had an occurrence of 12.5% each during the study period. However, decabromobiphenyl (deBB 209), which is one of the commercial PBBs contributed 0.0289 ng/m^3 to the total concentration (Σ_{10} PBB - 0.0653 ng/m^3) during sampling season Ab-8. The total concentration, Σ_{10} PBB - 0.0653 ng/m^3 in this study is higher than that detected by Chao *et al.* (2014) in Taiwan. They recorded 0.0265 pg/m^3 over the oceanic air and 0.144 pg/m^3 on land. Wang *et al.* (2010) also recorded lower concentration ranging from 0.149 to 0.556 pg/Nm^3 from a rural area.

4.2.11 Concentration of perfluorinated compounds

The groups of perfluorinated compounds (PFCs) measured in this study are

(1) perfluorinated sulfonic acids (PFSAs) / perfluoroalkyl sulfonates

(2) perfluorinated carboxylic acids (PFCAs) / perfluoroalkyl carboxylates and

(3) fluorotelomer alcohols.

4.2.11.1 Concentration of perfluorinated carboxylic acids

A total of eleven (11) perfluorinated carboxylic acids (PFCAs) were analysed. Perfluorobutanoate (PFBA), perfluoropentanoate (PFPA) perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTrDA), perfluorotetradecanoate (PFTeDA). Figure 4-14a is a graph depicting the concentration of the eleven perfluorinated carboxylic acids (PFCAs) in air measured in nanogram per meter cube (ng/m^3). Out of the eleven (11) perfluorinated carboxylic acids (PFCAs) analysed for, three namely, perfluoropentanoate (PFPA), perfluoroheptanoate (PFHpA) and perfluorononanoate (PFNA) were not detected throughout all sampling periods.

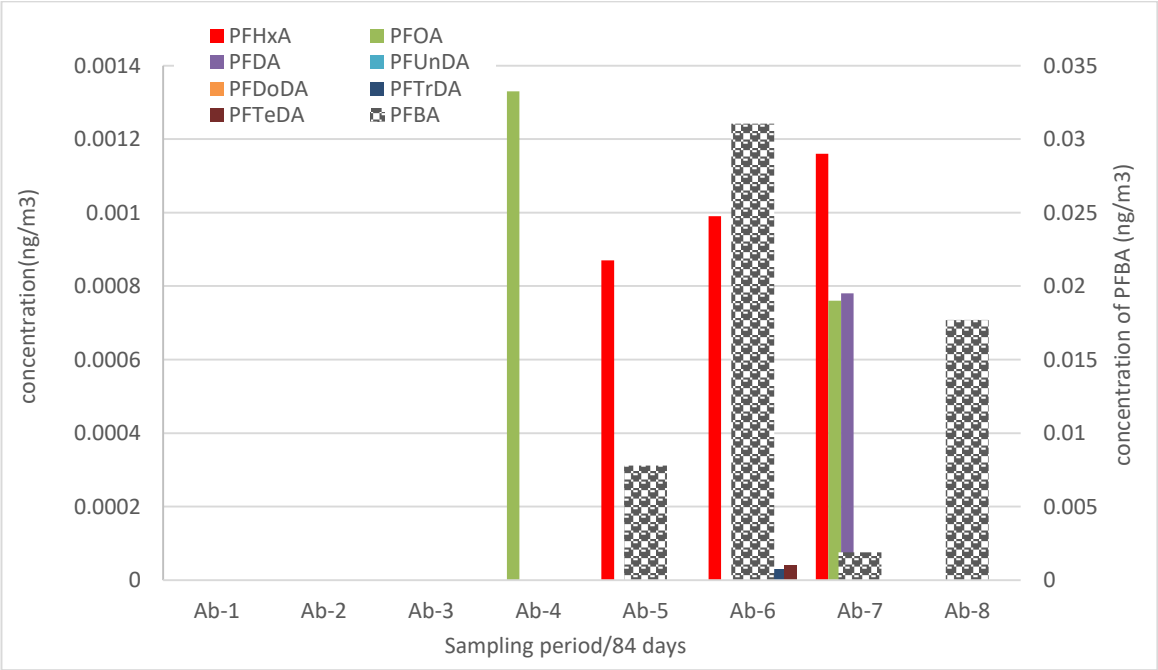


Figure 4-14a: Concentration of perfluorinated carboxylic acids (ng/m^3)

It is interesting to note that, in all the first three quarters of the sampling periods of the first year of sampling (Ab1-Ab-3), no perfluorinated carboxylic acids (PFCAs) were detected. In the fourth quarter of the first sampling year however, perfluorooctanoate (PFOA) was detected as the only carboxylate. PFOA concentration throughout the sampling period ranged from 0.0008 to 0.0013 ng/m^3 recorded in Ab-7 and Ab-4 respectively. The levels of PFOA in this work show very low concentrations as compared to Huber *et al.* (2011) and Jogsten *et al.* (2012) with concentrations of 0.388 ng/m^3 and 0.015–0.21 ng/m^3 respectively. Perfluorobutanoate (PFBA) showed great prevalence in the whole of the second sampling year with the highest concentrations being recorded during sampling period Ab-6, with 0.0311 ng/m^3 and followed by Ab-8 with 0.0177 ng/m^3. These were all lower than what was recorded in Norway (0.12 ng/m^3) by Huber *et al.* (2011) and in Spain by Jogsten *et al.* (2012) (0.072–0.25 ng/m^3). The trend is an indiction of an increasing levels of perfluorinated carboxylic acids in the atmosphere since such are used as surfactants and surface protectors in many consumer products and industrial applications.

4.2.11.2 Concentration of perfluorinated sulfonic acids in air

A total of five (5) perfluorinated sulfonic acids (PFSAs) and five (5) of their pre-cursors were also analysed in this study. The perfluorinated sulfonic acids (PFSAs) were perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS), perfluorododecane sulfonate (PFDS). The pre-cursors were N-methyl perfluorooctane sulfonamide (MeFOSA), N-ethyl perfluorooctane sulfonamide (EtFOSA), perfluorooctane sulfonamide (PFOSA or FOSA), N-methyl perfluorooctane

sulfonamide ethanol (MeFOSE) and N-ethyl perfluorooctane sulfonamide ethanol (EtFOSE).

From the results (Figure 4-14b) three out of the five perfluorinated sulfonic acids analysed for, were dominant. These were perfluorobutane sulfonate (PFBS), perfluorooctane sulfonate (PFOS) and perfluorododecane sulfonate (PFDS). Perfluorooctane sulfonate (PFOS) which is listed on the Stockholm Convention for persistent organic pollutants, was the only sulphonic acid detected during the first sampling year. It recorded 0.00004 ng/m^3 during the first sampling period (Ab-1). This is extremely low compared to 0.09 ng/m^3 measured in Norway (Huber *et al.*, 2011).

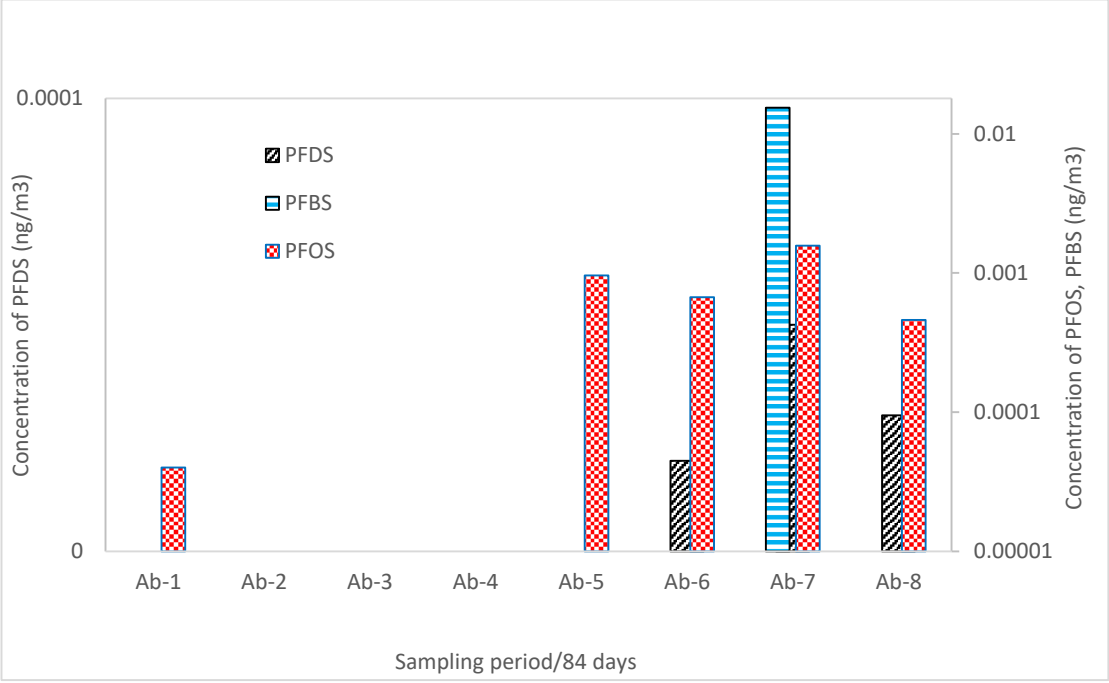


Figure 4-14b: Three prevalent perfluorinated sulfonic acids detected in air (ng/m^3)

In the second sampling year however, quantifiable concentrations were detected (Figure 4-14b). PFOS concentrations prevailed in most of the sampling seasons; except for Ab-7 where perfluorobutane sulfonate (PFBS) was highest with

concentration of 0.0154 ng/m^3. This is close to what was measured in Spain (0.019 ng/m^3) from indoor dust when 10 different houses were sampled. The other houses sampled gave much lower concentrations ranging from 0.0035–0.0058 ng/m^3 (Jogsten *et al.,* 2012).

The pre-cursors of the perfluorinated sulfonic acids analysed for, were all below the limit of quantification in all of the sampling periods except for Ab-6 where a total of three pre-cursors, (MeFOSA, PFOSA and EtFOSE) recorded 0.00006 ng/m^3. All the pre-cursors, N-methyl perfluorooctane sulfonamide (MeFOSA), perfluorooctane sulfonamide (PFOSA or FOSA), and N-ethyl perfluorooctane sulfonamide ethanol (EtFOSE) which basically were the main contributors to the total concentrations measured during the Ab-6, contributed 0.00002 ng/m^3 each. In Ab-8, only EtFOSE was detected. It recorded a concentration of 0.00013 ng/m^3, even higher than the total concentration recorded in Ab-6 (0.00006 ng/m^3) for thre pre-cursors. Comparatively, results from Korea by Kim *et al.* (2012) (0.026–0.027 ng/m^3) and Norway by Jahnke *et al.* (2007) (0.0012 ng/m^3) are much higher than this work. Likewise, results from work done in Japan (Harada *et al*., 2006, 2005), North-America (Shoeib *et al.*, 2011) and China (Zhang *et al.*,2010) are all generally higher than that from this study.

4.2.12 Cluster analyses and principal component analysis for source identification

In this section both Ward's hierarchical clustering analysis and principal component analysis were employed to give a clear classification of analytes as affected by the pollution sources.

The Ward's hierarchical clustering analysis (CA) was performed to visualize the groupings of the various analyte/pollutant groups recorded in this work. The CA used all the variance or information contained in the original data set with the squared Euclidean distance as a similarity measure. This method has minimal space distortion effect and makes use of more information on cluster contents than other methods and has been proven to be an extremely powerful grouping tool (Holland, 2008). As a confirmation tool for the results obtained in this study, the principal component analysis (PCA) was also used in this study to further explore the extent of air pollution by the organic pollutants and to aid in source identification. In the PCA, Varimax rotation with Kaiser Normalization was used to maximize the sum of the variance of the factor coefficients which better explained the possible groups/sources that influenced the air pollution.

4.2.12a Clustering analysis for analyte sources

From Figure 4-15, an R-mode cluster analysis revealed three pronounced clusters on the dendrogram observed at phenon line 10. Clusters 1 includes analyte 7 to 29, cluster 2 includes analyte 6 to 16 and cluster 3 included analyte 58 to 83. Cluster 2 has two subgroups. Subgroup 1 included analyte 6 to 68 and subgroup 2 includes analyte 4 to 16. Cluster 1 members are predominantly polychlorinated biphenyls (PCBs) and cluster 3, polycyclic aromatic hydrocarbons (PAHs). Cluster 2 (with the two subgroups) contains a mixture of dioxins, furans, organochlorine pesticides and polybrominated diphenyl ethers (PBDEs).

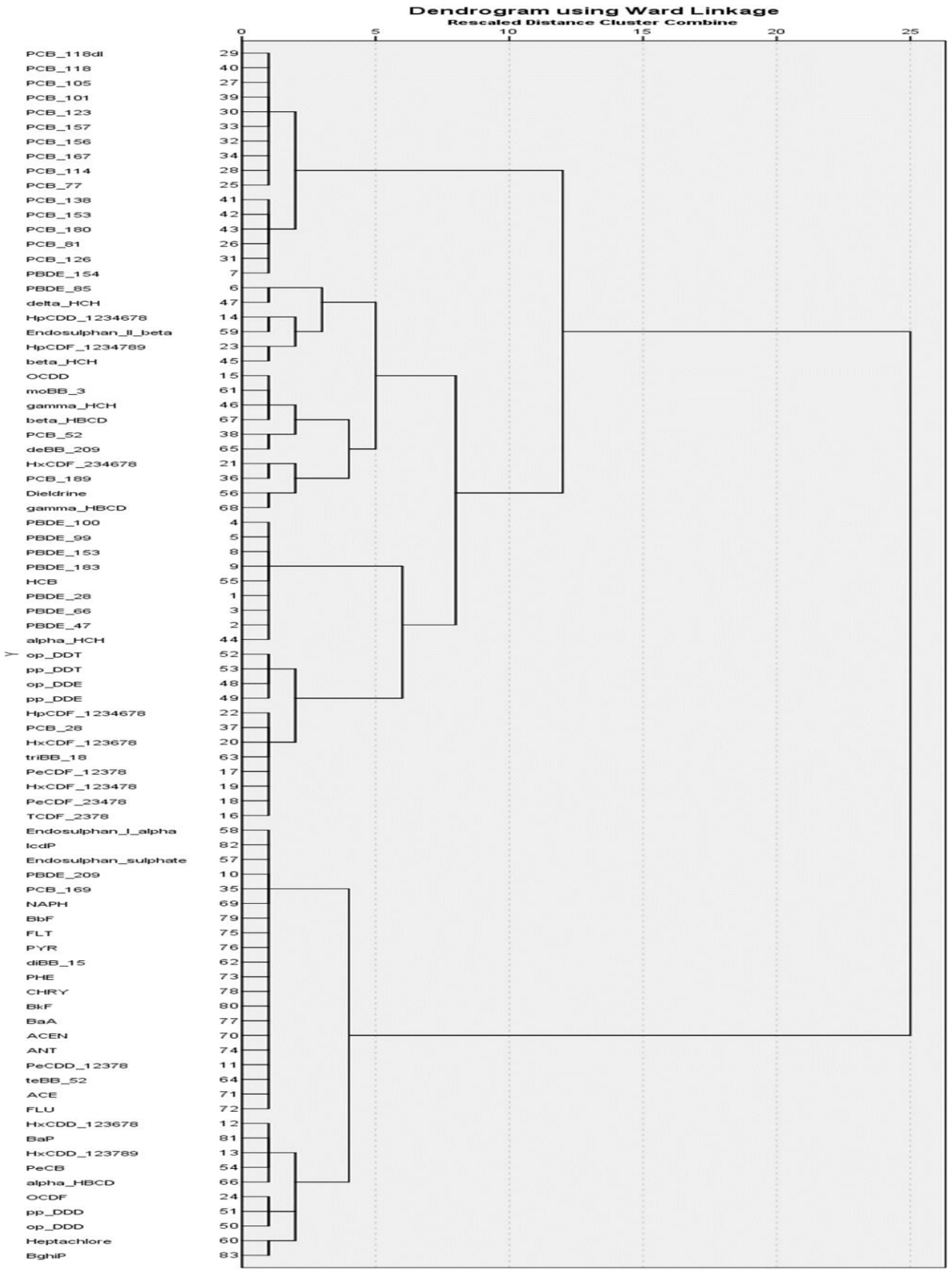


Figure 4-15: Dendogram of measured analytes/pollutants (variables) in air

4.2.12b Principal component analysis for analyte sources

The factor scores for all analytes (POPs) and their distributions are also shown in Tables 4-8. The calculated factor loadings, cummulative percent and percentages of variance explained by each factor in R-mode PCA are listed in Tables 4-9.

In the analysis, four factors with Eigen values >1 were extracted from the varimax-rotated factor analysis of all analytes in the data set. Factor scores represent cumulate contribution of all analytes loaded on a particular factor/principal component. Positive scores in the PCA is an indication that the quality of air is affected by the presence of the pollutants that are significantly loaded on that specific factor/component, whereas negative scores suggest that air quality is essentially unaffected by those pollutants. The Kaiser-Meyer-Olkin measure of sampling adequacy was a 0.791 with a significance of 0.000.

4.2.12c Source identification using cluster and PCA

From the PCA, the first principal component (PC1) in the air sample data sets explains more than 36% of total variance. This is heavily loaded on polycyclic aromatic hydrocarbons (PAHs) and slightly loaded on polychlorinated dibenzo-p-dioxins (PCDDs). The second principal component (PC2), explaining about 25.6% of total variance, has high loadings for polychlorinated biphenyls (PCBs) and a minimal load on polybrominated biphenyl (PBBs) which are flame retardants. The third principal component (PC3) in this study is one accounting for 12.4% of total variance and is heavily loaded on organochlorine pesticides and moderate positive loadings by polychlorinated dibenzo-p-furans (PCDFs). PC4 accounts for about 10% of the total variance and is mostly contributed both principally by polybrominated diphenyl ethers (PBDEs) and minimally on furans (PCDFs).

Table 4-8: The factor scores of analytes/pollutants and their distributions

	Component				
Analytes	PC1	PC2	PC3	PC4	Communalities
PBDE_28	-.152	-.072	.109	**.906**	.861
PBDE_47	-.219	.326	.104	**.809**	.820
PBDE_66	-.305	-.030	.040	**.890**	.887
PBDE_100	.057	**.698**	.180	**.670**	.972
PBDE_99	.130	**.573**	-.001	**.775**	.946
PBDE_85	-.415	-.027	-.245	**.636**	.364
PBDE_154	.285	**.603**	.368	**.687**	.818
PBDE_153	-.030	.411	-.064	**.813**	.835
PBDE_183	.213	.156	.281	**.793**	.778
PBDE_209	.127	.109	-.227	**.614**	.936
PeCDD_12378	**.957**	.105	-.257	-.028	.994
HxCDD_123678	**.881**	-.045	.123	-.077	.799
HxCDD_123789	**.732**	-.236	.055	.493	.838
HpCDD_1234678	**.601**	-.334	-.327	-.035	.580
OCDD	**.775**	-.272	-.326	-.099	.791
TCDF_2378	-.333	.345	**.545**	.279	.605
PeCDF_12378	-.304	.387	**.734**	.251	.842
PeCDF_23478	-.212	.217	**.735**	.235	.688
HxCDF_123478	-.283	.286	**.761**	.368	.877
HxCDF_123678	-.230	.054	**.739**	.470	.824
HxCDF_234678	.236	-.235	**.749**	-.122	.688
HpCDF_1234678	***-.530***	.165	**.680**	.394	.693
HpCDF_1234789	.252	-.609	**.561**	.479	.978
OCDF	**.734**	.146	**.617**	-.120	.955
PCB_77	.193	**.931**	.259	.037	.974
PCB_81	.064	**.755**	.543	.226	.920
PCB_105	.246	**.950**	-.081	-.014	.969
PCB_114	.369	**.920**	.023	.003	.983
PCB_118dl	.247	**.943**	-.109	-.012	.962
PCB_123	.364	**.877**	.169	.056	.934
PCB_126	.067	**.793**	**.534**	.138	.938
PCB_156	.339	**.919**	.097	.019	.970
PCB_157	.481	**.795**	.213	.016	.909
PCB_167	.288	**.923**	.154	.032	.959
PCB_169	.253	**.757**	-.429	-.116	.834
PCB_189	.137	**.548**	-.602	-.058	.684
PCB_28	.179	**.576**	.349	.452	.691
PCB_52	-.363	**.587**	-.323	.143	.602
PCB_101	.114	**.921**	-.050	.099	.874
PCB_118	.237	**.941**	-.112	-.033	.955
PCB_138	-.085	**.920**	.279	.110	.944
PCB_153	-.149	**.881**	.265	.156	.894
PCB_180	-.282	**.700**	.430	.154	.779

Table 4-8 cont: The factor scores of analytes/pollutants and their distributions

	Component				
Analytes	PC1	PC2	PC3	PC4	Communalities
alpha_HCH	-.117	.029	**.884**	.005	.797
beta_HCH	-.063	***-.507***	**.640**	.427	.854
gamma_HCH	.242	-.319	**.651**	.075	.590
delta_HCH	-.159	-.406	**.648**	.054	.394
op_DDE	-.313	.185	**.820**	.033	.805
pp_DDE	-.348	.002	**.870**	.067	.883
op_DDD	**.586**	.289	**.687**	-.052	.901
pp_DDD	**.621**	.073	**.695**	-.070	.880
op_DDT	-.140	.376	**.796**	.156	.818
pp_DDT	-.267	.298	**.861**	.103	.912
PeCB	**.730**	.273	**.505**	.052	.865
HCB	-.021	.067	**.874**	.421	.946
Dieldrine	-.162	-.401	**.522**	.472	.682
moBB_3	.221	**.797**	.041	-.393	.841
diBB_15	.127	**.925**	-.300	-.121	.977
triBB_18	-.004	**.699**	**.820**	**.548**	.982
teBB_52	.112	**.950**	-.275	-.024	.990
deBB_209	***-.653***	**.604**	-.068	.172	.825
alpha_HBCD	.127	-.110	-.095	**.598**	.395
beta_HBCD	-.490	-.071	-.030	***-.728***	.776
gamma_HBCD	.178	-.096	.345	***-.826***	.843
NAPH	**.921**	.101	-.366	.007	.993
ACEN	**.920**	.182	-.158	-.083	.911
ACE	**.950**	.083	-.273	-.009	.985
FLU	**.982**	.077	-.128	-.023	.986
PHE	**.954**	.141	-.197	-.101	.979
ANT	**.929**	.151	-.140	-.086	.912
FLT	**.914**	.152	-.301	-.146	.971
PYR	**.906**	.147	-.299	-.134	.950
BaA	**.864**	.151	-.358	-.092	.906
CHRY	**.872**	.138	-.374	-.179	.952
BbF	**.920**	.059	-.350	-.057	.976
BkF	**.887**	.148	-.375	-.107	.960
BaP	**.963**	-.077	.109	.017	.945
IcdP	**.854**	.295	.217	-.043	.865
BghiP	**.647**	.261	.219	-.494	.578

The Table 4-8 also shows a Varimax rotated factor loadings and communalities of the organic pollutants analysed in air from Abetifi (significant values, in bold type face).

Table 4-9: Factor loadings, cummulative percent and percentages of variance

	PC1	PC2	PC3	PC4
Eigen values	30.329	21.219	10.280	7.951
% of Variance	36.541	25.565	12.386	9.579
Cummulative %	36.541	62.106	74.492	84.072

The major groups revealed in both the cluster analysis and the principal component analysis are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides and polybrominated diphenyl ethers (PBDEs). The other pollutants were polychlorinated dibenzo-p-furans (PCDFs), which distributed itself partly with the organochlorine pesticide group and PDBE group, and polychlorinated dibenzo-p-dioxins (PCDDs) which also was associated with PAH group and organochlorine pesticide group.

PAHs are major emission products from vehicles as well as being a source of incomplete combustion of organic matter. The later source of PAH production also produces both dioxins and furans. This group compares very well with the cluster 3 observed in Figure 4-15. This pollution source can be said to be derived from vehicular fuel combustion sources. Abetifi which is the sampling site has close proximity to one busy highway in Ghana, Nsawam-Nkawkaw-Ejisu road where all types of vehicle ply (24 hours a day, seven days a week) including the very heavy duty trucks transporting goods from the hinterlands to the cities and to other neighbouring countries and vice versa. This therefore is a vehicular pollution source and partially from burning of inorganic matter.

The PCB pollutant group found in the atmosphere can be traced essentially to the combustion of some capacitor and transformer oils. Additionally, PCBs were also vitally added in small quantities to plastics, paints, flame retardants, plasticizers,

surface coatings, wire insulators and metal coatings and their combustion are also important atmospheric sources of PCBs. However, using the prevalent homologue source apportionment (section 4.2.5.1), long range atmospheric transport was observed. Consequently components in PC2 (which agrees to cluster 1), are derived from incineration of various PCB-containing items as afore mentioned but from a long range source.

In this group organochlorine pesticides may be considered the most important analytes. Organochlorine pesticides were extensively used in Ghana in the agricultural sector to curb crop pest in most farming communities. This third component (PC3 = cluster 2a) is a mixed source derived from farming activities, incineration and re-volatilization from sinks (soil and or sediment).

The fourth component (Table 4-8) includes groups of polybrominated diphenyl ethers (specifically, penta-brominated diphenyl ethers) and furans. This association could either be based on their emission sources and or their chemical compositions. Penta-brominated diphenyl ethers is a flame-retardant used in carpets, furniture and bedding and furans are also known basically to be produced from incomplete combustion of many processes including incineration of waste generated from furniture and upholstry. This pollution source may be one of incomplete inorganic combustion. Both groups of pollutants (PBDE and furans) are noted to contain an ether (-o-) group. This might be the shared similarity between them and the responsible factor for their clustering.

Table 4-10 shows the atmospheric pollution sources from Abetifi using cluster analysis & factor loadings. Conclusively, four clusters were observed and four major factor loadings were realized in this study and these point to the pollution sources prevailing

at Abetifi as being vehicular, incineration, farming, industrial and other anthropogenic activities.

Table 4-10: Air pollution source signatures from Abetifi using cluster analysis & factor loadings

Cluster Analysis	Factor Analysis	Principal Analyte	Possible pollution source
Cluster 1 =	PCA2 =	Polychlorinated biphenyls	Long range atmospheric transport & incineration
Cluster 2a =	PCA3 =	Organochlorine pesticides	Re-volatilization from farmland soils
Cluster 2b =	PCA4 =	Polybrominated diphenyl ethers	Burning of upholstry
Cluster 3 =	PCA1 =	Polycyclic aromatic hydrocarbons	Vehicular & burning of inorganic matter

4.2.12d Cluster and principal component analysis for sampling season identification

The cluster and factor (PCA) analyses were again used to identify the seasonal variations in the sampling periods (Figure 4-16a, Figure 4-16b, Figure 4-16c).

When observed at phenon line 10, two distinct clusters can be distinguished in the dendrogram obtained from the cluster analysis performed based on the analyzed parameters (Figure 4-16a). Cluster 1 includes season Ab-1, Ab-2, Ab-3 and Ab-4 and cluster 2 includes Ab-5, Ab-6, Ab-7 and Ab-8.

The relationship between the different sampling periods which were also investigated using principal component analysis and a scatter plot, generated using the first two principal components (Figure 4-16b) and the first and third principal components

(Figure 4-16c). The seasons Ab-2 and Ab-3 are located between 1 and 1.5 on the scale and same for Ab-6 and Ab-8 axcept that is found in the opposite direction.

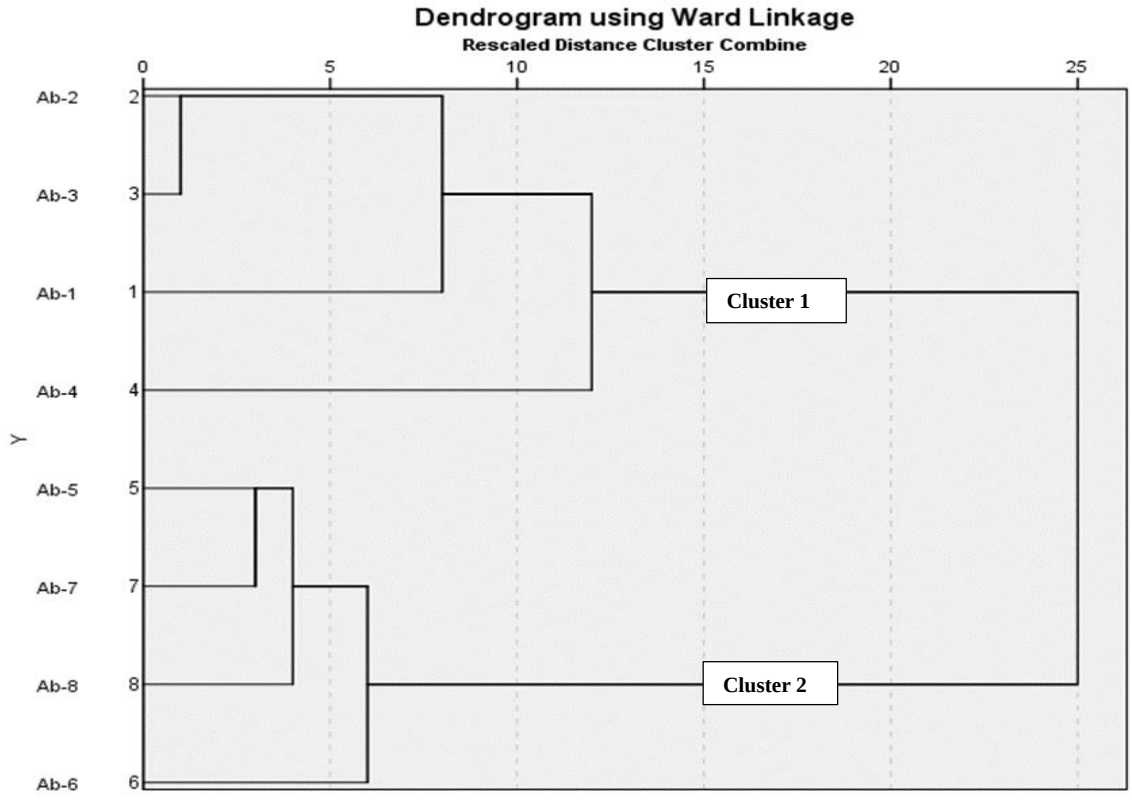


Figure 4-16a: A hierarchical dendrogram for the sampling seasons (cases)

Remarkably and interestingly, all the cases (Figure 4-16a, Figure 4-16b, Figure 4-16c) which can be distinguished by the two distinct groups represent the different sampling years. Sampling year one was in 2010 and year two, 2011. This means that there was no similarities or common factor strong enough to affect the concentration of analytes recorded in year 2010 and that of 2011.

Therefore, the individual quarterly sampling seasons in both years were not grouped together. The distinction was clearly an annual segregation.

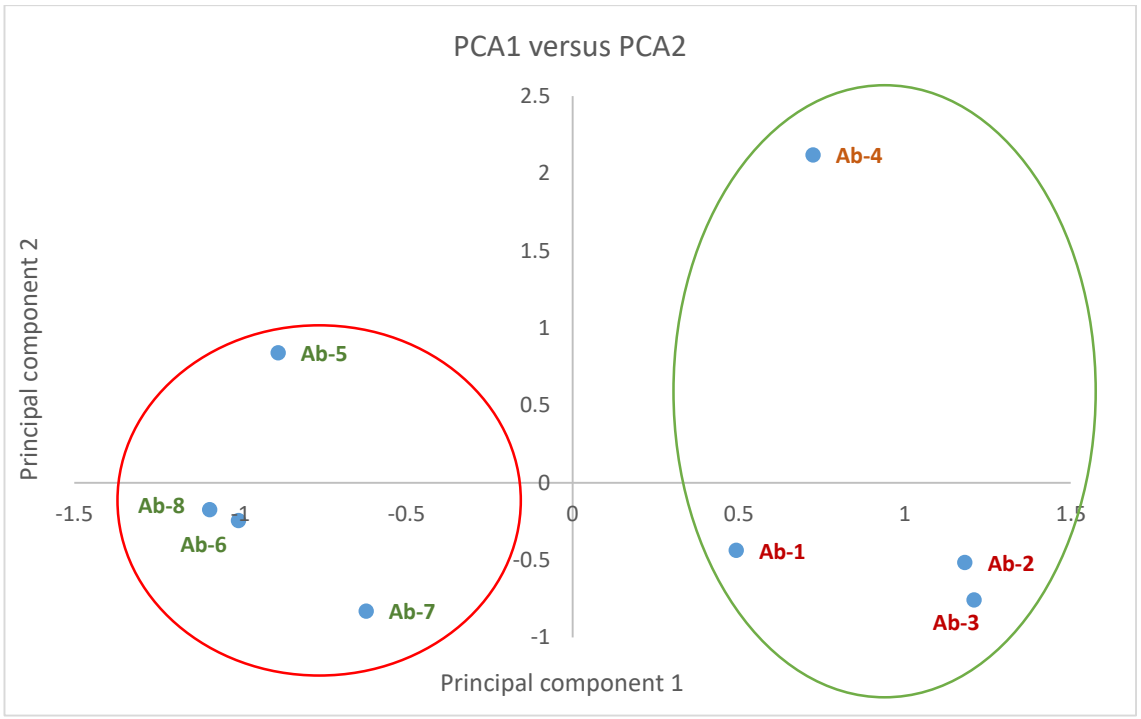


Figure 4-16b: A plot of principal component 1 versus principal component 2 showing two distinct sampling years

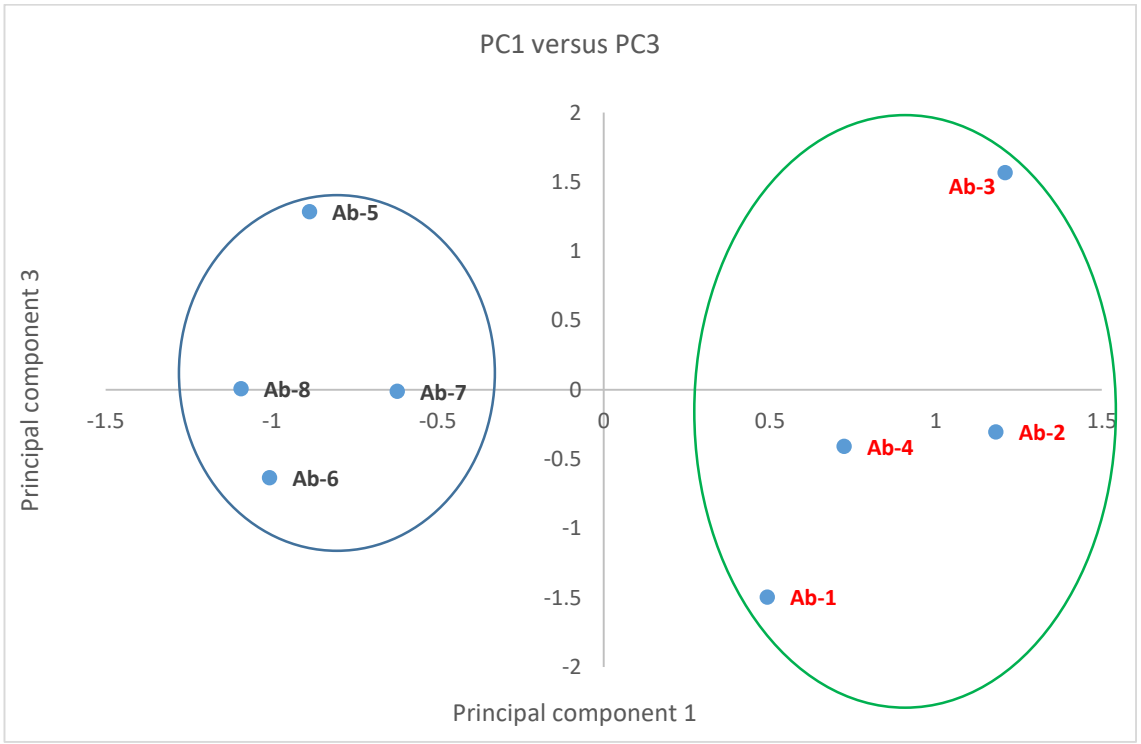


Figure 4-16c: A plot of principal component 1 versus principal component 3 showing two distinct sampling years

4.2.13 Heavy metal analysis using PUF

The Table 4-11 below is the research results from using polyurethane foams (PUFs) as a method modification. In this method, two PUFs each from MONET and Ghana were deployed at the same time and monitored for heavy metals. The samples were collected every 28-days.

From the study (Table 4-11), the concentrations from the MONET PUFs recorded lead (Pb) values that ranged from 0.007 to 0.074 µg/m^3, manganese (Mn) from 0.087 to 0.050 µg/m^3, cadmium (Cd) from 0.015 to 0.070 µg/m^3 and chromium (Cr) from 0.011 to 0.063 µg/m^3. Copper (Cu) concentrations were between 0.069 and 0.117 µg/m^3. Nickel (Ni) levels were from 0.006 to 0.024 µg/m^3.

The results from using the MONET PUFs, showed the highest concentration recorded for copper (0.117 µg/m^3) and this was detected in the first month of the monitoring whereas Ni recorded least concentration (0.006 µg/m^3) which was consistently noted in both first and second months.

The concentrations from the Ghana (locally-prepared) PUFs, recorded lead concentrations ranging from 0.004 to 0.077 µg/m^3, manganese (Mn) from 0.040 to 0.094 µg/m^3, cadmium (Cd) from 0.009 to 0.057 µg/m^3 and chromium (0.043 to 0.08 µg/m^3). Nickel (Ni) concentrations were from 0.003 to 0.028 µg/m^3 and Cu, between 0.039 and 0.108 µg/m^3.

Except for Cu and Cd that showed a one time significance each, p = 0.01 (month 4) and 0.04 (month 6), the results obtained from the two types of PUFs are comparable without any significant differences in all metals under consideration even though the MONET foams recorded higher values than those prepared in Ghana.

Lead (Pb) values that ranged from 0.004 to 0.077 μg/m^3. This might be due to the past use of Pb containing anti- knocking fuel additives in Ghana, playing a substantial role in the build-up of atmospheric levels of lead before the ban in 2004 and which are still being detected in our atmosphere. The mean level of Pb observed was lower than the WHO guidance level of 0.5 μg/m^3 but higher than that obtained by Safo-Adu *et al.,* 2014 in an urban environment.

Manganese concentrations in the air can be as a result of the change over from leaded anti-knocks to the use of methylcyclopentadienyl manganese tricarbonyl (MMT) (Affum *et al.,* 2011). Values obtained were high (0.050—0.087 μg/m^3) but lower than the World Health Organization air quality guideline (150 ng/m^3).

Cadmium and Nickel sources could be coming largely from vehicular emissions due to old and less efficient engines and from open burning of waste which are casually done in the towns near the sampling site. Both Cd and Ni in addition to Chromium could also be due to the small scale mechanic workshops and other workshops including electro-plating, textile manufacturing, leather tanning, and wood preservation, another common activity in a town near to the sampling site, Abetifi.

Copper levels, which were the highest amongst the reviewed elements could be due to natural, vehicular or small scale repair shops and from open source burning. Both polyurethane foams (PUFs) used in the study gave results in the order of Cu>Pb >Mn>Cd>Cr>Ni.

Table 4-11: Mean concentration (µg/m^3) and standard deviation of selected heavy metals in air filters from Abetifi.

	Element/	Pb conc. (µg/m^3)		Cu conc. (µg/m^3)		Cr conc. (µg/m^3)		Mn conc. (µg/m^3)		Ni conc. (µg/m^3)		Cd conc. (µg/m^3)	
	PUF type	mean	±std error	mean	±std error	mean	±std error	mean	±std error	mean	±std error	mean	±std error
	PUF1	0.059	±0.005	0.117	±0.008	0.007	±0.00	0.050	±0.003	0.006	±0.00	0.043	±0.005
	PUF2	0.051	±0.003	0.108	±0.011	0.014	±0.014	0.041	±0.002	0.002	±0.002	0.025	±0.005
Month1	*p*	*0.25*		*0.56*		*0.68*		*0.27*		*0.09*		*0.07*	
	PUF1	0.074	±0.007	0.090	±0.008	0.063	±0.006	0.061	±0.004	0.006	±0.00	0.063	±0.002
	PUF2	0.074	±0.007	0.094	±0.008	0.043	±0.005	0.040	±0.003	0.013	±0.001	0.057	±0.004
Month2	*p*	*0.96*		*0.72*		*0.39*		*0.22*		*0.04*		*0.44*	
	PUF1	0.039	±0.002	0.103	±0.019	0.018	±0.002	0.087	±0.007	0.024	±0.002	0.070	±0.007
	PUF2	0.034	±0.001	0.095	±0.016	0.016	±0.003	0.085	±0.006	0.011	±0.011	0.049	±0.003
Month3	*p*	*0.70*		*0.75*		*0.91*		*0.84*		*0.36*		*0.06*	
	PUF1	0.037	±0.003	0.111	±0.016	0.024	±0.009	0.053	±0.003	0.014	±0.007	0.061	±0.004
	PUF2	0.035	±0.004	0.031	±0.002	0.015	±0.001	0.056	±0.004	0.007	±0.007	0.045	±0.003
Month4	*p*	*0.83*		*0.01*		*0.60*		*0.91*		*0.50*		*0.41*	
	PUF1	0.073	±0.006	0.070	±0.008	0.021	±0.002	0.082	±0.008	0.012	±0.004	0.039	±0.001
	PUF2	0.056	±0.004	0.070	±0.008	0.008	±0.001	0.082	±0.008	0.026	±0.002	0.032	±0.001
Month5	*p*	*0.39*		*1*		*0.07*		*1*		*0.62*		*0.73*	
	PUF1	0.007	±0.00	0.069	±0.004	0.022	±0.002	0.055	±0.004	0.023	±0.002	0.015	±0.001
	PUF2	0.004	±0.00	0.069	±0.004	0.010	±0.003	0.055	±0.004	0.021	±0.001	0.009	±0.00
Month6	*p*	*0.07*		*1*		*0.16*		*1*		*0.95*		*0.04*	

PUF1- Polyurethane foam from MONET

PUF2- Polyurethane foam from Ghana.

The elements selected in this study for testing efficiency of the polyurethane foam (PUF) prepared in Ghana was basically due to their toxicological nature and to see how much is available in the atmosphere at Abetifi to which people are exposed.

The study reveals the usefulness and effectiveness of using locally laboratory-prepared polyurethane foam (PUFs) for heavy metal sampling and data generation. It is conclusive therefore that, the locally laboratory-prepared PUF (Ghana produced-PUF) is good tool for heavy metal sampling.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

From the study, various atmospheric persistent organic pollutants (POPs) were characterized and a forested mountainous environmental baseline data generated. Changing temporal concentrations of the POPs under review were also identified. Data is generated for different pesticides grouped under the term/ group names: ΣDRINs, ΣDDTs, ΣHCBs and ΣHCHs and their pollution sources identified. Baseline data too is generated for polychlorinated biphenyls (ΣIn-PCBs).

The atmospheric human health exposure at Abetifi was assessed considering the contributions from such carcinogenic chemicals as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs). In addition, data for flame retardants such as polybrominated diphenyl ethers (PBDEs), hexanbromocyclododecanes (HBCDs) and polybrominated biphenyls (PBBs) is now available in Ghana as a result of this work and baseline data is also generated for such emerging POPs as perfluorinated compounds. Finally in this study the suitability of using polyurethane foam in sampling heavy metals in the atmosphere is established.

5.1 Conclusions

In this study, persistence of the pollutants under review were revealed. All groups of pollutants were in quantifiable measures. The mean concentration of all various persistent organic pollutants (POPs) were in the increasing order of PCDFs < PCDDs < Dl-PCBs < PBDEs < In-PCBs < HBCDs < PFOA < PFOS < HCBs < HCHs < DDTs < DRINs < PBBs.

DDT recorded values as high as 0.046 ng/m^3 with a pollution source signature of degradation fingerprint and of fresh input. Gamma-HCH isomer (Lindane, sold in Ghana under the trade name Gamalin 20) recorded a maximum concentration of 0.019 ng/m^3 revealed a pollution source of solely fresh input. Indicator PCB congeners had a maximum concentration of 0.014 ng/m^3 and showed an atmopsheric signature of long-range transport (58%) and fresh input (42%).

From the study, it can be concluded that all dioxin-like and indicator PCBs were emitted from a specific point source at any point in time as results show a very strong positive association (Pearson's correlation of 0.972) between the two PCB groups.

Furthermore it is conclusive from this study that although concentrations are as low as 0.009 pg/m^3 for furans, its most toxic form- 2, 3, 7, 8-tetrachlorodibenzo furan (TCDF) was consistently recorded in the air at Abetifi throughout all samplimg season.

It is also worth noting that there was an increase in concentration of the total atmospheric dioxin (polychlorinated dibenzo-p-dioxin) measured in from year 2010 to year 2011.

The human health exposure to dioxin-like chemicals (dioxin, furan & dioxin-like PCBs), on a daily basis was calculated to give an exposure value of between 0.0014 pg/kg bw per day minimum and 0.0067 pg/kg bw per day, maximum.

As regards the emerging POPs levels in Ghana, the trend observed for brominated flame retardants in this study (Abetifi) reveals the global production trend and release of the commercial polybrominated diphenyl ethers (PBDEs) into the environment where deca-BDEs < penta-BDEs< octa-PBDEs. Levels were quantifiable in pg/g with the PBDE concentration trend being affected by the relative humidity (for deca-BDEs) and rainfall pattern (for penta-BDEs) in the study area. HBCD revealed a decreasing

but not linear. Perflourinated compounds (PFCs) in the atmosphere at Abetifi gave a total mean concentration (Σ_8) for the two years as 0.015 ng/m^3.

Conclusively, mixed pollution sources have been identified for the air pollution state in Abetifi: vehicular, agricultural and burning. The main vehicular emission source specifically was diesel combustion and that of agricultural source was from both fresh input and re-volatilization from sinks (which is a secondary source pollution). The pollution produced from burning was from the open burning of biomas, upholsteries and furniture.

The results of this study indicate not only a very good capability of passive air samplers with polyurethane foam (PUF) adsorbent, to reveal the spatial concentration trend of persistent organic pollutants in ambient air.

The integration of the passive air sampling technique in the analysis of such carcinogenic pollutants (dioxins, dl-PCBs, PAHs) may provide an effective tool for the screening of such human and ecotoxicological chemicals as POPs in ambient air samples, which can be used for exposure assessment as a part of human health risk assessment process (as demonstrated in this work).

Heavy metals in air using PUF in PAS

This research is noted to have successfully and effectively collected heavy metal samples using locally fabricated and assembled passive air sampling (PAS) dome chambers, fixed with locally laboratory-prepared polyurethane foams (PUFs) (prepared as adsorption air filters). Prior to this research, such method or study has not been done in Ghana, besides analysing for both “legacy” and new POPs from one location in Ghana using PUFs in a method of passive sampling.

5.2 Recommendations

The study found background data for persistent organic pollutants (POPs) in air. It is recommended therefore that this data be used by regulatory bodies such as the Environmental Protection Agency for their regulatory purposes. Additionally, it is recommended that further studies be done in this area, extending the baseline study to others regions, to help establish a national baseline data and a yearly POP concentration trends in Ghana's atmosphere.

It is recommended that more work be done in using polyurethane foam (PUF) to sample heavy metals in order to establish a mathematical relationship between different densities of PUFs and the concentration of heavy metals adsorbed.

The PUFs treated in Ghana (prepared as adsorption filters) were effectively used to collect heavy metals in air and quantified. It is recommended that, this aspect should be monitored for consistently inorder to ensure efficiency and roll out of this method in this part of our world.

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APPENDICES

Appendix I: World Health Organization toxic equivalency factors

Congener		California TEF	I-TEF	TEF_{WHO-97}	TEF_{WHO-05}
PCDDs					
2,3,7,8-TCDD		1	1	1	1
1,2,3,7,8-PeCDD		1	0.5	1	1
1,2,3,4,7,8-HxCDD		0.03	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD		0.03	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD		0.03	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD		0.03	0.01	0.01	0.01
1,2,3,4,6,7,8,9-OCDD			0.001	0.0001	0.0003
PCDFs					
2,3,7,8-TCDF		1	0.1	0.1	0.1
1,2,3,7,8-PeCDF		1	0.05	0.05	0.03
2,3,4,7,8-PeCDF		1	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF		0.03	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF		0.03	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF		0.03	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF		0.03	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF		0.03	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF		0.03	0.01	0.01	0.01
1,2,3,4,6,7,8,9-OCDF			0.001	0.0001	0.0003
PCBs	(IUPAC#, Structure)				
77	3,3',4,4'-TCB			0.0001	0.0001
81	3,4,4',5-TCB			0.0001	0.0003
105	2,3,3',4,4'-PeCB			0.0001	0.00003
114	2,3,4,4',5-PeCB			0.0005	0.00003
118	2,3',4,4',5-PeCB			0.0001	0.00003
123	2',3,4,4',5-PeCB			0.0001	0.00003
126	3,3',4,4',5-PeCB			0.1	0.1
156	2,3,3',4,4',5-HxCB			0.0005	0.00003
157	2,3,3',4,4',5'-HxCB			0.0005	0.00003
167	2,3',4,4',5,5'-HxCB			0.00001	0.00003
169	3,3',4,4',5,5'-HxCB			0.01	0.03
170	2,2',3,3',4,4',5-HpCB			0	-
180	2,2',3,4,4',5,5'-HpCB			0	-
189	2,3,3',4,4',5,5'-HpCB			0.0001	0.00003

TEF values used/proposed in California (TSD, 2010)

Appendix IIa: Chemical & toxicological properties of selected persistent organic pollutants –DRINS, DDT, HCB

Trade Name	Type of pesticide	Toxicity	Half-life	Reference
Aldrin	Insecticide	• Inhibition of activation of the GBA-A receptor. • Affect calmodulin level, for regulation of calcium (Ca^{2+}) transport in the brain.		UNEP, 2002 WHO, 1989, EHC 91,IPCS, GNIP on POPs, 2007
Dieldrin		• Inhibition of activation of the GBA-A receptor • Affect calmodulin level, for regulation of calcium transport in the brain • Inhibit chloride flux		UNEP, 2002 Mariussen and Fonnum, 2006 WHO, 1989, EHC 91,IPCS GNIP on POPs, 2007
Endrin	Rodenticide	• Inhibition of activation of the GBA-A receptor • Affect calmodulin level, for regulation of calcium (Ca^{2+}) transport in the brain		UNEP, 2002 WHO, 1989,EHC 91,IPCS, GNIP on POPs, 2007
DDT	Insecticide	• Paralysis of the tongue, lips, and face. • Apprehension, • Irritability • Dizziness • Tremors, • Convulsions • Cardiac and respiratory failure	37 hours	ATSDR, 2002:Toxicological profile of DDT, DDE &DDD Hoffman *et al.*, 1995
DDE			17 hours	
DDD			30 hours	
HCB	Fungicide	• Death, Probable carcinogen • Neurological & Developmental toxicity • Endocrine toxicity • Immunological toxicity in humans & animals	182—1533 days	GNIP on POPs, 2007 ATSDR, 2013

Appendix IIb: Chemical & toxicological properties of selected persistent organic pollutants –PeCB, HCH, PBDE, DIOXIN

Trade Name	Type of pesticide	Toxicity	Half-life	Reference
PeCB	Fungicide Flame Retardants	• Decreased in red and white blood cells, • Body weights loss • Nephrotoxic effects • Hepatotoxic effects	45 to 467 days (*Estimated data*)	POPs convention on DRP for PeCB, 2007 CEPA, 1993
			277 days (*Calculated data*)	POPs convention on DRP for PeCB, 2007; Vulykh *et al.*, 2005
			155 days (Due to degradation process)	
			65 days (*modelled data*)	
HCH	Insecticide	• Neurotoxin • Hepatotoxin • Nephrotoxin • Human carcinogens	2.3—13 days	Wurl, 2006; Codex Alimentarius Commission. Reports of 13th session on pesticide residues, FAO/WHO, 1998; National Toxicology Programme, 2011
PCDD/ PCDF	No use	• Dermal toxicity • Immunotoxicity, • Reproductive effects • Teratogenicity • Endocrine disruption and carcinogenicity • Chlor-acne		TSD for Cancer Potency Factors, 2010 GNIP on POPs, 2007
PBDE	Industrial compound	• Carcinogenicity • Neurotoxicity • Endocrine disruption		Syed *et al*., 2010

Appendix IIc: Chemical & toxicological properties of selected persistent organic pollutants –PCB

Trade Name	Type of pesticide	Toxicity	Half-life	Reference
Tri- PCB	Industrial compound		550 hours	Wurl, 2006 cited Mackay, 1997,
Di-PCB		Occupational Exposure- • Abnormal liver function • chlor-acne • kidney cancer.	170 hours	Tan, 2008; Wurl, 2006; Longnecker *et al.*, 1997. Wurl, 2006 cited Mackay, 1997,
Penta-PCB			1500 hours	Tan, 2008; Wurl, 2006; Wurl, 2006 cited Mackay, 1997, Longnecker *et al.*, 1997
Hexa-PCB			5500 hours	Tan, 2008; Wurl, 2006; Wurl, 2006 cited Mackay, 1997, Longnecker *et al.*, 1997
PCBs		Background exposure- subtle effects on neurologic development, immune function, and, in susceptible groups, thyroid function	3- 500 days in air	Sinkkonen and Paasivirta, 2000 Longnecker *et al.*, 1997
Dioxin-like PCBs		• Dermal toxicity • Immunotoxicity • Reproductive effects • Teratogenicity • Endocrine disruption • Carcinogenicity. • chlor-acne- in humans		TSD, 2010; Gh EPA, 2007

Appendix III: IUPAC numbers & chlorine positions of PCB congeners

No.	Structure	No.	Structure	No.	Structure	No.	Structure
1	2	56	2,3,3',4'	111	2,3,3',5,5'	166	2,3,4,4',5,6
2	3	57	2,3,3',5	112	2,3,3',5,6	167**	2,3',4,4',5,5'
3	4	58	2,3,3',5'	113	2,3,3',5',6	168	2,3',4,4',5',6
4	2,2'	59	2,3,3',6	114**	2,3,4,4',5	169*	3,3',4,4',5,5'
5	2,3	60	2,3,4,4'	115	2,3,4,4',6	170***	2,2',3,3',4,4',5
6	2,3'	61	2,3,4,5	116	2,3,4,5,6	171	2,2',3,3',4,4',6
7	2,4	62	2,3,4,6	117	2,3,4',5,6	172	2,2',3,3',4,5,5'
8	2,4'	63	2,3,4',5	118**	2,3',4,4',5	173	2,2',3,3',4,5,6
9	2,5	64	2,3,4',6	119	2,3',4,4',6	174	2,2',3,3',4,5,6'
10	2,6	65	2,3,5,6	120	2,3',4,5,5'	175	2,2',3,3',4,5',6
11	3,3'	66	2,3',4,4'	121	2,3',4,5',6	176	2,2',3,3',4,6,6'
12	3,4	67	2,3',4,5	122	2',3,3',4,5	177	2,2',3,3',4',5,6
13	3,4'	68	2,3',4,5'	123**	2',3,4,4',5	178	2,2',3,3',5,5',6
14	3,5	69	2,3',4,6	124	2',3,4,5,5'	179	2,2',3,3',5,6,6'
15	4,4'	70	2,3',4',5	125	2',3,4,5,6'	180***	2,2',3,4,4',5,5'
16	2,2',3	71	2,3',4',6	126*	3,3',4,4',5	181	2,2',3,4,4',5,6
17	2,2',4	72	2,3',5,5'	127	3,3',4,5,5'	182	2,2',3,4,4',5,6'
18	2,2',5	73	2,3',5',6	128	2,2',3,3',4,4'	183	2,2',3,4,4',5',6
19	2,2',6	74	2,4,4',5	129	2,2',3,3',4,5	184	2,2',3,4,4',6,6'
20	2,3,3'	75	2,4,4',6	130	2,2',3,3',4,5'	185	2,2',3,4,5,5',6
21	2,3,4	76	2',3,4,5	131	2,2',3,3',4,6	186	2,2',3,4,5,6,6'
22	2,3,4'	77*	3,3',4,4'	132	2,2',3,3',4,6'	187	2,2',3,4',5,5',6
23	2,3,5	78	3,3',4,5	133	2,2',3,3',5,5'	188	2,2',3,4',5,6,6'
24	2,3,6	79	3,3',4,5'	134	2,2',3,3',5,6	189**	2,3,3',4,4',5,5'
25	2,3',4	80	3,3',5,5'	135	2,2',3,3',5,6'	190	2,3,3',4,4',5,6
26	2,3',5	81	3,4,4',5	136	2,2',3,3',6,6'	191	2,3,3',4,4',5',6
27	2,3',6	82	2,2',3,3',4	137	2,2',3,4,4',5	192	2,3,3',4,5,5',6
28	2,4,4'	83	2,2',3,3',5	138	2,2',3,4,4',5'	193	2,3,3',4',5,5',6
29	2,4,5	84	2,2',3,3',6	139	2,2',3,4,4',6	194	2,2',3,3',4,4',5,5'
30	2,4,6	85	2,2',3,4,4'	140	2,2',3,4,4',6'	195	2,2',3,3',4,4',5,6
31	2,4',5	86	2,2',3,4,5	141	2,2',3,4,5,5'	196	2,2',3,3',4,4',5,6'
32	2,4',6	87	2,2',3,4,5'	142	2,2',3,4,5,6	197	2,2',3,3',4,4',6,6'
33	2',3,4	88	2,2',3,4,6	143	2,2',3,4,5,6'	198	2,2',3,3',4,5,5',6
34	2',3,5	89	2,2',3,4,6'	144	2,2',3,4,5',6	199	2,2',3,3',4,5,6,6'
35	3,3',4	90	2,2',3,4',5	145	2,2',3,4,6,6'	200	2,2',3,3',4,5',6,6'
36	3,3',5	91	2,2',3,4',6	146	2,2',3,4',5,5'	201	2,2',3,3',4',5,5',6
37	3,4,4'	92	2,2',3,5,5'	147	2,2',3,4',5,6	202	2,2',3,3',5,5',6,6'
38	3,4,5	93	2,2',3,5,6	148	2,2',3,4',5,6'	203	2,2',3,4,4',5,5',6
39	3,4',5	94	2,2',3,5,6'	149	2,2',3,4',5',6	204	2,2',3,4,4',5,6,6'
40	2,2',3,3'	95	2,2',3,5',6	150	2,2',3,4',6,6'	205	2,3,3',4,4',5,5',6
41	2,2',3,4	96	2,2',3,6,6'	151	2,2',3,5,5',6	206	2,2',3,3',4,4',5,5',6
42	2,2',3,4'	97	2,2',3',4,5	152	2,2',3,5,6,6'	207	2,2',3,3',4,4',5,6,6'
43	2,2',3,5	98	2,2',3',4,6	153	2,2',4,4',5,5'	208	2,2',3,3',4,5,5',6,6'
44	2,2',3,5'	99	2,2',4,4',5	154	2,2',4,4',5,6'	209	2,2',3,3',4,4',5,5',6,6'
45	2,2',3,6	100	2,2',4,4',6	155	2,2',4,4',6,6'		
46	2,2',3,6'	101	2,2',4,5,5'	156**	2,3,3',4,4',5		
47	2,2',4,4'	102	2,2',4,5,6'	157**	2,3,3',4,4',5'		
48	2,2',4,5	103	2,2',4,5',6	158	2,3,3',4,4',6		
49	2,2',4,5'	104	2,2',4,6,6'	159	2,3,3',4,5,5'		
50	2,2',4,6	105**	2,3,3',4,4'	160	2,3,3',4,5,6		
51	2,2',4,6'	106	2,3,3',4,5	161	2,3,3',4,5',6		
52	2,2',5,5'	107	2,3,3',4',5	162	2,3,3',4',5,5'		
53	2,2',5,6'	108	2,3,3',4,5'	163	2,3,3',4',5,6		
54	2,2',6,6'	109	2,3,3',4,6	164	2,3,3',4',5',6		
55	2,3,3',4	110	2,3,3',4',6	165	2,3,3',5,5',6		

NB: Marked congeners have been assigned "toxic equivalency factors"(TEFs):*non-ortho congener;**mono-ortho congener;*** di-ortho congener. These congeners are also chlorinated in both para and at least two meta-positions (WHO 2000a).

Appendix IV: Relative carcinogenic activity of PAHs

Name	Abbreviation	Carcinogenic	Activity
Naphthalene	NAPH	-	Not determined
Acenaphthylene	ACEN	-	Not determined
Acenaphthene	ACE	-	Not determined
Fluorene	FLU	-	Not determined
Phenanthrene	PHE	-	Not determined
Anthracene	ANT	-	Not determined
Fluoranthene	FLT	0	Inactive
Pyrene	PYR	0	Inactive
Chrysene	CHRY	+	Weakly active
Benzo(a)anthracene	BaA	+	Weakly active
Benzo(k)fluoranthene	BkF	-	Not Determined
Benzo(b)fluoranthene	BbF	++	Moderately active
Benzo(a)pyrene	BaP	++++	Extremely active
Indeno(1,2,3cd)pyrene	IcdP	+	Weakly active
Benzo(g,h,i)perylene	BghiP	+	Weakly active
Dibenzo(a,h)anthracene	DBahA	+++	Very active

(Fern´andez-S´anchez *et al.*,2004).

Appendix V: Physical and chemical properties of selected persistent organic pollutants

Trade Name	Chemical Name	Chemical Formula	Molecular Mass g/mol	Solubility/ ugL^{-1} @ 20ºC	Vapour Pressure /mmHg	Log Kow
Aldrin	1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene	$C_{12}H_8Cl_6$			6.5 x 10^{-5} @ 25ºC	
Dieldrin	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5-8-dimethanonaphthalene	$C_{12}H_8Cl_6O$		140	1.78 x 10^{-7} @ 20ºC	3.69 - 6.2
Endrin	3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b] oxirene	$C_{12}H_8Cl_6O$		200	2.7 x 10^{-7} @ 25ºC	5.6
DDT	1,1,1 -trichloro-2,2-bis-(4-chlorophenyl)-ethane	$C_{14}H_9Cl_5$	354.50	0.025 mg/L	2.53 x 10^{-5} @ 20ºC	6.79 and 6.91
DDE	1,1-dichloro-2,2-bis-(4-chlorophenyl)-ethylene	$C_{14}H_8Cl_4$	318.02	0.12 mg/L	6.5 x 10^{-6} @ 20ºC	6.51 and 7
DDD	1,1-dichloro-2,2-bis-(4-chlorophenyl)-ethane	$C_{14}H_{10}Cl_4$	320.04	0.09mg/L	1.35 x 10^{-6}	5.87 and 6.02
HCB	Hexachlorobenzene	C_6Cl_6	284.8		1.09 x 10^{-5} @ 20ºC	6.18
PeCB	Pentachlorobenzene	C_6Cl_5	230.34		0.11 @ 20ºC	5.17 and 5.18 @ 25 ºC
HCH	Hexachlorocyclohexane - alpha (α) HCH	$C_6H_6Cl_6$	290.8 mg/mol	0.002 g/L	4.5x10^{-5} @ 20ºC	3.8
	Hexachlorocyclohexane - beta (β) HCH	$C_6H_6Cl_6$	290.8 mg/mol	0.0002 g/L	3.6x10^{-7} @ 20ºC	3.78
	Hexachlorocyclohexane - gamma (γ) HCH	$C_6H_6Cl_6$	290.8 mg/mol	0.0073 g/L	4.2x10^{-5} @ 20ºC	3.72
	Hexachlorocyclohexane - delta (δ) HCH	$C_6H_6Cl_6$	290.8 mg/mol	0.0314 g/L	3.5x10^{-5}@ 20ºC	4.14

Appendix VI: Physical and chemical properties of selected industrial chemicals

Chemical Name	Type of PCB (Degree of chlorination /bromination)	Chemical Formula	Molecular Mass g/mol	Solubility/ mgL^{-1} @ 25°C	Vapour Pressure /mmHg @ 25°C	Log Kow @ 25°C
Polychlorinated biphenyls (PCBs)	Di-PCB	$C_{12}H_8Cl_2$	223.1	0.06 – 2.0	0.0018 - 0.279	4.9 – 5.3
	Tri- PCB	$C_{12}H_7Cl_3$	257.5	0.015 to 0.5	0.0136 - 0.143	5.5 – 5.9
	Tetra-PCB	$C_{12}H_6Cl_4$	292	0.0043 – 0.1	$5.9x10^{-5}$ - 0.0059	5.6 – 6.5
	Penta-PCB	$C_{12}H_5Cl_5$	326.4	0.004 – 0.02	$3x10^{-4}$ - 0.009	6.2 – 6.5
	Hexa-PCB	$C_{12}H_4Cl_6$	360.9	$2x10^{-5}$ – 0.001	$2x10^{-5}$ - $1.6x10^{-3}$	
	Hepta-PCB	$C_{12}H_3Cl_7$		$4.5\ x10^{-4}$ – 0.002	$2.7\ x10^{-5}$	
	Octa- PCB	$C_{12}H_2Cl_8$		$2x10^{-4}$- $3x10^{-4}$	$2.7\ x10^{-5}$	
	Nona-PCB	$C_{12}HCl_9$		$1.8\ x10^{-5}$ -$1.1\ x10^{-4}$		
	Deca-PCB (Full chlorination)	$C_{12}Cl_{10}$		$1.2\ x10^{-6}$		
Polybrominated Diphenyls Ethers	Tetra-PBDE	$C_{12}H_6Br_4O$			$2.7 – 3.3\ x10^{-4}$ @ 20°C	5.9 – 6.2
	Penta-PBDE	$C_{12}H_5Br_5O$		0.0009 µg/L @ 20°C	$2.9 - 7.3\ x10^{-5}$ @ 20°C	6.5 – 7.0
	Octa-PBDE	$C_{12}H_2Br_8O$			$1.2 - 2.7\ x10^{-5}$ @ 20°C	8.4 -8.9
	Deca-PBDE	$C_{12}Br_{10}O$			$< 1.0\ x\ 10^{-4}$ @ 20°C	10
Hexabromocyclododecane	HBCD	$C_{12}H_{18}Br_6$				5.6

Appendix VII: Physical and chemical properties of selected polycyclic aromatic hydrocarbons

Chemical Name	Type of PAHs	Molecular Mass g/mol	Solubility/ mgL^{-1} @ 25ºC	Boiling Point ºC	Log Kow @ 25ºC
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene	128	31.7	218	3.5
	Phenanthrene	178	1.29	339	4.45
	Anthracene	178	0.075	340	4.46
	Fluoranthene	202	0.26	375	4.9
	Pyrene	202	0.135	393	4.9
	Benz(a)anthracene	228	0.014	435	5.61
	Benz(a)pyrene	252	0.004	496	6.5

Appendix VIIIa: Results of Standard Reference Material for PCB for Urban Dust 1649a (ng/g) from NIST

Compound	Certified value	± Std. Error	Present study	± Std. Error	% Recovery
PCB 28	18.5	1.2	17.81	1.8	96.25
PCB 52	24.65	0.97	23.12	1.26	93.78
PCB 101	52.9	1	51.93	1.9	98.17
PCB 118	25.7	1.5	24.48	1.7	95.25
PCB 153	82.5	8	82.38	7.8	99.85
PCB 138	69.7	7.5	67.09	8.3	96.26
PCB 180	78.7	8.2	73.40	8.7	93.26

Appendix VIIIb: Results of Standard Reference Material for PAH in Urban Dust 1649a (μg/g) from NIST

Compound	Certified value	± Std. Error	Present study value	± Std. Error	% Recovery
phenantrene	4.14	0.37	3.88	0.34	93.7
anthracene	0.432	0.082	0.407	0.071	94.2
fluoranthene	6.45	0.18	5.99	0.27	92.9
pyrene	5.29	0.25	5.28	0.22	99.9
benzo(a)anthracene	2.208	0.073	2.093	0.117	94.8
chrysene	3.049	0.06	2.906	0.045	95.3
benzo(b)fluoranthene	6.45	0.64	5.97	0.52	92.6
benzo(k)fluoranthene	1.913	0.031	1.699	0.05	88.8
benzo(a)pyrene	2.509	0.087	2.256	0.062	89.9
indeno(123cd)pyrene	3.18	0.72	3.15	0.57	98.9
dibenz(ah)anthracene	0.288	0.023	0.284	0.026	98.7
benzo(ghi)perylene	4.01	0.91	3.95	0.33	98.6

Appendix IX: Results of standard reference material for air particulate on filter-NIST 2783 (μg/g)

Element	Certified value	± Std. Error	Present study value	± Std. Error	% Recovery
Cu	404	± 42	416	± 42	103
Ni	68	± 12	65	± 15	96.3
Pb	317	± 54	304	± 52	95.9
Cd	n/a		n/a		n/a
Cr	135	± 25	128	± 25	95.2
Mn	320	± 12	314	± 10	98.2