

**THE DETERMINATION OF ORGANOCHLORINATED PESTICIDES
AND POLYCHLORINATED BIPHENYLS IN SEDIMENT, SOIL AND
WATER OF THE MSUNDUZI RIVER, KWAZULU-NATAL, SOUTH
AFRICA**

GBADEBO CLEMENT ADEYINKA

Submitted in fulfilment of the academic requirements for the degree of

Master of Science

School of Chemistry and Physics
College of Agriculture, Engineering and Sciences
University of KwaZulu-Natal
Westville, Durban, South Africa

Supervisor: Dr. B. Moodley

December 2014

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MSUNDUZI RIVER, KWAZULU-NATAL, SOUTH AFRICA**

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2014

A dissertation submitted to School of Chemistry and Physics, College of Agriculture, Engineering and Sciences, University of KwaZulu-Natal, Westville, Durban, South Africa for the degree of Master of Science in the School of Chemistry and Physics.

The chapters in this dissertation were written as a set of discrete research papers and contain general introduction, background and experimental details as well as general conclusion.

As the candidate's Supervisor, I have approved this dissertation for submission

Supervisor

Name: Dr. B. Moodley

Signed.....

Date.....

PREFACE

The research work described in this dissertation was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Westville, Durban from April 2013 to November 2014, under the supervision of Doctor Brenda Moodley.

These studies represent the original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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B.Sc (OOU)

I hereby certify that the above statement is correct

SIGNED: -----

Dr. B. Moodley

Ph.D (UKZN)

DECLARATION 1 – PLAGIARISM

I, GBADEBO CLEMENT ADEYINKA declare that

1. The research reported in this dissertation, except where otherwise indicated, is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other person's data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
4. This dissertation does not contain other person's writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted then:
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DECLARATION 2 – PUBLICATIONS

DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/ or include research presented in this dissertation (include publications in preparation, submitted, in press and published and give details of each author to the experimental work and writing of each publication). Publication manuscripts have been reformatted from the original journal styles to maintain style format of the thesis.

Publication 1

- **Gbadebo Clement Adeyinka**, Brenda Moodley, Grace Birungi, Patrick Ndungu (2014). **Quantitative Analyses of Selected Polychlorinated Biphenyl (PCB) Congeners in Water, Soil and Sediment during Winter and Spring Seasons from Msunduzi River, South Africa** (Manuscript ready for submission).

Contribution: The experimental was done by me under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as write-up, and edited by my supervisor. Other co-authors were involved in the sampling process, provided useful ideas and edited the manuscript.

Publication 2

- **Gbadebo Clement Adeyinka**, Brenda Moodley, Grace Birungi, Patrick Ndungu (2014). **Evaluation of Organochlorine Pesticide (OCP) Residues in Soil, Sediment and Water during Winter and Spring Seasons from Msunduzi River, South Africa** (Manuscript ready for submission).

Contribution: The experimental work was done by me under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as write-up, and edited by my supervisor. Other co-authors were involved in the sampling process, provided useful ideas and edited the manuscript.

Publication 3

- **Gbadebo Clement Adeyinka**, Brenda Moodley, Grace Birungi, Patrick Ndungu (2014). **Assessment of Selected Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs) in Sediment, Soil and Surface Water During Autumn Season from Msunduzi River, KwaZulu-Natal, South Africa** (Manuscript ready for submission).

Contribution: The experimental work was done by me under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as write-up, and edited by my supervisor. Other co-authors were involved in the sampling process, provided useful ideas and edited the manuscript.

Publication 4

- **Gbadebo Clement Adeyinka**, Brenda Moodley, Grace Birungi, Patrick Ndungu (2014). **Spatial Distributions of Selected Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs) in Sediment, Soil and Surface Water During Summer Season from Msunduzi River, KwaZulu-Natal, South Africa** (Manuscript ready for submission).

Contribution: The experimental work was done by me under the supervision of Dr. B. Moodley (my supervisor). I also analysed the data as well as write-up, and edited by my supervisor. Other co-authors were involved in the sampling process, provided useful ideas and edited the manuscript.

Conference contribution

- ❖ **Gbadebo Clement Adeyinka** and Brenda Moodley (2013). Analyses of persistent organic pollutants (POPs) in the Msunduzi River KwaZulu-Natal, South Africa. College of Agriculture, Engineering and Science, Postgraduate Research Day, Howard College Campus, Durban, South Africa. 1st November, 2013 (Poster).
- ❖ **Gbadebo Clement Adeyinka** and Brenda Moodley (2013). Analyses of persistent organic pollutants (POPs) in the Msunduzi River KwaZulu-Natal,

South Africa. South Africa Chemical Institute (SACI) 2013 International Conference, East London, South Africa, Dec. 1-6, 2013 (Poster).

- ❖ **Gbadebo Clement Adeyinka**; Brenda Moodley; Grace Birungi; Patrick Ndungu (2014). Sample protocols and extraction details for the analysis of persistent organic pollutant (POPs) in the Msunduzi River, South Africa. Water Research Commission (WRC) annual project meeting Westville Campus, UKZN 2014 (oral presentation).
- ❖ **Gbadebo Clement Adeyinka** and Brenda Moodley (2014). Evaluation of Organochlorine Pesticides (OCPs) Residues in Sediment and Water during winter season of Msunduzi River, South Africa. Analitika 2014 International Conference.
- ❖ **Gbadebo Clement Adeyinka** and Brenda Moodley (2014). Evaluation of Organochlorine Pesticides (OCPs) Residues in Sediment and Water during winter season of Msunduzi River, South Africa. College of Agriculture, Engineering and Science Postgraduate Research Day, Westville Campus, Durban, South Africa. 27th October, 2014 (Poster).

Signed.....

ABSTRACT

Persistent organic pollutants (POPs) are a major class of organic contaminants of serious global concern due to their persistence in the environment because of their stability to photolytic, chemical and biological degradation. POPs are mostly semi volatile organic compounds (SVOCs) and include polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), which are toxic and capable of causing serious health disorders, such as, developmental and cancer related problems in animals and humans. Organic pollutants, such as, organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are as well toxic as inorganic pollutants. There is limited information available on the concentration level and distribution pattern of organic pollutants within the KwaZulu-Natal Rivers as well as many studies done within this area have also only focused on inorganic pollutants. The lack of information and the need for knowledge on the organic pollutants in these rivers together with global concern for quality water has therefore prompted an investigation of the organic pollutants in the selected river. Therefore, the results and outcomes of this study could serve as a baseline assessment for various levels of government and scientific communities for future planning on the state of this river. The concentration patterns of selected priority pollutants (dirty dozen) made up of eight polychlorinated biphenyl (PCB) congeners and seven organochlorine pesticides (OCPs) together with six DDT metabolites were evaluated in sediment, soil and surface water during autumn, winter, spring and summer seasons from the Msunduzi River of KwaZulu-Natal, South Africa. Sediment, soil and water samples were collected at ten sites along the river in April 2013, July 2013, September 2013 and February 2014 that represented autumn, winter, spring and summer sampling seasons. Soil and sediment samples were dried and sieved while water samples were kept at 4 °C prior to the extraction. Soil and sediment samples were extracted by ultrasonication with dichloromethane (DCM) and water samples were subjected to liquid-liquid extraction using DCM. All sample extracts were cleaned up using multi-layered acidic/basic silica gel and all quality assurance steps were carefully observed. Both PCB congeners and OCPs were analysed and quantified in the sample extracts using gas chromatography–mass spectrometry (GC-MS). All the PCB congeners and OCPs analysed were detected in sediment, soil and water samples during all seasons. The results showed that sediment and soil samples contained the highest concentrations of both PCBs and OCPs with water samples having the lowest concentrations of all the analytes throughout the seasons. Concentrations of PCB

congeners detected in the environment were found to be dependent on the number of chlorine atoms on the phenyl ring of PCB congeners, were PCB 180 exhibited the highest concentration and PCB 138 was found to be present in the lowest concentration. Total DDTs and endrin were the most predominant OCPs. The result of indicative indices suggested that the presence of DDTs could be attributed to the aged long degradation of DDT to its metabolites. The concentration patterns of the pollutants during the seasons were found to be in decreasing order of winter, spring, autumn and summer seasons. The concentrations detected in water samples during the seasons were also found to exceed the United State Environmental Protection Agency (USEPA) of 0.014 ng/mL and European Union (EU) 0.01 ng/mL recommended tolerable levels in surface and underground water respectively.

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DEDICATION

This thesis is dedicated to God Almighty for seeing me through this stage of my life, may your name be glorified forever. Also to my family, for their love and understanding while I was away from them.

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LIST OF ABBREVIATIONS

ACE	Associated Chemical Enterprises
ACGIH	American Conference of Governmental Industrial Hygienists
ADI	Acceptable Daily Intake
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Chemical Abstracts Service
CEC	Commission for Environmental Cooperation
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DHHS	Department of Health and Human Services
FAO	Food and Agriculture Organization of the United Nations
GC	Gas Chromatography
GEMS	Global Environment Monitoring System
GPS	Global Positioning System
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer

IPCS	International Programme on Chemical Safety
IQ	Intelligent Quotient
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
LD50	Median Lethal Dose
LOAEL	Lowest-Observed-Adverse-Effect Level
LOD	Limit of Detection
LOQ	Limit of Quantification
MCL	Maximum Contaminant Level
MPL	Maximum Permissible Level
MS	Mass Spectrometry
NCI	National Institutes of Health
NOAEL	No-Observed-Adverse-Effect Level
NTP	National Toxicology Program
OCPs	Organochlorine Pesticides
PCBs	Polychlorinated
PEL	Permissible Exposure Limit
POPs	Persistent Organic Pollutants
PTDI	Provisional Tolerable Daily Intake
RCRA	Resource Conservation and Recovery Act
RSC	Royal Society of Chemistry
SC	Stockholm Convention
SPE	Solid-Phase Extraction
SVOCs	Semi Volatile Organic Compounds

TCCH	Toxic Chemicals and Children's Health
TEF	Toxicity Equivalence Factor
TEQ	Toxicity Equivalence
TLV-TWA	Threshold Limit Value – Time-Weighted Average
UNEP	United Nations Environment Programme
USA	United States of America
USITC	United States International Trade Commission
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 General Overview

Water pollution is a serious global problem that requires urgent attention, evaluation and revision of policies in water resource provision at all levels. The prevailing environmental conditions in some of the African sub-regions have been a concern to Governments, scientific communities and stake holders involved in the provision of portable water. Provision and adequate supply of portable and fresh clean water is essential for healthy living. However, the delivery of freshwater has been hindered not only by an increase in population numbers and management problems but also by an increase in urbanization, reduced rainfalls due to climate changes and as well as ecological degradation. Water pollution has been linked to health problems in both humans and aquatic ecosystems globally and a million new cases of diseases related to water pollution are reported each year, leading to the death of over ten million people with about 70% of them occurring in tropical regions (Mcfeter, 1990).

Water is typically referred to as unsafe when its suitability and accessibility have been compromised by anthropogenic and natural contaminants. Water pollution could be a result of point source pollution such as industrial and wastewater discharge or non-point sources such as leaching of nutrients and pesticides from agricultural land. These pollutants could be either inorganic such as heavy metals or organic in nature such as persistent organic pollutants (POPs). POPs are carbon containing organic compounds of anthropogenic origin such as industrial waste processes, vehicular activities and agricultural practices as well as sanitation processes, while few may originate from natural sources such as volcanic eruptions (UNEP, 1999; Ritter *et al.*, 2005; Yao *et al.*, 2013). POPs are semi volatile organic compounds (SVOCs) and may evaporate from soil, sediment or water to air (Wania and Mackay, 1993; Ritter *et al.*, 2005). They are transported from warmer regions to the colder Polar Regions *via* air currents (Wania and Mackay, 1993; Wania and Mackay, 1996). This important class of organic pollutants once released into the environment persists and remains intact for a long period, due to their stability against chemical, thermal, photolytic and biological degradation (Buccini, 2003; Wang *et al.*, 2005; Zhao *et al.*, 2006). POPs are lipophilic, have long range of transportation, are bio accumulating in the food chain as well

as are characterized as acutely toxic. POPs are therefore found almost everywhere even where they have never been generated (Buccini, 2003).

The initial group of POPs was known as the dirty dozen as rectified by the Stockholm Convention (SC) on POPs in 2001 which included, aldrin, dieldrin, endrin, heptachlor, toxaphene, chlordane, mirex, hexachlorobenzene (HCB), 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT), polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH) which are known as industrial chemicals and polychlorinated dioxins and polychlorinated dibenzofurans (PCDD/Fs) which are unintentional by-products of industrial chemicals (Buccini, 2003; Bouwman, 2004; Ritter *et al.*, 2005). The Stockholm Convention (SC) on POPs was established and adopted in May, 2001 but was only fully functional in 2004, in most of the member countries. It is a global treaty under the watch of United Nations Environmental Programme (UNEP) which is aimed at stopping the release and usage of hazardous and persistent organic chemicals, bans and reduces the production of many POPs, canvases and supports the member countries financially in the clean-up of the old stockpiles of materials containing POPs, protecting humans and the environment as well as intensifying public awareness on the dangers of POPs (Bouwman, 2004; Xu *et al.*, 2013). South Africa being a member of the convention finally signed the treaty in 2004 and undertook to support research, and control the release of POPs in the environment (Bouwman, 2004; Burger and Nel, 2008). As a result, protection of water sources continues to present challenges to government and regulatory authorities, and industries and other agencies involved are required to adhere to the stricter water safety standards.

Whilst much research on water pollution by organic pollutants has been carried out in some of the developed countries in the world, there is limited information on the level and distribution pattern of POPs in the South African environment. Previous studies indicated the presence of these pollutants in various rivers in South Africa, such as Western Cape, where six pesticides were detected in Elgin farm dams at a concentration of 626 µg/L (Davies, 1997). The total endosulfan concentration in Lourens River in the Western Cape was found to be between 0.03-0.16 µg/L and 3.9-245 µg/kg in both water and sediment respectively (Schultz *et al.*, 2001b). A study by Awofolu and Fatoki on the OCP concentration levels in sediment samples from marine and freshwater sources in the Eastern Cape province of South Africa, showed that the *o,p*-DDD, aldrin and *beta*-benzene hexachloride (*β*-BHC) concentrations ranged between trace for *o,p*-DDD to 450 ng/L for *β*-BHC and from trace (aldrin and *o,p*-DDD) to 184 ng/g (*β*-BHC) in water and sediment samples respectively

(Awofolu and Fatoki, 2003). A study conducted on 13 OCP compounds from the Jukskei River catchment area in Gauteng, indicated high concentrations of these organic pollutants which ranged between 4.26-22914 ng/g and 1.07-15400 ng/mL in sediment and water samples respectively (Sibali *et al.*, 2008). A study by Polder and co-workers found that higher concentrations of polybrominated-diphenyl ethers (PBDEs) were present in bird eggs obtained from around the Vaal River, which is situated downstream of one of the industrialized areas in South Africa (Polder *et al.*, 2008). Nieuwoudt and co-workers studied the concentration levels of PCDD/Fs and 12 PCBs in soil and sediment samples collected from residential and industrial areas in central South Africa. The authors found that total PCDD, PCDF and PCB concentrations in soil were 5.20-870 ng/kg, 2.5-160 ng/kg and 300-4700 ng/kg respectively, while total concentrations of PCDDs, PCDFs and PCBs were 0.99-170 ng/kg, 0.41-3.90 ng/kg and 120-1800 ng/kg in sediment samples respectively (Nieuwoudt *et al.*, 2009). Studies on the Isipingo estuary in Durban showed the presence of PCBs, OCPs and lindane in fish and water samples at concentration levels of 5.70-869 ng/g arochlor 1254¹, 0.29-123 ng/g, < 0.23-23 ng/g and 0.23-175 ng/g for *p,p*-DDE, *p,p*-DDT and Σ DDT as well as < 0.07-4.12 ng/g for lindane (Grobler *et al.*, 1996). Sereda and Meinhardt studied the *p,p*-DDE, *p,p*-DDD and endosulfan concentrations in water and sediment of the Ubombo and Ingwavuma districts in northern KwaZulu-Natal. The following concentrations were found: < 0.7-2 ng/L in water and < 0.3-586 ng/kg in sediment of *p,p*-DDE; < 0.7 ng/L in water and < 0.3-950 ng/kg in sediment of *p,p*-DDD and 90-236 ng/kg of endosulfan in sediment (Sereda and Meinhardt, 2003). Residues of these OCPs, most especially DDT metabolites, were attributed to their higher usage in agriculture and malaria control in the area. Also, Channa and co-workers studied the regional variation in pesticide concentrations in delivering women plasma within three coastal sites of KwaZulu-Natal, South Africa. Significantly higher lindane and endosulfan concentrations were found to be predominant pesticides in the blood plasma samples collected from expectant mothers in the studied areas. Among the three sites studied, Empangeni (an intermittent malaria prone area) was reported to have the highest lindane and endosulfan mean concentration of 956 ng/g and 141 ng/g

¹ Aroclor 1254 is the trade name for a commercial mixture of PCBs. The first two digits represent the number of carbon atoms in the rings while the last two digits indicate the percentage (degree) of chlorination by mass in the mixture. Therefore Aroclor1254 has a mixture of PCBs having 12 carbons and 54% of chlorine by mass.

compared to the other two sites (Manguzi, a malaria endemic area and Port Shepstone, a non-malaria prone area) (Channa *et al.*, 2012). Other pesticides such as *cis*-permethrin, cyfluthrin, deltamethrin, cypermethrin which are pyrethroids, as well as HCH, β -HCH and α -HCH were reported to be found in low concentrations. Detectable levels of POPs were also found in river fish and sediments in KZN such as Pongolo floodplain and Pongolapoort (Naude *et al.*, 1998; McHugh *et al.*, 2011).

Of all the studies done on POPs in South African rivers there is currently no scientific report on the levels and distributions of OCP and PCB organic pollutants in the Msunduzi River which is the major river to the larger population of Pietermaritzburg and Msunduzi municipality. Furthermore, this river is a source of drinking water, agricultural water for crops and animals as well as is widely used for recreational activities where people and animals including aquatic organisms may be exposed to varying degrees of contamination due to the organic pollutants. Many studies done within this area have also only focused on inorganic pollutants. The lack of information and the need for knowledge on the organic pollutants in this river has therefore prompted an investigation of the organic pollutants in this river and the results and outcomes of this study could serve as a baseline assessment for various levels of government and scientific communities for future planning on the state of this river.

1.2 Aim and Objectives

1.2.1 Aim

To investigate and quantitatively determine the seasonal variations in the concentrations of some selected persistent organic pollutants (POPs) in soil, sediment and water of the Msunduzi River in Pietermaritzburg, South Africa.

1.2.2 Objectives

- a) To identify the presence of the targeted POPs in the Msunduzi River
- b) To quantify the selected POPs in the environmental media of the chosen sites
- c) To determine the distribution pattern of the selected POPs in sediment, soil and water samples from the Msunduzi River
- d) To determine the seasonal and spatial variation of the selected POP concentrations along the Msunduzi River.

1.3 Hypothesis of the Study

Concentrations of persistent organic pollutants (POPs) are significant in sediment, soil and water from the Msunduzi River, and are dependent on the season and location of sampling sites.

1.4 Research Scope

The geographical area in this study is the province of KwaZulu-Natal (KZN) with focus on the Msunduzi River. This river is one of the major tributaries of the uMgeni River which is the main source of water to the greater region of KwaZulu-Natal. It passes through highly industrialized areas as well as rural and agricultural areas, which all contribute to the levels of organic pollution in the river. This river is also used for national water sports (The Dusi canoe marathon) where people could potentially be exposed to these pollutants. Therefore, it is a suitable river for this study and will provide much needed information to a wide variety of stakeholders including the municipality and scientific community. Studies have shown

detectable levels of POPs in the various rivers in South Africa as well as in KwaZulu-Natal, but there is little or no information about the concentration levels of PCBs and OCPs in most of the tributaries of the uMgeni River with particular reference to the Msunduzi River. Therefore, this river was chosen as a suitable site of investigation and the results will fill a gap in information on the presence and quantity of selected POPs in this river.

CHAPTER 2

2.0 BACKGROUND ON PERSISTENT ORGANIC POLLUTANTS (POPS)

2.1 Introduction

POPs are a group of chemicals that includes 12 priority organic compounds (known as the dirty dozen): aldrin, chlordane, DDT, dieldrin, dioxins, endrin, furans, heptachlor, hexachlorobenzene (HCB), mirex, polychlorinated biphenyls (PCBs), and toxaphene (Ritter *et al.*, 2005). These groups of chemicals have been widely used as pesticides or as industrial chemicals that pose serious environmental and human health risks as well as risks to water ecosystems (Ritter *et al.*, 2005). POPs have been produced and released into the environment by anthropogenic activity. They are characterized as chemicals with high environmental persistence, high resistance to chemical, biological as well as photochemical degradation. Some of them do break down but often into more toxic substances. POPs can accumulate in animals and human fatty tissues; they tend to bioconcentrate and move up into higher trophic levels in the food chain in higher concentrations than is acceptable (CEC/TCCH, Buccini, 2003). POPs have also been reported to pose various health challenges to humans, wildlife as well as aquatic organisms (USEPA, 2007).

2.2 Polychlorinated Biphenyls (PCBs)

2.2.1 General Overview

PCBs are a group of chlorinated synthetic organic chemicals that have relatively low water solubility and have relatively long environmental and biological half-lives of 8-15 years (ATSDR, 2000). They consist of a biphenyl structure with two linked benzene rings in which some or all of the hydrogen atoms on the benzene ring have been substituted by chlorine atoms. They have a basic chemical formula of $C_{12}H_{10-n}Cl_n$, where n is the number of chlorine atoms substituted in the benzene ring. There are 209 different PCB congeners that can be formed depending on the number of chlorine atoms involved in the substitutions. PCB congeners are lipophilic and hydrophobic in nature with the lipophilicity of the congener's increasing with an increase in the number and degree of substitution. The lower congeners with the lower degree of substitution are relatively more volatile than those with a higher

number of chlorine atoms. Due to their high flash point (between 170-380 °C), they are practically fire resistant (ATSDR, 2002). They have high resistance to thermal degradation, poor electrical conductivity and high thermal conductivity which is the reason for their use as fire retardants. The molecular structure, physical and chemical properties of the selected PCB congeners in this study are shown in Figure 2.1 and Table 2.1 respectively.

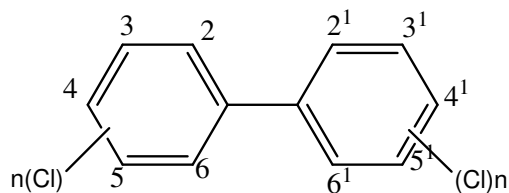


Figure 2.1 General basic structure of PCBs.

Table 2.1 Physical and chemical properties of PCB congeners.

PCB Congeners	Molecular weight (g/mol)	Molecular formula	Melting point (°C)	Boiling Point (°C) (at 20 mmHg)	Solubility	Partition coefficient		Vapour pressure (mm Hg at 25 °C)	Henry's law constant (atm-m ³ /mol at 25 °C)
					Water (mg/L)	Log K _{ow}	Log K _{oc}		
PCB 28	257.54	C ₁₂ H ₇ Cl ₃	57-58	206-207	0.0085	5.69	5.28	2.8 x 10 ⁻²	32.20
PCB 52	291.98	C ₁₂ H ₆ Cl ₄	87-89	268	0.046	6.09	5.91	7.3 x 10 ⁻³	31.41
PCB 77	291.98	C ₁₂ H ₆ Cl ₄	173	360	0.18	6.53	4.41-5.75	4.4 x 10 ⁻⁷	0.43 x 10 ⁻⁴
PCB 101	326.43	C ₁₂ H ₅ Cl ₅	77	380	0.00012	6.31	**	2.9 x 10 ⁻³	35.5
PCB 105	326.43	C ₁₂ H ₅ Cl ₅	**	**	0.0034	5.66	**	6.5 x 10 ⁻⁶	8.24 x 10 ⁻⁴
PCB 138	360.9	C ₁₂ H ₄ Cl ₆	78.5-80	400	0.016	7.44	5.21-7.3	4.0 x 10 ⁻⁶	1.07 x 10 ⁻⁴
PCB 153	360.88	C ₁₂ H ₄ Cl ₆	103-104	No data	0.00091	7.75	4.75-7.68	3.8 x 10 ⁻⁷	2.78 x 10 ⁻⁴
PCB 180	395.32	C ₁₂ H ₃ Cl ₇	109-110	240-280	0.00031-0.0066	7.37	5.78-6.9	**	1.07 x 10 ⁻⁴

Source: HSDA, 2000; ATSDR, 2000. **== data not available

2.2.2 Sources of Polychlorinated Biphenyls

PCB distribution in the environment was first noted in 1966 by Jensen who carried out research on human and wildlife samples (Jensen, 1966). Polychlorinated biphenyls are aromatic man-made chemicals, which do not occur in the natural environment and are formed as a consequence of anthropogenic activities such as industrial by-products. PCBs are also introduced to the environment by uncontrolled combustion processes of PCB-containing waste, incineration of hazardous and medical waste, wood treated with pentachlorophenol and certain industrial chemical processes involving chlorine such as polyvinyl chloride, as well as emissions from vehicle exhausts (Safe, 1994; Ritter *et al.*, 2005; Davis *et al.*, 2007). Polychlorinated biphenyl (PCBs) are mixtures of chlorinated hydrocarbons that had a wider commercial usage between 1929 until late 1980 in various industrial applications such as carbonless copy paper, in plastics, as paint additives, dielectrics in transformers and large capacitors and heat exchange fluids (Tolosa *et al.*, 1997; Vallack *et al.*, 1998). PCBs have been found to be useful for industrial applications because they are resistant to heat are non-flammable, fairly unreactive, have low vapour pressure and high dielectric constants (Ritter *et al.*, 2005).

2.2.3 Environmental and Biological Fate of PCBs

PCBs are endocrine disruptors, and exposure to them has been linked to some health related problems such as acne-like skin conditions in adults, neurobehavioral and immunological changes in infants (Klanova *et al.*, 2007; ATSDR, 2000). Other related health issues associated with PCB exposure are cancer related illnesses, mental disorders, behavioural and learning disorders in children as well as toxicity problems such as endocrine and neurotoxicity effects in humans (Lemesh, 1992; Kimbrough, 1995). Some of the environmental and biological health related issues are discussed below.

2.2.4 Skin, Hepatic and Ocular Problems

Various dermal related problems such as skin irritation (skin rashes), chloracne, and pigmentation of skin and nails and alterations in liver enzymes have been linked to PCB occupational exposure in humans and accidental ingestion of contaminated food containing high levels of PCBs and other halogenated chemicals. Episodes such as the Belgian dioxin and PCB contamination of food products in 1999 (Van Larebeke *et al.*, 2002), the *Yusho* (Japan 1968), and *Yu-Cheng* (Taiwan 1979) incidents (Aoki, 2001), that resulted from

ingesting contaminated rice oil, showed that PCBs can pose an important risk in the accidental contamination of food. Major ocular effects that are associated with PCB exposure include hyper secretion of the Meibomian glands, abnormal pigmentation of the conjunctiva, and swelling of the eyelids in some cases, which is associated with fatigue, nausea and vomiting. These occurrences have been reported in monkeys exposed to a dose of PCBs as low as 0.005 mg/kg/day (ATSDR, 2000).

2.2.5 Reproductive and Developmental Effects

Research data on the reproductive systems of both women and men, who have had long term exposure to PCBs, show disruption to women's menstrual cycles, and changes to sperm morphology resulting in problems with conception (Taylor *et al.*, 1989; ATSDR, 2000; ATSDR, 2001). Some health related effects on fertility and reproductive organs have been reported in rats, mice, and monkeys exposed to PCBs through food. Studies on monkeys exposed to PCBs showed that some reproductive and developmental problems are low birth weights, skin hyperpigmentation and behavioural disturbances (Sager, 1983; Sager *et al.*, 1991). Research has also shown children born up to 7-12 years post maternal exposure to the Taiwan PCB incident had poorer cognitive development up to 7 years of age, behavioural problems, deformed nails, hyperpigmentation and intrauterine growth delay (Sager *et al.*, 1991; Sager and Girard, 1994; ATSDR, 2001). Exposure to PCBs may also result in decreased thyroid hormone levels (Schell *et al.*, 2008). Unintentional exposure could be attributed to the persistence and long half-life of PCBs in the human body as well as in the environment.

2.2.6 Neurological and Immunological Effects

Reports by Chia and Chu, and Chen and co-workers showed a reduction in the sensory and motor nerve conduction velocities, in patients exposed to the outbreak of PCBs that occurred in *Yusho* and *Yu-Cheng* in Japan and Taiwan (Chia and Chu, 1984, 1985; Chen *et al.*, 1985). Various neurological symptoms, in the victims of *Yusho* and *Yu-Cheng* were also reported which include numbness, weakness and neuralgia of limbs, hypaesthesia, and headaches (Chia and Chu, 1984, 1985; Kuratsune, 1989; Rogan, 1989). Studies on the victims exposed to PCBs in the *Yu-Cheng* incident were reported to have poorer immune systems, and suffered from a variety of infections. Epidemiological findings in infants and children in Michigan exposed to PCBs before birth, revealed poor performance in verbal and memory activities, abnormal reflexes and deficiencies in memory, learning, and intelligent quotient

(IQ) (Jacobson *et al.*, 1990a; Jacobson and Jacobson, 1996; Lantin *et al.*, 1998c; Patandin *et al.*, 1999). These problems were found to be associated with prenatal exposure to PCBs. Studies of children born to mothers who had consumed PCB contaminated fish from the Great Lakes showed neurodevelopmental toxicity at birth as well as into early childhood. Research had also shown that chronic and low level exposure to Aroclor 1254 affected rhesus monkeys' immune systems by altering their T-cells and/or macrophage function (ATSDR, 2000; Ritter *et al.*, 2005).

2.2.7 Carcinogenic Effects

Generally, human studies have shown that there is a link between cancer-related problems and PCB exposure in humans. A research report generated on liver cancer from the victims of the *Yusho* PCB outbreak in Japan has since been used as evidence to support the occupational hepatocarcinogenicity data on human carcinogenicity status. Cancer related cases and deaths have also been reported in both male and female workers involved in electrical capacitor manufacturing plants in New York and Massachusetts (Brown and Jones, 1981; Brown, 1987b) which was as a result of PCB exposure.

2.3 Organochlorine Pesticides (OCPs)

OCPs are chemicals designed to combat, prevent, or control the attack of various pests and vectors on agricultural crops, domestic animals and human beings (FAO, 1989; UNEP, 1990). They are toxic organic chemical agents that are intentionally released into the environment to alleviate the spread of pests and vector diseases. Among the OCPs, the following were studied in this research; HCB, HCH (lindane), aldrin, heptachlor, dieldrin, endrin, mirex and DDT with its metabolites *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT and *p,p*-DDT. Their physical and chemical properties have been summarized in Table 2.2

Table 2.1 Physical and chemical properties of organochlorine pesticides

OCPs	Molecular weight	Molecular formula	Melting point (°C)	Boiling point (°C)	Solubility	Partition coefficient		Vapour pressure (mm Hg at 20 °C)	Henry's constant at 20 °C (atm·m ³ /mol)
					Water (µg/L) at 25 °C	Log K _{ow}	Log K _{oc}		
HCB	284.8	C ₆ Cl ₆	231.8	325	4.7	5.73	3.10	1.09 x 10 ⁻⁵	**
HCH	290.83	C ₆ H ₆ Cl ₆	112.5	323.4	17	3.72	3.00	4.20 x 10 ⁻⁵	3.50 x 10 ⁻⁶
Heptachlor	373.32	C ₁₀ H ₅ Cl ₇	95-96	135-145	0.056	5.44	**	3.00 x 10 ⁻⁴	**
Aldrin	364.93	C ₁₂ H ₈ Cl ₆	104-105	145	0.20	5.17	2.61	2.31 x 10 ⁻⁵	3.20 x 10 ⁻⁴
Dieldrin	380.93	C ₁₂ H ₈ Cl ₆ O	175-177	330	0.1-0.20	5.40	3.84	5.89 x 10 ⁻⁶	5.80 x 10 ⁻⁵
Endrin	380.93	C ₁₂ H ₈ Cl ₆ O	200	245	0.20	5.60	4.53	7.00 x 10 ⁻⁷	4.40 x 10 ⁻⁷
Mirex	545.59	C ₁₀ Cl ₁₂	485	**	0.60	5.28	3.76	3.00 x 10 ⁻⁷	5.16 x 10 ⁻⁴
<i>o,p</i> -DDE	318.03	C ₁₄ H ₈ Cl ₄	**	**	0.14	6.00	5.19	6.00 x 10 ⁻⁵	1.80 x 10 ⁻⁵
<i>p,p</i> -DDE	318.03	C ₁₄ H ₈ Cl ₄	89	336	0.12	6.51	4.70	6.00 x 10 ⁻⁶	2.10 x 10 ⁻⁵
<i>o,p</i> -DDD	320.05	C ₁₄ H ₁₀ Cl ₄	76-78	**	0.10	5.87	5.19	1.94 x 10 ⁻⁶	8.17 x 10 ⁻⁶
<i>p,p</i> -DDD	320.05	C ₁₄ H ₁₀ Cl ₄	109-110	350	0.09	6.02	5.18	1.35 x 10 ⁻⁶	4.00 x 10 ⁻⁶
<i>o,p</i> -DDT	354.49	C ₁₄ H ₉ Cl ₅	74.2	**	0.085	6.79	5.35	1.10 x 10 ⁻⁷	5.90 x 10 ⁻⁷
<i>p,p</i> -DDT	354.49	C ₁₄ H ₉ Cl ₅	109	***	0.025	6.91	5.18	1.60 x 10 ⁻⁷	8.30 x 10 ⁻⁶

=no data, * = decomposes (HSDB, 1995; HSDB, 2010; Ritter *et al.*, 2005)

2.3.1 Hexachlorobenzene (HCB)

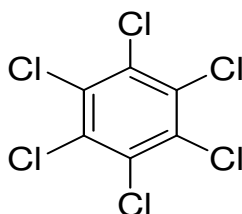


Figure 2.2 Structure of hexachlorobenzene.

HCB belongs to a group of chlorinated aromatic compounds that are found as white needle-like crystalline solids at room temperature (HSDB, 2010). It has hydrophobic interactions with water, low solubility in cold alcohol and carbon tetrachloride, and readily soluble in organic solvents such as benzene, chloroform, ether, and carbon disulfide. It is relatively stable under standard temperature and pressure (Akron, 2010). It is volatile and can be expected to transfer to the atmosphere. When HCB degrades, it gives off highly toxic fumes of hydrochloric acid as well as other oxides of carbon such as carbon monoxide, and carbon dioxide (USEPA, 2011). It is also known to bioconcentrate in the fatty tissues of living organisms.

2.3.1.1 Sources of hexachlorobenzene

HCB was first manufactured on a commercial scale in 1933 in the United States (IARC, 1979). Approximately 2.5 to 4.9 million pounds of HCB was produced in 1972 in the United States as a by-product from the manufacture of carbon tetrachloride, perchloroethylene, trichloroethylene, tetrachloroethylene and pentachlorobenzene, propazine, atrazine, simazine, vinyl chloride, pentachlorophenol and chlorothalonil. HCB is also known to be a product of combustion processes of municipal waste, or waste streams from wood-preserving and chlor-alkali plants (IARC, 1979; ATSDR, 2002). It was formally used as a fungicide for sorghum, onion and wheat (IARC, 1979) as well as seed treatment. It is also a by-product of the manufacture of industrial chemicals such as carbon tetrachloride, pentachlorobenzene and trichloroethylene.

2.3.1.2 Environmental and biological health effects of hexachlorobenzene

HCB is known to be highly stable to both chemical and biological degradation and is persistent in the environment; thus the general population may be exposed to low concentrations of this chemical (ATSDR, 2002). Some populations are at higher risk of exposure to certain concentrations of HCB most especially if they live near former HCB manufacturing or waste disposal sites or have a diet of fish caught from contaminated water sources (USEPA, 2011). When HCB is released into the environment, it is taken-up by both plants and animals through the food chain and bioaccumulates. Researchers have also identified the presence of HCB in terrestrial, freshwater and marine food chains in the Great Lakes and even Arctic regions (ATSDR, 2002). This is because when it is released into the atmosphere it remains in the vapour phase and therefore can make its way from temperate regions to Polar Regions due to trans boundary effects. When HCB is released into water, it strongly adsorbs onto organic particulate matter and sediment and does not decompose or hydrolyse (ATSDR, 2002). In the early 1970s, it was found in areas where it was formerly used as a pesticide, at low levels in urban soils as well as at high concentrations in soils near uncontrolled hazardous-waste sites. Health associated problems with HCB exposure include severe weakness, photosensitive skin lesions, hyperpigmentation, colic, and porphyrinuria² effects. All these were symptoms reported from people who had ingested HCB-treated seed grain in eastern Turkey in the mid to late 1950s. In this incident, a large number of victims had developed porphyria turcica, a disorder of heme biosynthesis. Pregnant women exposed to HCB were reported to have passed the HCB to their babies *via* placental fluid transfer and breast feeding. Most children born to these women were reported to develop “pembe yara” (pink sore), with a higher mortality rate (up to 90%) reported during this particular period. A study conducted years after the incident reported that some individuals still had porphyria related illnesses due to the persistence of HCB (ATSDR, 2002). HCB has been reported to be carcinogenic. Oral exposure of rodents to HCB was reported to cause tumours. Oral administration of HCB to female rats, mice and male and female hamsters were reported to cause liver tumours. Both male and female hamsters also developed tumours in the blood-

² Porphyrinuria is an excessive release of porphyrin and related compounds in the urine. It is a consequence of genetic or acquired deficiencies of enzymes of the heme biosynthetic pathway. It sometimes results in the accumulation of heme precursors thereby causing toxicity. Heme is an iron-containing pigment which is an essential co-factor of many hemoproteins.

vessels of the liver (hemangioendothelioma) and benign thyroid-gland and adrenal-gland tumours (follicular-cell adenoma) (IARC, 1979). HCB is considered a hazardous substance and therefore special standards have been set by various agencies for manufacturing, usage, labelling and transportation of this substance. USEPA set a maximum contaminant level (MCL) at 1 $\mu\text{g/L}$ and the Food and Drug Administration (FDA) set the maximum permissible level (MPL) in bottled water for HCB at 1 $\mu\text{g/L}$ (USEPA, 2002). The Resource Conservation and Recovery Act (RCRA) set the toxic characteristic leaching procedure threshold for HCB at 130 $\mu\text{g/L}$ and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold limit value – time-weighted average (TLV-TWA) was set at 2 $\mu\text{g/m}^3$ in air (USEPA, 2002).

2.3.2 Hexachlorocyclohexane (γ -HCH) (Lindane)

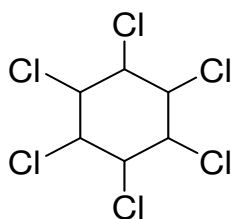


Figure 2.3 Structure of hexachlorocyclohexane.

HCH consists of eight isomers (Safe, 1993). Only γ -HCH, α -HCH, β -HCH, and δ -HCH are of commercial significance. Lindane is one of the major isomers of HCH with a common name γ -HCH. It is a brownish to white crystalline solid that is volatile and fairly insoluble in water but readily soluble in ether, benzene, ethanol and chloroform (USEPA, 1999). The technical-grade of lindane has almost 99% of γ -HCH, and is stable in the environment under standard temperature and pressure (Akron, 2009; HSDB, 2009).

2.3.2.1 Sources of hexachlorocyclohexane

HCH was first manufactured as a technical mixture of α , β , γ , δ , and ϵ HCB isomers through photochlorination of benzene, *via* free-radical initiation with ultraviolet light, X-rays, or gamma rays (Ritter *et al.*, 2005). The resulting solution is concentrated and γ -HCH (lindane) is crystalized at 99.9% purity. It was commercially produced in the United States in the mid 1940's and its production has since stopped but it is still produced worldwide in many

countries across the globe, such as India and China (IARC, 1974). The import of this chemical by the United States has declined from 1.4 million pounds between 1989 and 1999 to zero in 2005 (ChemSources, 2009; SRI, 2009; USITC, 2009). Lindane may also be released into the environment during its formulation or use as an insecticide, from wind erosion of contaminated soil, or released from hazardous waste sites (ATSDR, 1997). HCH has been banned a long time ago but traces of this chemical are continuously found in the environment because of its persistence and bioaccumulation in the environmental media (USEPA, 1994; ATSDR, 1997).

2.3.2.2 Environmental and biological health effects of hexachlorocyclohexane

The main sources of human exposure to HCH (lindane) has been through ingestion, inhalation, dermal contact, as well as from eating contaminated food or by breathing air contaminated during formulation or use of HCH (HSDB, 2009). A survey conducted by the U.S. FDA's Total Diet on HCH revealed that about 279 out of 2168 samples collected and at least one sample of 54 different food items analysed were found to contain HCH (FDA, 2006). HCH is harmful to humans. The short-term effects of HCH exposure through inhalation in humans results in irritation of the nasal passage and throat. Its long-term exposure affects the cardiovascular, liver, nervous, immune and blood systems (ATSDR, 1997; HSDB, 1993). Oral exposure to HCH in humans affects the nervous system and causes seizures and convulsions, vomiting and nausea as well as affects the musculoskeletal systems (ATSDR, 2000; ATSDR, 1997; HSDB, 1993). Acute toxicity, from oral exposure to HCH, conducted on mice and rats have reported reproductive effects such as decreased sperm count, increased testicular weight, and disruption of spermatogenesis in males. Disrupted ovarian cycling and reduced ovulation rate have also been reported in female animals exposed to HCH, while developmental effects have not yet been reported (RTECS, 1993). Oral exposure studies on animals have also shown HCH to be a liver carcinogen. The EPA has classified lindane as a Group B2/C, possible human carcinogen. The USEPA have set a maximum contaminant level (MCL) at 2 µg/L and the FDA has set the maximum permissible level (MPL) in bottled water at 2 µg/L (USEPA, 2002). Resource Conservation and Recovery Act (RCRA) set a toxic characteristic leaching procedure threshold for HCB at 400 µg/L and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold limit value – time-weighted average (TLV-TWA) was set at 500 µg/m³ in air (USEPA, 2002).

2.3.3 Heptachlor

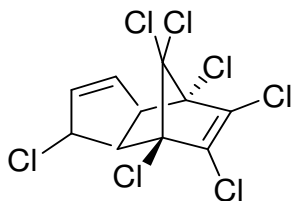


Figure 2.4 Structure of heptachlor.

Pure heptachlor is a white crystalline solid with a camphor-like odour however the technical-grade heptachlor is a tan coloured powder. Heptachlor is highly insoluble in water, and is readily adsorbed onto particulate matter and organic solvents. It is expected to partition into the atmosphere because of its volatile nature. It is persistent and has a half-life of up to 2 years in temperate soil and because of its high partition coefficient ($K_{ow} = 4.4-5.5$), it adsorbs strongly to aquatic sediments and bioconcentrates in organisms (WHO, 2004). Heptachlor is very stable, is a semi volatile chemical and is sparingly soluble in water which makes it suitable for trans boundary movement which has resulted in the parent molecule and its metabolites being detected in Arctic water, air and bioorganisms (WHO, 2008).

2.3.3.1 Sources of heptachlor

Heptachlor is a man-made chemical and a constituent of technical grade chlordane, approximately 10 percent by weight (ATSDR, 1993). It is a targeted stomach and contact insecticide, used mainly against soil insects and termites. Heptachlor was formally used from 1953 to 1974 as a soil and seed treatment to protect corn, small grains, and sorghum from pests. It was also used against grasshoppers, cotton insects and some crop pests to control ants, cutworms, maggots, termites, and other pests in agriculture and it was used in homes to combat malaria (Worthing, 1991, ATSDR, 1993). Production, sale and usage of heptachlor were voluntarily stopped in 1987 by its sole U.S. manufacturer. In 1988, the sale, distribution, and shipment of existing stocks of all cancelled heptachlor and chlordane products were prohibited in the United States and in most of the countries across the globe however heptachlor application by subsurface injection still continues (ATSDR, 1993). The only commercial use of heptachlor products still permitted is fire ant control in power

transformers. In addition, homeowner's use of existing stocks of heptachlor-containing termite control products is allowed in most developing countries (ATSDR, 1993).

2.3.3.2 Environmental and biological health effects of heptachlor

Heptachlor is moderately persistent in the environment most especially in soil, where it can be readily oxidised to its epoxide form (heptachlor epoxide). In animals, heptachlor metabolises to the epoxide form, which has similar toxicity to heptachlor and which may also accumulate in animal fat. In addition, it may undergo significant photolysis, oxidation and volatilization reactions (Mabey *et al.*, 1981). It binds to soil particles and migrates slowly in the environment (Tzapko *et al.*, 1967). The main source of exposure to heptachlor is through food (Handerson *et al.*, 1969; Johnson and Manske, 1977). Acute inhalation of heptachlor by humans has been associated with nervous system effects in a few case studies, while gastrointestinal effects, such as nausea and vomiting, have been reported following accidental ingestion of heptachlor (ATSDR, 1993; HSDB, 1993). Acute exposure to heptachlor *via* the oral route has shown effects on the liver and central nervous system in animals (ATSDR, 1993; HSDB, 1993). Heptachlor has been shown to cross the placenta to the developing foetus in humans. Developmental effects of oral exposure to heptachlor in animal studies have been reported. These include foetal resorptions, decreased postnatal survival, as well as reproductive effects such as failure of animals to reproduce (ATSDR, 1993). Oral administration of heptachlor has been shown to increase the incidence of liver tumours in mice (IARC, 1987). The EPA considers heptachlor to be a possible cancer-causing agent and has classified it as a Group B2 carcinogen (USEPA, 1999). However, due to low concentrations of heptachlor and its epoxide form in drinking-water, lower than is toxic, it is not considered necessary to derive a guideline value (Handerson *et al.*, 1969; Johnson and Manske, 1977).

2.3.4 Aldrin and Dieldrin

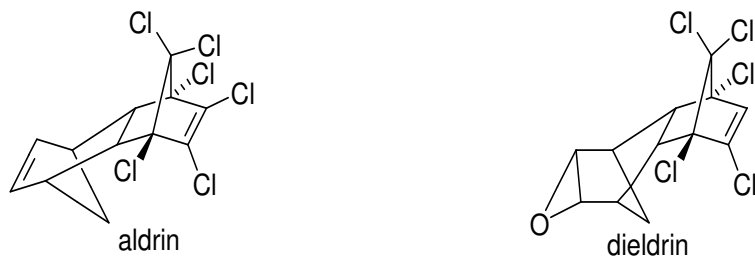


Figure 2.5 Structures of aldrin and dieldrin.

Both aldrin and dieldrin will be discussed together because they share some common traits and because aldrin readily converts into dieldrin once it enters either the environment or body (Ritter *et al.*, 2005). Aldrin and dieldrin have similar structures and were previously used as insecticides. Technical grades of powdered aldrin and dieldrin have a tan colour while their pure forms are white powders. Both compounds evaporate slowly in air although aldrin evaporates more readily than dieldrin. They both have mild chemical odours. Aldrin/dieldrin are known to be very stable to organic and inorganic alkalies, diluted acids, and hydrated metal chlorides (Budavari *et al.*, 1989; Lewis, 1993), while dieldrin in some cases may react with sunlight to produce photodieldrin (IARC, 1974b). Aldrin has minimal corrosive ability towards steel, brass, copper, nickel, and aluminium. Both aldrin and dieldrin have relatively passive corrosive tendencies to metals upon storage as a result of the slow formation of hydrogen chloride (HSDB, 2000a; IPCS, 1989b). Most fertilizers, herbicides, fungicides, and insecticides were reported to be compatible with aldrin and dieldrin (Lewis, 1993). Generally, contact with concentrated mineral acids, acid catalysts, acid oxidizing agents, phenols, or active metals with aldrin and dieldrin should be highly avoided (IPCS, 1989a, b). Dieldrin is formed by the epoxidation of aldrin with peracetic or perbenzoic acid (IARC, 1974a, b), and is a stereoisomer of endrin (Budavari *et al.*, 1989). Dieldrin has been reported to react with hydrogen bromide to give bromohydrin (HSDB, 2000b). Because of their persistent nature and hydrophobicity, aldrin and dieldrin are known to bioconcentrate (WHO, 1989).

2.3.4.1 Sources of aldrin and dieldrin

Aldrin and dieldrin are man-made chemicals (laboratory chemicals) and do not occur naturally in the environment. They may be found in soil and water and in homes where they were mostly used to combat termites. These chemicals could also be found in plants and animals close to hazardous waste sites. Both chemicals are no longer produced and used in the environment. They were both used extensively in the 1950s till 1970s as insecticides on crops such as corn and cotton. The Department of Agriculture in the United States stopped the usage of these chemicals in 1970. Consequently in 1972, they were both approved by the EPA for the eradication of termites where their usage continued until 1987, but in that year the registration of these chemicals were voluntarily cancelled by the manufacturers.

2.3.4.2 Environmental and biological health effects of aldrin and dieldrin

Aldrin is normally introduced into the environment through application to soil as an insecticide. A large percentage is rapidly converted to dieldrin *via* epoxidation, which in turn persists in the environment because of its high hydrophobicity and extremely low volatility. Dieldrin can travel long distances by wind by attaching to dust particles. Dieldrin is highly retained in animal fats, plant waxes and organic particulates due to its lipophilic and hydrophobic interaction with water. Since dieldrin is fat soluble, it has the potential to progressively accumulate in the food chain, which in turn could lead to build up of high concentrations in organisms that exceed the lethal limits (USEPA, 1980). Dieldrin evaporates slowly from surface water or soil and changes to photodieldrin within a few days in air. The primary exposure route to aldrin and dieldrin is through eating contaminated food. These contaminated foods may be seafood harvested from contaminated water sources, root crops, dairy products, and meats. Exposure could also be through breathing air, drinking water or possibly coming into contact with contaminated soil at hazardous waste sites. Skin contact and inhalation of aldrin and dieldrin by workers using it as an insecticide have also been reported (ATSDR, 2002). People living in homes that had been treated for termites using aldrin or dieldrin have shown the highest levels of exposure. Infants' exposure to aldrin and dieldrin had been reported to be through drinking their mother's milk containing these chemicals. Health effects of people exposed to low concentrations of aldrin or dieldrin may not be noticed immediately because these chemicals build up in the body with time. Exposure to moderate levels of aldrin or dieldrin for a long period may lead to symptoms such as vomiting, dizziness, irritability, headaches and uncontrollable muscle movements.

The EPA has classified both chemicals as probable human carcinogens based on animal studies, but the International Agency for Research on Cancer (IARC) has determined that the two chemicals are not classifiable in their carcinogenicity to humans (IARC, 1987). Studies on animals show that high concentrations of aldrin and dieldrin affect the nervous system and the kidneys similar to those seen in humans (ATSDR, 2002). Other associated effects of aldrin and dieldrin in animals include liver changes and immune suppression. In addition, children born to mothers who have consumed large quantities of aldrin or dieldrin, have a high mortality rate however the reproductive and developmental effects of aldrin and dieldrin have yet to be established. The EPA recommendation for a lifetime drinking water exposure concentration limit for aldrin and dieldrin was set at 1 µg/L and 2 µg/L respectively (USEPA, 2000). This guideline protects against adverse non cancer health effects that make the assumption that all exposure is from consuming contaminated drinking water (USEPA, 2002). According to the FDA, the maximum allowable aldrin and dieldrin residue in raw food should be from 0 to 100 µg/kg depending on the type of food product. Both Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) recommended a maximum average value of 250 µg/m³ in air for an 8 and 10-hour workday over a 40-hour workweek for aldrin and dieldrin manufacturing workplaces to protect workers (USEPA, 2003).

2.3.5 Endrin

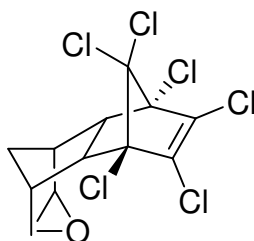


Figure 2.6 Structure of endrin.

Endrin is an endo stereoisomer of dieldrin and is a white, odourless, crystalline solid substance in its pure state with the technical grade having a light tan colour and a faint chemical odour. Technical endrin has a purity of at least 92% (WHO, 1992a). The persistent nature of endrin together with its high partition coefficient enables it to bioconcentrate in

particulate matter and organisms. Endrin appears to biomagnify only slightly through various levels of the food chain (Metcalf *et al.*, 1973). Its low water solubility, high stability in the environment as well as semi-volatility favours its long-range transport, which has resulted in it being detected in as far out regions as Arctic fresh water (Lockhart *et al.*, 1992). Endrin is known for its quick metabolism in animals without accumulation in the fat with the same rate as other compounds of the same structures. Endrin enters the atmosphere through volatilization, and soil run-off can contaminate surface water (ATSDR, 1999; Ritter, 2005).

2.3.5.1 Sources of endrin

Endrin is synthesized by condensing vinyl chloride with hexachloro-cyclopentadiene, dehydrochlorination of the adducts and then reacting with cyclopentadiene to form isodrin, which is then epoxidized with acetic or benzoic acid (IARC, 1974; WHO, 1992a). Commercial preparations of solid endrin are typically known to contain 95-98% pure endrin. Endrin is an insecticide used mainly on cotton and grain crops. It was first introduced as an insecticide, rodenticide, and avicide in early 1951 to control cutworms, grasshoppers, borers, and other pests on cotton, sugarcane, tobacco, apple orchards and grain (EPA, 1979e). It was also used as an insecticide on bird perches. It was never used as extensively for termite-proofing or other applications in urban areas as aldrin/dieldrin (HSDB, 1995). Endrin was first registered for use in the USA in 1952 (Smith, 1991). Its toxicity to non-target populations of raptors and migratory birds led to its use as a pesticide agent being stopped. Except for use as a toxicant on bird perches, which was stopped in 1991, all other uses of endrin in the United States were voluntarily withdrawn by the manufacturer in 1986 (EPA, 1983e; USDA, 1995).

2.3.5.2 Environmental and biological health effects of endrin

The main sources for potential human exposure to endrin are through food residue items, unused stocks, unregistered use, inappropriate disposal, and from hazardous waste sites. However, there is no established evidence of significant exposure originating from any of these sources (ATSRD, 1996). Symptoms of endrin poisoning may range from convulsions, nausea, vomiting, dizziness, nervousness, confusion and headaches. Some of these symptoms may persist for some time, after exposure to high doses of endrin. Exposure to endrin has caused death as well as severe central nervous system (brain and spinal cord) injury, probably because the brain and other parts of the nervous system contain much fatty tissue where

endrin tends to remain. Swallowing large amounts of endrin (more than 0.2 mg/kg of body weight) may also result in convulsions and sudden death. Studies have shown that endrin causes birth defects such as abnormal bone formation in animals, but no such cases have been reported in humans. There have not been any reports of cancer related cases yet through exposure to endrin. Thus far, no significant excess of cancer has been found in factory workers exposed to an endrin prone work place, although endrin metabolites have been reported to be detected in their urine. The EPA and the Department of Health and Human Services, (DHHS) also known as International Agency for Research on Cancer (IARC), have not yet classified endrin as a potential human carcinogen because not enough information is available for its classification (IARC, 1987). The EPA's proposed maximum contaminant level (MCL) for endrin in drinking water is 0.2 µg/L (USEPA, 2002). The 1-day and 10-day health advisories set by the EPA for endrin in water for both children and adults is 20 µg/L, while the longer-term health advisories for children and adults are 3 µg/L and 10 µg/L, respectively (USEPA, 2007). The EPA recommends an ambient water quality criteria level of 1 µg/L to protect human health (USEPA, 2007). The limit set by NIOSH and OSHA for endrin in the atmosphere is 100 µg/m³ (USEPA, 1994; USEPA, 2007).

2.3.6 Mirex

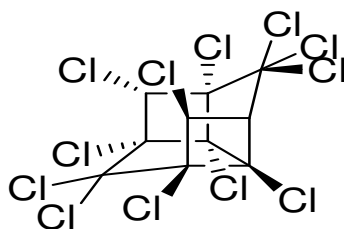


Figure 2.7 Structure of mirex.

Mirex is a major organochlorinated insecticide which is odourless, inflammable and a snow-white crystal at room temperature (HSDB, 2009). It is insoluble in water, but highly soluble in carbon tetrachloride, dioxane, methyl ethyl ketone, xylene and benzene. It is relatively stable at standard temperature and pressure (Akron, 2009). It is considered as one of the most stable and persistent pesticides with a very long half-life of up to 10 years. Due to its persistence and lipophilicity, it bioconcentrates, bioaccumulates and biomagnifies in organisms. Also, its low water solubility, high stability, high lipid solubility, as well as semi-

volatility encourages it to bind strongly to aquatic sediments resulting in long-range transport where it has also been found in Arctic fresh water and terrestrial organisms.

2.3.6.1 Sources of mirex

Mirex was first produced in the mid-1940s, but only became commercially available in the United State in 1958 (IARC, 1979; Smith, 1991). Technical grade mirex is a mixture of 95.12% mirex and 2.58% chlordecone. Mirex is produced by the dimerization of hexachlorocyclopentadiene in the presence of aluminium chloride (WHO, 1980). Mirex is famously known for its insecticidal properties and is used in South America to combat leaf cutters, harvester termites in South Africa and to control mealy bugs of pineapples in Hawaii. It was also investigated for possible use against yellow jacket wasps in the USA. Mirex was also used extensively as a fire retardant in electrical goods, paint, paper, plastics and rubber (ATRSD, 1995).

2.3.6.2 Environmental and biological health effects of mirex

Although, production and usage of mirex was banned in the environment a long time ago in many countries across the world, the residues of this chemical may still be present in the environment today, because of its persistence in the environment and high resistance to degradation (ATSDR, 1995). Other factors that may encourage its presence in the environment could be as a result of its historical use, improper disposal, accidental spillages or leaching, incineration and volatilization from old stockpiles. The primary routes of mirex exposure to humans is through food, most especially meat, fish from contaminated water bodies, residence near a former mirex manufacturing plant or waste-disposal site, or living in areas where mirex was previously used to control fire ants. Some of the effects on plants associated with mirex exposure include a reduction in plant germination as reported by Rajanna and de la Cruz (1975). Reports also indicated that, there is a possibility of uptake, accumulation and translocation of mirex by a variety of plant species (Mehendale *et al.*, 1972; Rajanna and de la Cruz, 1975). But the reasons for these occurrences are not fully understood because mirex being lipophilic should not be taken up and translocated by plants. Plants are mostly contaminated on the surface due to mirex depositing itself on the aerial parts of the plant (Fries, 1995). Short term effects of mirex in animals include a decrease in body weight, and morphological changes in liver cells. In addition, reduced litter sizes and parental mortality as well as formation of cataracts have been observed in animal studies.

Mirex has been reported as a reasonably anticipated human carcinogen because of evidence of its carcinogenicity from experimental studies on animals. Mirex has been reported to cause malignant liver tumours in both rats and mice (Akron, 2009; ATSDR, 1995; Bloom, 2005). IARC has classified mirex as a possible human carcinogen (Group 2B). The FDA has set a limit for mirex at 100 µg/kg in the edible portion of fish (ATSDR, 1995).

2.3.7 DDTs

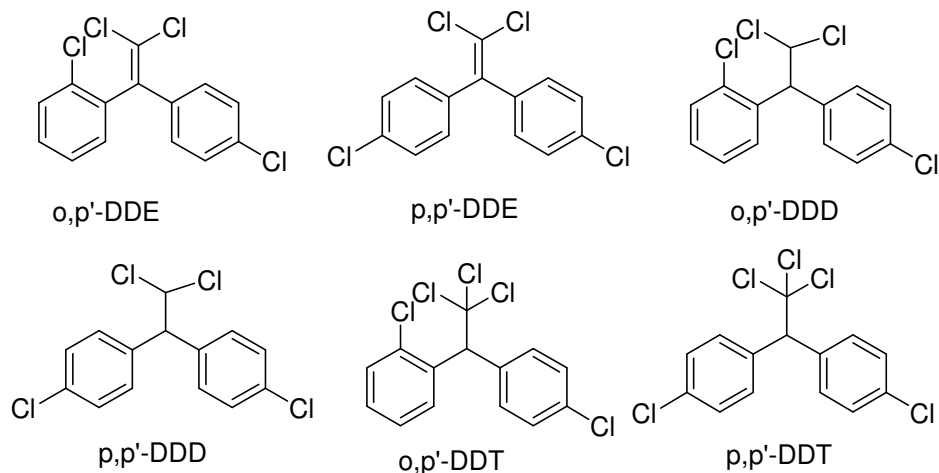


Figure 2.8 Structures of *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT and *p,p*-DDT.

DDT is a chlorinated aromatic hydrocarbon insecticide and the grade that was generally used as an insecticide was made up of fourteen chemical compounds of which only 65-85% was the active ingredient, *p,p*-DDT (NCI, 1978; ATSDR, 2002). Generally, technical DDT is a mixture of three isomers of DDT, mainly containing about 75% *p,p*-DDT, 15% *o,p*-DDT, 5% *p,p*-DDE, and < 5% *p,p*-DDD (Metcalf, 1973; Bopp *et al.*, 1982). DDT is a semi-volatile compound in its pure form and exists at room temperature as a colourless to off-white solid with a slight aromatic odour (Akron, 2009; HSDB, 2009). It is sparingly soluble in water, but readily soluble in most organic solvents such as benzene, benzyl benzoate, carbon tetrachloride, chlorobenzene, acetone, isopropanol, kerosene, morpholine, peanut oil, cyclohexanone, ethanol, ethyl ether, gasoline pine oil, tetralin, and tributyl phosphate as well as lipids (IARC, 1974; HSDB, 2009). DDT and its metabolites are very stable and exceptionally persistent in the environment and resistant to complete decomposition by

microorganisms although photochemical degradation does occur under aerobic conditions to DDE and under anaerobic condition to DDD (IPCS, 1989; Bossi *et al.*, 1992). DDT and its metabolites are readily adsorbed onto sediments and soils, which can both act as sinks and as long-term sources of exposure. The breakdown products of DDT, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD or TDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (DDE), are also present almost everywhere in the environment and tend to be even more persistent than DDT. Due to its lipophilicity and high partition coefficient it has a strong tendency to be adsorbed onto surfaces. Most DDT that enters water bodies adheres firmly to soil particulate matter and has demonstrated the ability to bioconcentrate and biomagnify (Ritter *et al.*, 2005). In most cases, when it does get into water, its concentration in the water is gradually reduced by adsorption onto surfaces (IPCS, 1989).

2.3.7.1 Sources of DDT

DDT is a non-systemic contact insecticide with a broad spectrum of activity. Its technical form was first synthesized in 1874, and its commercial production began around 1945 in the United States (ATSDR, 2002; HSDB, 2009). During this period it was widely used especially in the Second World War to control typhus³ and malaria vectors, and was thereafter extensively applied as an insecticide in agriculture. DDT is sold in a variety of different forms such as aerosols, dustable powders, emulsifiable concentrate, granules and wettable powders (RSC, 1991; Meister, 1992). It can be used with many other pesticides but it is incompatible with basic substances (RSC, 1991). Its production was however banned in most countries in 1972, due to ecological considerations, and many other countries have more recently restricted or banned its use except when it is needed for the protection of human health. Despite its banning in most countries across the globe and by the Stockholm Convention on POPs (UNEP, 2001), DDT is still used in some countries (including South Africa) for the control of vectors that transmit typhus, sleeping sickness, malaria, yellow fever and other insect-transmitted diseases and is illegally sold with different names used in

³ Typhus is sometimes called jail fever caused by a certain bacteria: *Rickettsia typhi* or *Rickettsia prowazekii*. *Rickettsia typhi* causes endemic or murine typhus. Endemic typhi is very common in an area where hygiene is very poor and a colder environment most especially during the winter period, while murine typhi is usually prevalent during the summer period with high precipitation rate (usually with high temperature).

agricultural practices in many developing countries (Van Dyk *et al.*, 1982; Awofolu and Fatoki, 2003; Bouwman, 2004).

2.3.7.2 Environmental and biological health effects of DDT

DDT was classified as a POP in 1997 by the Governing Council of the United Nations Environment Programme (UNEP, 1997). Human exposure to DDT still continues due to its extensive former use, current input in some developing countries across the world, as well as the persistent nature of DDT and its metabolites in the environment (ATSDR, 2002). Currently DDT is still being released into the atmosphere through spraying in some parts of the world. However, it volatilizes most especially in temperate regions from soil, in areas where it was used previously. Volatilization and deposition processes of DDT may be continuous for long periods, resulting in its worldwide distribution. Due to extremely low water solubility of DDT, it is highly sorbed onto organic matter and very slightly mobile where it could be ingested by aquatic animals and thereby bioaccumulate in animal fats through the food chain which could be a possible factor responsible for its presence in the environment (USEPA, 1989; WHO, 1989). DDT and its metabolites have been found across the world, from the Arctic to the Antarctic and have been detected in indoor environments, through snow and rain in water, soil, and animal and plant tissues. Its residue levels in the environment have diminished but due to the high persistence of DDT, it will be present at low levels for some time (DHHS, 2011). The primary source of DDT to humans is through ingestion of contaminated foods particularly meat, fish, poultry, and root and leafy vegetables as well as through inhalation. Inhalation results in the carcinogen being trapped in mucous secretion which is then swallowed thus exposing the individual to DDT (ATSDR, 1994). Adverse effects of DDT have been reported in animals such as eggshell thinning and altered gonadal development in birds of prey exposed to DDT which has resulted in the severe decline of the population. Also, DDT has been reported to cause some health related effects in animal organs such as the liver, the central nervous system, as well as estrogenic and anti-androgenic effects. DDT has also been linked to reproductive or teratogenic, immunological and epidemiological effects in animals but no such adverse effects have been reported in humans (FAO/WHO, 2001). A study on animal exposure to DDT found that it caused primary liver-cell tumors, increased incidences of lung tumors and malignant lymphoma (IARC, 1991). A recent study on cancer as a risk factor in human organs as a consequence of DDT exposure has been documented. Studies have shown that there is a link between

exposure to DDT and its metabolites, and cancer related issues in some tissue sites in humans such as liver, gallbladder prostate and adipose tissue (Shukla *et al.*, 2001; Settimi *et al.*, 2003). Morris-Brown and co-workers reported a case of leukemia among the agricultural workers exposed to DDT (Morris-Brown *et al.*, 1990).

Plasma related cancer (multiple myeloma⁴) was reported in a case study of farmers who were exposed to DDT (Eriksson and Karlsson, 1992; Cocco *et al.*, 1997). An increased risk of liver cancer was also reported to be linked to DDT found in serum and DDE found in adipose tissue (Cocco *et al.*, 1997; McGlynn *et al.*, 2006). Other associated risks of cancer at other tissue sites, such as the gallbladder, prostate and testes have also been reported (Shukla *et al.*, 2001; Settimi *et al.*, 2003; McGlynn *et al.*, 2008). IARC has determined that there is insufficient evidence for the carcinogenicity of DDT in humans but sufficient evidence has been found in experimental animals. Thus IARC has labelled DDT as a possible human carcinogen (Group 2B). The Food and Agriculture Organization of the United Nations and World Health Organization recommended guideline value for DDT and its metabolites is set at 1 µg/L (USEPA, 2000) in drinking-water to protect human health. The Water Quality Criteria based on fish or shellfish and water consumption recommended a guideline of 0.00022 µg/L for DDT in water (EPA, 2000). The FDA acceptable levels for DDT in food items and in animal feed is set between 50 to 5000 µg/kg (USEPA, 2000). The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold limits value – time-weighted average (TLV-TWA) for DDT is set at 1 mg/m³ (NTP/DHHS, 2011). OSHA and NIOSH recommended a permissible exposure limit (PEL) of DDT at 1000 and 500 µg/m³ respectively (FAO/WHO, 2001).

⁴ Myeloma is a cancer resulting from plasma cells. The plasma cell becomes abnormal in a myeloma condition, replicates in an uncontrolled manner and releases only one type of antibody called paraprotein which has no useful function. Myeloma unlike other cancers does not exist as a lump or tumour. The majority of medical related problems of myeloma are caused by build-up of the abnormal plasma cells in the bone marrow and the presence of paraprotein in the blood or in the urine.

2.4 The *n*-Octanol/Water Partition Coefficient - K_{ow} (Log K_{ow})

$$K_{ow} = \frac{\text{Concentration in } n\text{-octanol phase}}{\text{Concentration in water phase}} = \text{Log}_{10}K_{ow} \text{ ----- (i)}$$

The octanol-water partition coefficient (K_{ow}), is a measure of the hydrophobicity (water repulsing) of an organic compound. The more the hydrophobicity of a compound, the less soluble it is in water, therefore the more likely it will adsorb to soil or sediment particles (Bedient, 1994). An organic compounds octanol-water partition coefficient, K_{ow} , is the ratio of the compound's concentration in equal volumes of *n*-octanol and water after equilibrium has been reached. Both temperature and water solubility are the major determinant factors for the partition coefficient (Smith *et al.*, 1988; Pontolillo and Eganhouse, 2001). It is also a measured ratio (at equilibrium) of the dissolved mass of the substance between equal layers of *n*-octanol and water. It is dimensionless which provides a useful predictor of the other physical properties for most pesticides and other organic substances with molecular weights less than 500 g/mol. Values of K_{ow} for organic chemicals can be quite large, and therefore for convenience it is often expressed as Log K_{ow} where the values range from -3 to 7. K_{ow} is found to be a good indicator of bioaccumulation of pesticides in organisms and food chains (Lyman *et al.*, 1990). K_{ow} values are generally influenced by the polarity of the pesticide. Non polar compounds have higher K_{ow} values and Log K_{ow} can be used to determine the relative ability of an organic compound to adsorb to soil. High Log K_{ow} values mean low aqueous solubility and are generally directly proportional to molecular weight, molar volume, and density (Mallhot & Peters, 1988; USEPA, 2009).

2.5 Soil Adsorption Coefficient K_{oc}/K_d

$$K_d = \frac{\text{Concentration of a chemical in soil}}{\text{Concentration of a chemical in water}} \text{ ----- (ii)}$$

$$K_{oc} = \frac{K_d \times 100}{\% \text{ organic carbon}} \text{ ----- (iii)}$$

Adsorption of pesticides on soils and sediments is an important parameter that determines the destination of pesticides in the environment and their eventual degradation processes. The K_d value is a measure of how tightly the pesticide binds or sticks to soil particles. The greater the K_d value, the more strongly the compound will adsorb onto soil and organic matter and not move within the soil resulting in it less likely to leach or contribute to runoff. Most pesticides

are non-polar and have more hydrophobic interactions, that is, they are insoluble in water. The non-polar pesticides are more likely to move out of water and adsorb onto soils and sediments which contain non-polar organic matter. The values for K_d varies greatly because the organic matter content of the soil is not considered in the equation. Therefore K_{oc} is most preferred to determine the capacity of soil to adsorb pesticides because it considers the organic matter content of the soil. K_{oc} is the ratio at equilibrium of mass of a substance, adsorbed onto a unit mass of soil, relative to the mass of the substance remaining in the water solution. K_{oc} is a dimensionless parameter; its value is greatly dependent on the physicochemical parameters such as pH, temperature and organic matter content of soil as well as polarity of the chemicals (USEPA, 2001; Zacharia, 2011).

2.6 Vapour Pressure (VP) and Henry's Law Constant-H (K_h)

$$K_h = \frac{16.04 \times \text{vapour pressure } (P) \times \text{molecular mass } (M)}{\text{temperature } (T) \times \text{solubility } (S)} \text{----- (iv)}$$

Vapour pressure is a measure of the tendency of a compound to turn into a gaseous state. The higher the vapour pressure of a compound, the faster it will move to the atmosphere and the lesser will be the available residues to leaching. This occurrence could, on one hand, be an advantage but does not necessarily mean that pesticides with high vapour pressures pose no threat to groundwater. A high vapour pressure can cause vapour drift and environmental pollution. Pesticides with high vapour pressure need to be handled in such a way so that the vapours do not escape into the atmosphere. A pesticide with low vapour pressure does not move into air, so there is potential to accumulate in water if it is water soluble or in soil or biota if it is not water soluble. The tendency of a pesticide to volatilize is dependent on its vapour pressure, molecular mass, temperature as well as solubility. This function is expressed by Henry's Law Constant (K_h). The lower the value of Henry's Law constant of the pesticide, the greater its leaching potential. K_h is defined as the concentration of pesticide in air over its concentration in water. The value can be determined using the pesticide's vapour pressure and solubility. K_h characterizes the tendency for a pesticide to move between the air and the river soil. This is highly influenced by the climatic condition of a given location based on seasonal changes. Higher temperature results in an increase in vapour pressure which together with high values of K_h cause pesticides to volatilize more easily into air. The greater

the value of Henry's law constant, the higher the tendency for the pesticide to volatilize from soil to water and into air.

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CHAPTER 3

MATERIALS AND METHODS

3.1 Sampling Sites

The geographical area in this research work is the province of KwaZulu-Natal (KZN) with focus on the Msunduzi River which is one of the main tributaries of the uMgeni River (one of the largest rivers in the KZN province). The Msunduzi River is popularly known by its anglicised name, the Dusi River, located in the uMgungundlovu district municipality and has a mean annual precipitation ranging from 684 to 1186 mm (Gericke *et al.*, 2004). It passes through highly industrialized areas, receives runoff from rural communities and the municipality along its course as well as agricultural areas; which all contribute to the levels of organic pollution in the river. Ten sampling sites were carefully selected along the Msunduzi River that represents various anthropogenic activities such as domestic, industrial, agricultural and municipal activities. Soil, sediment and water samples were collected along the course of the river in May 2013, July 2013, September 2013 and February 2014 which represented autumn, winter, spring and summer seasons respectively. Global positioning system (GPS) was used to locate each sampling site during each sampling period. The map of the sampling sites, site coordinates, site activities as well as physicochemical parameters of the river water during the sampling seasons are shown in Figure 3.1 and Table 3.1 respectively.

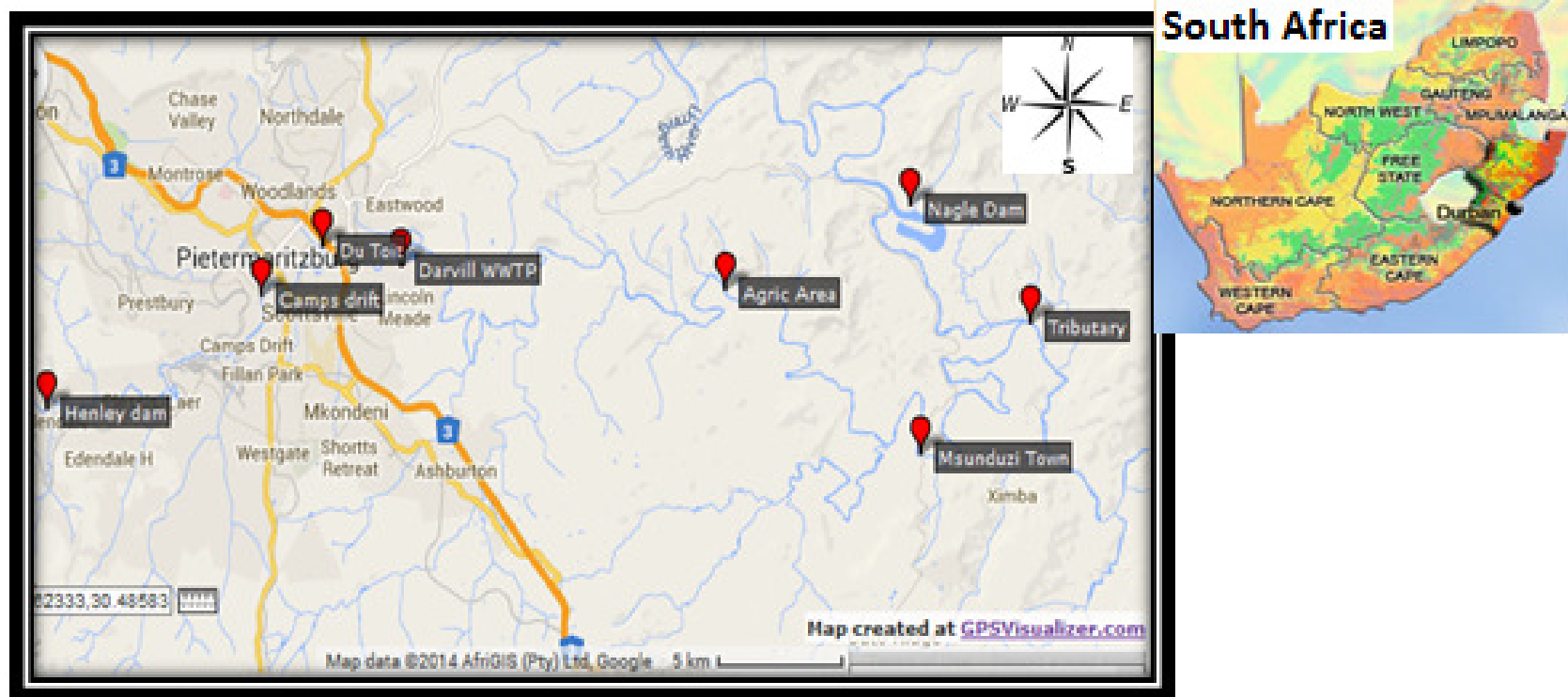


Figure 3.1 Map showing the sampling sites during the study seasons along the Msunduzi River, South Africa.

Table 3.1 GPS coordinates for sample sites, physicochemical parameters and description of sampling site activities.

Site code	Sample coordinates		Physicochemical parameters								Description of the sampling site
			pH during sampling seasons				Water Temperature (°C) during sampling seasons				
	Latitude	Longitude	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	
M 1	29° 38'51"	30° 17'32"	5.51	6.21	7.52	6.21	13.8	14	19	24.3	Domestic activities and surface runoff.
M 2	29° 36'47"	30° 22'36"	6.36	5.15	8.05	6.86	15.1	21	21	27.1	Domestic and Commercial activities.
M 3	29° 35'52"	30° 24'01"	6.01	7.20	7.49	6.62	15.3	15	18	25.0	Domestic and Commercial activities.
W 1	29° 36'15"	30° 25'52"	5.77	5.31	7.24	7.95	21.8	19	22	25.5	Influent of various wastes from the city of Pietermaritzburg.
W 2	29° 36'15"	30° 25'52"	5.95	5.54	7.85	6.32	20.7	19	22	27.7	Effluent of treated waste from the waste water treatment plant.
W 3	29° 36'15"	30° 25'52"	6.16	**	7.70	**	17.1	**	22	**	Effluent of treated waste discharged and agricultural activities.
M 4	29° 36'40"	30° 33'32"	5.50	5.12	8.72	6.68	14.2	14	24	30.1	Agricultural runoff and domestic activities.
M 5	29° 39'40"	30° 38'10"	5.75	4.77	8.92	6.19	15.1	15	26	30.9	Domestic and agricultural activities
M 6	29° 37'08"	30° 09'30"	6.07	5.56	8.87	6.10	22.8	15	21	30.6	Dam for water supply and agricultural runoff.
M 7	29° 37'16"	30° 40'46"	6.70	5.07	7.60	6.36	19.8	15	25	30.3	Domestic, agricultural and Surface Water runoff.

**= Samples were not collected due to major renovation at that particular sampling point during the sampling period M 1 = Henley Dam Outlet. M 2 = Camps Drift; M 3 = Du Toit; W 1 = Darvill Wastewater Treatment Plant 1 (inlet); W 2 = Darvill Wastewater Treatment Plant 2 (after chlorination); W 3 = Darvill Wastewater Treatment Plant 3 (discharge); M 4 = Agricultural Area; M 5 = Msunduzi Town; M 6 = Nagle Dam; M 7 = uMgeni, Msunduzi River joining point.

3.2 Reagents and Materials

All reagents and chemicals were of HPLC-grade and the eight PCB and thirteen OCP standards were purchased from Sigma-Aldrich® South Africa. They were PCB 28, PCB 52, PCB 77, PCB 101, PCB 105, PCB 138, PCB 153, and PCB 180 while OCPs studied were HCB, HCH, heptachlor, aldrin, *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT, *p,p*-DDT, dieldrin, endrin and mirex. High purity anhydrous sodium sulfate Gold line (CP) with CAS No. 7757-82-6 was obtained from Associated Chemical Enterprises (ACE) and used as a desiccant throughout the study, while silica gel, grade 634, of 100-200 mesh (0.063-0.2 mm) size, obtained from Merck, was used for both basic and acidic silica gel prepared in the laboratory for the clean-up of the extracts prior to analyses. Reagent grade sulfuric acid (specific gravity 1.84) obtained from Promark Chemicals was used for acidification. All glassware were baked in the oven at about 150 °C for 12 hours prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

3.3 Sampling and Sample Treatment

3.3.1 Sample collection

Soil and sediment samples were collected using the same method. Sediment samples were collected by scooping 0-10 cm of the sediment from the river bed with a stainless steel spade, while the soil samples were collected at a depth of 0-15 cm on the banks of the river close to the water using a grab sampler and stainless steel soil auger. The samples were stored in glass bottles. Water samples were collected in 2.5 L amber reagent bottles, which were washed with phosphate free, soap (dDyna Chem), rinsed with tap water and distilled water and finally rinsed with HPLC grade acetone, and *n*-hexane to eliminate both polar and non-polar contaminants prior to sampling. The bottles were rinsed twice with the river water to be sampled before the actual water sample was collected. A grab sampling technique was used to collect water samples from a depth of 1-2 cm from the water surface. The bottles were filled to overflowing to prevent headspace which could lead to loss of volatiles. A 1 mL aliquot of 50% sulfuric acid was added to each of the water samples immediately after collection to prevent microbial degradation of the samples. The lids of the glass bottles were lined with acetone pre-washed aluminium foil to prevent possible sample contamination from phthalates which could leach from the plastic lining of the lid (Derek and Sverko, 2006).

Samples were kept cool under ice during transportation to the laboratory. Samples were stored at 4 °C prior to extraction to prevent break down and bio-degradation of compounds of interest (Hilscherova *et al.*, 2003). Soil and sediment samples were air dried in the fume hood for five days; the dried samples were sieved with 75 µm, 300 µm, and 450 µm stainless steel sieves (purchased from DLD South Africa) and stored in the fridge prior to extraction. All samples were extracted and cleaned up within two weeks of sample collection.

3.3.2 Sample extraction

3.3.2.1 Soil and sediment:

The dried and homogenized sample (20 g) was mixed with 10 g of anhydrous sodium sulfate to remove excess moisture from the sample. An ultrasonic bath (UMC 20, 90022112 Kenmare) was used for the extraction due to its efficiency for organic pollutants as well as it required less solvent compared to the conventional soxhlet extraction method which requires much solvent and is time consuming (Zhou *et al.*, 2006; Adegbenro *et al.*, 2011). Soil and sediment samples were extracted with three times 30 mL dichloromethane (DCM), at 30 °C for 30 minutes each. Extracts were combined, filtered and concentrated to 2 mL using rotary evaporation (Hei-Vap, Heidolp version, Germany).

3.3.2.2 Water extraction:

Liquid-liquid extraction was adopted in this work because the method offered better results (Fatoki and Awofolu, 2003; US EPA, 1668B 2008) compared to the solid-phase extraction (SPE) method. The use of SPE cartridges during sample preparation has been shown to introduce interferences to the analytes of interest. Extraneous peaks, which appeared in the gas chromatograms, have been attributed to the phthalate esters contained in the housing materials of the cartridges (Fatoki and Awofolu, 2003). A 30 mL aliquot of dichloromethane was added to the empty separating flask, capped and shaken for 45 seconds to rinse the inner surface of the separating flask and decanted. A 500 mL aliquot of the water sample was transferred to the separating flask together with 40 mL of fresh DCM, and the sample was extracted by shaking the closed flask for 5 minutes with periodic venting. The organic layer was allowed to separate from the aqueous phase for 15 minutes. The DCM extract was removed, 10 grams of anhydrous sodium sulfate was added to it and the solution filtered. The procedure was repeated two more times; and the filtered extract fractions were combined and

reduced to 2 mL using rotary evaporation. Only the water sample collected from the waste water treatment plant was filtered through a vacuum sintered glass funnel to remove the solids and suspended particles due to the high turbidity of the water sample prior to the extraction.

3.3.3 Separation (Clean-up)

All samples were subjected to clean-up after extraction. Clean-up is an important step after extraction because it removes interferences from unwanted compounds leading to unambiguous results. It is important to remove and separate interferences from halogenated POPs using a suitable technique to reduce co-eluting peaks in chromatography. Two major steps were needed to reduce interferences, such as lipid removal by treating the extracts with concentrated sulfuric acid; and elemental sulfur can be removed as an interferent during sample analysis particularly if sediment or sewage samples are of interest. This was achieved by treating the extracts with activated copper powder set as a top layer on the silica column. In this research a multi-layer silica gel column was used as recommended by the United States Environmental Protection Agency (USEPA, method 1668B, 2008; Kumar *et al.*, 2013) for anthropogenic and organic pollutants. The column (Quickfit D1/11 England 50 mL) was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel, activated copper powder and 10 g anhydrous sodium sulfate (Na_2SO_4). The column was pre-eluted with 20 mL *n*-hexane before the extract was loaded; 50 mL of *n*-hexane:DCM:toluene solvent combinations were used for the elution in the ratio 2.5:1.5:1. The eluent was reduced to 2 mL using rotary evaporation and thereafter evaporated to dryness and weighed. The samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45 μm filter (acrodisc) prior to GC-MS analyses.

3.3.3.1.0 Preparation of basic and acidic silica gel for the clean-up

3.3.3.1.1 Basic silica (100 g)

A 4 gram sample of sodium hydroxide (NaOH) pellets was weighed into a beaker, distilled water was added and the solution stirred until homogeneous. The solution was then transferred into a 100 mL volumetric flask and made up to the mark with distilled water to make 1 N NaOH. About 33 g of this solution was combined with 67 g of silica gel in a beaker. The aggregates were broken up with a stirring rod until a uniform mixture was

obtained. The mixture was transferred into a 500 mL conical flask, covered with aluminium foil and agitated for 2 hours on the mechanical shaker, thereafter activated in the oven overnight at 250 °C and cooled in a desiccator prior to use.

3.3.3.1.2 Acidic silica (100 g 33% w/w)

A 44 g sample of concentrated sulfuric acid was thoroughly mixed with 66 g of activated silica gel in a clean 250 mL beaker. The aggregates were broken up with a stirring rod until a uniform mixture was obtained, transferred into a 500 mL conical flask and covered with aluminium foil and agitated for 2 hours on a mechanical shaker. The mixture was activated in an oven overnight at 250 °C, and cooled in a desiccator prior to use.

3.4 Standards

Stock Solution:

A 1000 ppm stock solution of mixed PCB and OCP standards was prepared by transferring 100 mg of each standard to a 100 mL volumetric flask and dissolving it in a small amount of *n*-hexane. Once completely dissolved, the solution was made up to the mark with *n*-hexane, the flask capped and shaken to homogenise the solution. The stock solution was kept in a fridge at 4 °C prior to use. The lower working standards of the mixed standard solutions were thereafter prepared from the stock solution using appropriate dilutions.

3.4.1 Preparation of stock and working standard solutions

Calculation:

$$100 \text{ mg} = \frac{1000 \text{ mg} \times 0.1 \text{ L}}{1 \text{ L}}$$

Lower working standards were prepared using the dilution factor method and the following equation:

$$C_1V_1 = C_2V_2 \text{ ----- (1)}$$

For example, a 0.125 mg/L of PCB was prepared from a stock of 1000 mg/L solution of PCB by transferring 1.25 µL of the stock solution to a 10 mL volumetric flask and making it up to

mark with *n*-hexane. The following calculations show the determination of the volume that needed to be transferred:

$$1000 \text{ mg/L} \times V_1 = 0.125 \text{ mg/L} \times 0.01 \text{ L}$$

$$V_1 = \frac{0.125 \frac{\text{mg}}{\text{L}} \times 0.01 \text{ L}}{1000 \text{ mg/L}}$$

$$V_1 = 1.25 \times 10^{-6} \text{ L}$$

$$V_1 = 1.25 \text{ } \mu\text{L}$$

Table 3.2 Volumes of 1000 mg/L stock solution that were transferred to 10.00 mL volumetric flasks for the preparation of calibration standards.

Required concentration (mg/L)	Required volume (μL)
0.125	1.25
0.250	2.50
0.500	5.00
1.000	10.00
1.500	15.00
2.500	25.00
5.000	50.00
10.00	100.00

Thus, 1.25 μL of stock solution was required to prepare a 0.125 mg/L solution of PCB in a 10 mL volumetric flask. In the same way calibration standards in the range 0.125 – 10.00 mg/L were prepared.

3.5 Instrumental Analyses and Quality Control.

3.5.1 GC-MS Analysis

The details of the GC-MS conditions as well as quality control measures such as procedural blanks, instrument sensitivity check, limits of detection and quantification (LOD/LOQ) as well as recovery studies have been reported in the papers. Two GC-MS instruments were used because the first Agilent GC-MS used, experienced hardware problems that took time to repair due to financial constraints and also because it was an old instrument, its maintenance budget was cut. Hence the autumn and summer samples were analysed on the Agilent GC-MS and the winter and spring samples were analysed on a Shimadzu GC-MS. Their conditions were as follows:

Winter and spring samples were analysed using gas chromatography/mass spectrometry (GC/MS) (Shimadzu QP-2010 Ultra Japan), with a DB-5MS capillary column of length 30 m (0.25 μ m internal diameter and 0.25 μ m film thickness). Helium was the carrier gas with a flow rate of 0.72 mL/min and a total flow of 31.8 mL/sec, a linear velocity of 32.2 cm/s at purge flow of 3.0 mL/min using splitless injection mode. The injection and detector temperatures were set at 220 °C and 320 °C respectively. Oven temperature was set at 150 °C and held for 2 min, raised to 295 °C at 14 °C/min and held for a further 2 min. A 1 μ L injection volume was used.

Autumn and summer samples were analysed using an Agilent gas chromatography/mass spectrometry (GC/MS) (GC-6890-MS-5973 series Germany), with a ZB-5MS fused-silica capillary column of length 30 m (0.25 μ m internal diameter and 0.25 μ m film thickness). Helium was used as a carrier gas with a flow rate of 1.0 mL/min, a total flow of 43.8 mL/sec and a linear velocity of 28 cm/s using splitless injection mode. The injection and detector temperatures were set at 250 °C and 325 °C respectively. Oven temperature was set at 125 °C and held for 1 min, raised to 295 °C at 15 °C/min and held for a further 2 min. A 1 μ L injection volume was used.

An external calibration method was used in determining the analyte concentrations in both water and sediment samples (EPA 1686B, 2008).

3.5.2 Calculations

3.5.2.1 Determination of percentage recoveries in sediment and soil for PCBs and OCPs.

Percentage recoveries for sediment and soil samples were determined using the method adopted by McCarty and co-workers for matrix spiked data (McCarty *et al.*, 2008).

$$\text{Percentage Recovery (\%R)} = \frac{X_s - X_u}{K} \times 100 \text{ ----- (2)}$$

$$\%R = \frac{X_s}{X_u + K} \times 100 \text{ ----- (3)}$$

Where X_s is the measured value for a spiked sample ($\mu\text{g/kg}$), X_u is the measured value for an unspiked ($\mu\text{g/kg}$) sample and K is the known amount ($\mu\text{g/kg}$) that was spiked in the sample.

For example, two 20 g sediment samples were weighed into four separate beakers; two portions were spiked with an 80 $\mu\text{g/kg}$ OCP standard mixture each and homogenised while the other two portions were left unspiked. The spiked and unspiked samples were both extracted after four days and subjected to the same clean up procedure as done for the original sample. The value of X_s and X_u for one pair of spiked and unspiked samples were determined as, 157.39 $\mu\text{g/kg}$ and 71.54 $\mu\text{g/kg}$ respectively for *o,p*-DDE at a retention time of 9.631 min. The percentage recovery calculation is as follows:

$$\%R = \frac{X_s - X_u}{K} \times 100.$$

$$\%R = \frac{157.39 - 71.54}{80} \times 100 = 107.31 \%$$

$$\%R_{o,p\text{-DDE}} = 107.31 \%$$

The percentage recovery was performed in on the other pair as a duplicate and the average was then determined.

3.5.2.2 Determination of percentage recoveries in water sample.

Water recovery was evaluated using tap water and was based on the EPA 1668B method.

$$\text{Percentage Recovery (\%R)} = \frac{\text{Concentration found in } \frac{\mu\text{g}}{\text{L}}}{\text{Concentration spiked in } \mu\text{g/L}} \times 100 \text{ ----- (4)}$$

Two samples of tap water were spiked with 8 µg/L of mixed PCB standards each (two samples for duplicate analysis) and homogenised. The homogenised samples were extracted after three days and subjected to the same analytical procedure as the original samples. PCB 153 concentrations were found to be 6.70 µg/L and 7.05 µg/L in the two samples.

$$\%R = \frac{6.70}{8.00} \times 100 = 83.75 \%$$

$$\text{and } \frac{7.05}{8.00} \times 100 = 88.13 \%$$

Average of duplicate analyses = 85.94 % PCB 153.

3.5.2.3 Determination of LOD and LOQ

The LOD/LOQ values were determined using the method employed by Shrivastava and Gupta based on the equation of the calibration graph (Shrivastava and Gupta, 2011).

$$\text{LOD} = 3.3 * \mathbf{Sm} / \mathbf{b} \text{-----} (5)$$

$$\text{LOQ} = 10 * \mathbf{Sm} / \mathbf{b} \text{-----} (6)$$

Where **Sm** is the standard deviation of the response and **b** is the mean of the slope of the calibration curve.

Peak areas were plotted against concentrations ranging between 0.125 µg/mL – 10 µg/mL (a six point calibration curve). Each standard was analysed in triplicate and three calibration graphs were plotted. The gradient and y-intercept was determined for each calibration graph from their straight line equations and the standard deviation of the average intercept was determined. This standard deviation was used in equations 5 and 6 together with the average slope and intercept to determine the LODs and LOQs for each analyte. For example, the values of both standard deviation of the intercept (**Sm**) and mean of the slope (**b**) of the triplicate values were found to be 74.85 and 62012.33 respectively.

$$\text{LOD} = \frac{3.3 \times 74.8455}{62012.33} = 0.00398$$

$$\text{LOQ} = \frac{10 \times 74.8455}{62012.33} = 0.01207$$

The same average intercept and slope was used in the determination of the concentration of the analytes in the samples discussed in 3.5.2.4.

3.5.2.4 Determination of individual concentration of analytes in water samples.

The following equation was used to determine the individual concentration of the analyte in the sample:

$$\text{Concentration (ng/mL)} = \frac{(C_{ex})(V_{ex})}{(V_s)} \times 1000 \text{-----} (7)$$

Where C_{ex} is the concentration ($\mu\text{g/L}$) of the compound in the extract, V_{ex} is the volume of the total extract (mL) and V_s is the volume of water extracted (mL).

For example, in the analysis of PCB 77, a 500 mL water sample was extracted, cleaned-up and concentrated to a final volume of 2 mL. For GC-MS analysis, 1 mL of the filtered extracted sample was combined with 1 mL of a 1 $\mu\text{g/mL}$ standard and analysed in duplicate. Each peak area (spiked concentration + original concentration) obtained was then used to determine the concentration of the analyte using the equation of the straight line (see Appendix A). The spiked concentration was then subtracted from this concentration (spiked + original) to give the actual original concentration that was present in the sample taking into account the dilution factors. Finally the average of the duplicate results was determined. For example, the spiked concentration of 1 $\mu\text{g/mL}$ was subtracted from the final concentration obtained to give an actual concentration of 0.085 $\mu\text{g/mL}$:

$$\text{Concentration of PCB 77 found } (\mu\text{g/mL}) = \frac{0.085 \frac{\mu\text{g}}{\text{mL}} \times 2 \text{ mL}}{500 \text{ mL}} = 0.00034 \mu\text{g/mL}$$

Concentration (ng/mL) = 0.00034 $\mu\text{g/mL} \times 1000 = 0.34 \text{ ng/mL}$ of PCB 77 was found in water sample.

3.5.2.5 Determination of the actual concentrations of the analytes in sediment and soil samples

Equation 8 was used to determine individual concentrations of each analyte in both sediment and soil.

$$\text{Concentration (ng/g)} = \frac{(C_{ex})(V_{ex})}{W_s} \text{-----} (8)$$

Where W_s is the amount of solid sample (in dry weight) extracted in kg.

For example, a 20 g sediment sample was extracted, cleaned-up and concentrated to a final volume of 2 mL. The same procedure as discussed above was used to give a value of 0.136 µg/mL after subtraction of the spiked standard. Using equation 8,

$$\text{Concentration (ng/g) of PCB 77 congener in sediment sample} = \frac{0.136 \frac{\mu\text{g}}{\text{mL}} \times 2 \text{ mL}}{20 \times 10^{-3} \text{ kg}} = 13.6 \text{ ng/g}.$$

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CHAPTER 4

RESULTS AND DISCUSSION

Paper 1: Quantitative Analyses of Selected Polychlorinated Biphenyl (PCB) Congeners in Water, Soil and Sediment during Winter and Spring Seasons from Msunduzi River, South Africa

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ABSTRACT

Persistent organic pollutants such as polychlorinated biphenyls are bio accumulating as well as non-biodegradable in the environment. Many studies done within KwaZulu-Natal Rivers have only focused on inorganic pollutants. The lack of information and the need for knowledge on the organic pollutants within this area together with the global problem of water supply has prompted our investigation into the analyses of eight PCB congeners in the Msunduzi River of KwaZulu-Natal, South Africa and the results and outcomes of this study serve as a baseline assessment for various levels of government and scientific communities for future planning on the state of this river. Soil, sediment and water samples were collected at ten different sites along the river during winter and spring seasons. Soil and sediment samples were extracted using ultra sonication with dichloromethane while water samples were liquid-liquid extracted using dichloromethane. All sample extracts were cleaned-up using a multi-layer silica gel column and analysed with gas chromatography-mass spectrometry. Quality assurance measures were also determined. The percentage recoveries for water were 51.96-128.16 for all the PCBs analysed, while sediment recoveries ranged between 69.27-104.47 %. The highest total concentrations of the PCBs were 214.21-610.45 ng/g and 30.86-444.43 ng/g in winter and spring respectively. Soil PCB concentrations were 76.53-397.75 ng/g and 20.84-443.49 ng/g in winter and spring respectively. Water samples showed the lowest PCB concentrations of 0.68-22.37 ng/mL and 2.53-35.69 ng/mL for winter and spring seasons respectively. In all the

sampling sites selected for this study, Du Toit afforded the highest PCB concentration levels and the lowest was after chlorination at the Darvill wastewater treatment plant. The results presented are new and it is the first study of organic pollutants such as PCBs that have been carried out on this river.

Keywords: *Organic pollutants, polychlorinated biphenyls (PCBs), Msunduzi River, gas chromatography-mass spectrometry*

4.1 Introduction

Persistent organic pollutants (POPs) have been a serious environmental concern to both the local and the international community. This important class of organic pollutants, once released into the environment, persists and remains intact for a long period, due to their stability against chemical, photolytic and biological degradation (Buccini, 2003; Yenisoy-Karakas *et al.*, 2012). POPs are lipophilic, have long-range transportation, are bio accumulating in the food chain and are characterized as acutely toxic. POPs are found almost everywhere even where they have never been generated (Buccini, 2003). They tend to travel from hotter regions towards colder areas and settle in the soil and sediment for very long periods because temperature and light does not encourage their degradation (Zhao *et al.*, 2006).

Polychlorinated biphenyls (PCBs) are one of the twelve major organic pollutants known as the dirty dozen listed under the Stockholm Convention. They are a group of chlorinated synthetic organic chemicals that have relatively low water solubility and relatively long environmental and biological half-lives of 8-15 years (ATSDR, 2000). PCBs are introduced into the environment by anthropogenic activities such as incineration of PCB-containing waste, burning of many materials that may contain chlorine; wood treated with pentachlorophenol as well as uncontrolled landfills and hazardous waste sites (Safe, 1994; Davis *et al.*, 2007). PCBs were once widely used as dielectric and coolant fluids in electrical appliances such as transformers and, capacitors. PCBs were also used as, pesticide extenders, heat exchange fluids and as flame-retardants but such applications of PCBs have since decreased (Fiedler, 2001). Due to their environmental toxicity and classification as a POP, PCB production was banned in the United States in 1979 and by the Stockholm Convention (SC) on POPs in 2001 which South Africa was a party to (Porta and Zumeta, 2002; Bouwman, 2004). However, because of their persistency and tendency to bioaccumulate in the sediment they are still found in the environment today. In addition they bioaccumulate in

organisms and transfer to higher trophic levels and thus progress through the food chain posing serious health problems to animals and humans (Tanabe, 2002; Chau, 2005). PCBs are ubiquitous in the environment; and humans are primarily exposed to this organic pollutant *via* the ingestion of contaminated foods containing commercial mixtures of PCB congeners (Kreiss, 1985; Rose *et al.*, 2001; Shadel *et al.*, 2001). PCBs are endocrine disruptors and exposure to them has been linked to some health related problems such as acne-like skin conditions in adults and neurobehavioral and immunological changes in infants (Klanova *et al.*, 2007; ATSDR, 2000). Other related health issues associated with PCB exposure are cancer related illnesses, mental disorders as well as toxicity problems such as endocrine and neurotoxicity effects in humans. In the South African context, there is limited information on the concentrations and distributions of POPs particularly in KwaZulu-Natal. Previous research on KwaZulu-Natal's rivers focused on inorganic pollutants and very little research has been carried out on POPs, which are just as toxic and accumulating as the inorganic pollutants. Any research that has been carried out on POPs was also undertaken many years ago which is now out dated and new studies are required to provide a more updated scenario of the state of the rivers. This, together with the global problem of water supply, has stimulated our investigation into the analysis of POPs most especially PCBs in the Msunduzi River of KwaZulu-Natal province, South Africa. This research investigated the presence and concentration of selected PCBs: PCB 28, PCB 77, PCB 101, PCB 52, PCB 153, PCB 105, PCB 138 and PCB 180 in soil, sediment and water samples of the Msunduzi River during winter and spring seasons. Figure 4.1 shows the structures for the selected PCBs.

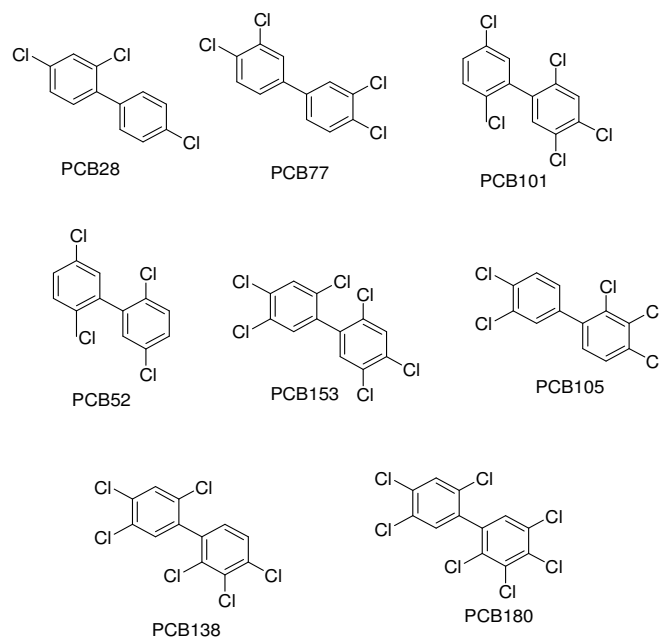


Figure 4.1 Structures of PCB congeners studied in this research.

4.2 Materials and Methods

4.2.1 Site Selection

The Msunduzi River is one of the main tributaries of the uMgeni River, which is the main source of water to the greater region of KwaZulu-Natal. The Msunduzi River passes through highly industrialized areas as well as rural and agricultural areas, which all contribute to the levels of organic pollution in the river. This river is also used for various national water sports competitions (e.g. The Dusi canoe marathon) where people could possibly be exposed to these pollutants. Therefore, it is a suitable and important river for this type of study and the results will provide much needed information to a wide variety of stakeholders including the Municipality and the scientific community. Winter and spring samples were collected in July 2013 and September 2013 respectively. Soil, sediment and water samples were collected from ten different sites along the river course as indicated in Figure 4.2 and Table 4.2 Global Positioning System (GPS) was used to locate each sampling site along the river.

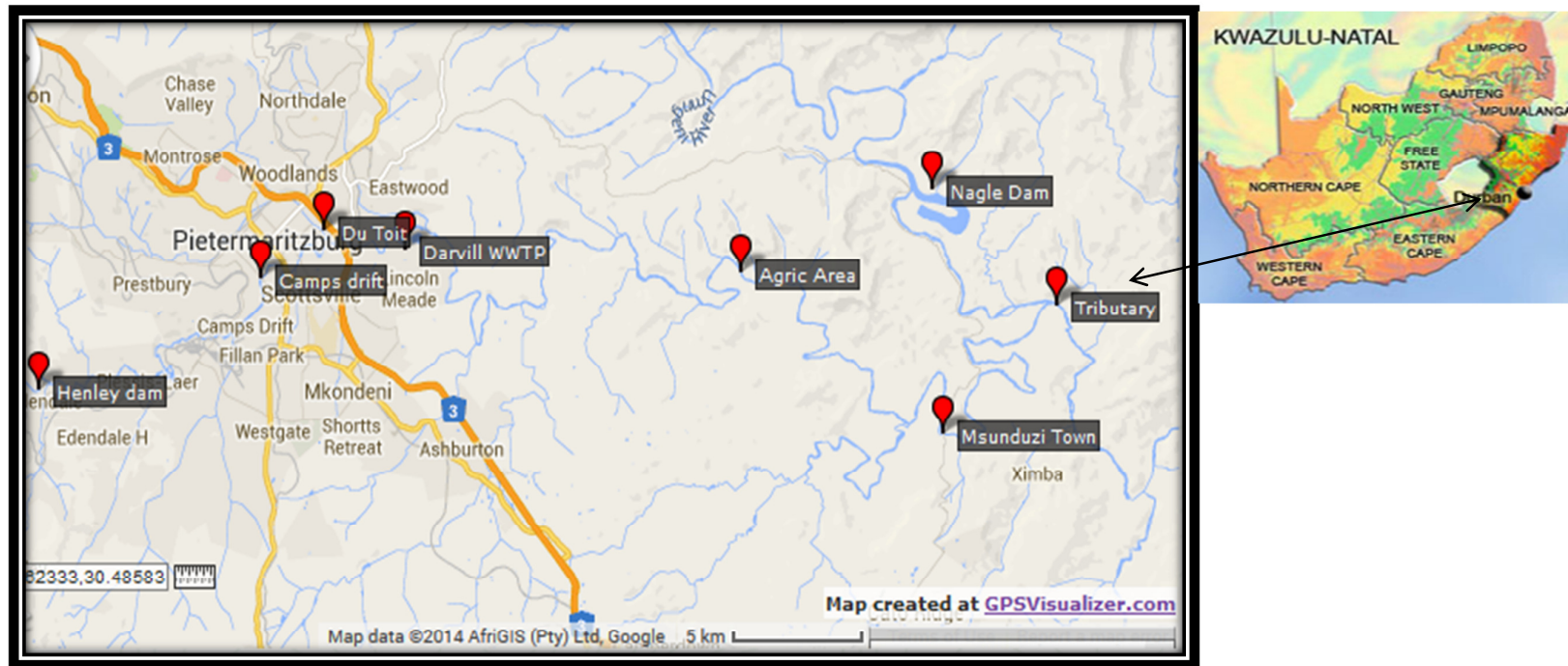


Figure 4.2 Map showing the sampling sites for this study along the Msunduzi River, South Africa.

4.2.2 Reagents and Materials

All reagents and chemicals were of HPLC-grade and the eight-selected PCB standards were purchased from Sigma-Aldrich® (South Africa). PCB stock solutions of 200 mg/L of individual standards were prepared by dissolving about 0.02 g of the individual PCB standards in 100 mL of *n*-hexane and stored in the refrigerator at 4 °C. The lower working concentrations for the PCB standards were prepared by appropriate dilution in *n*-hexane. High purity anhydrous sodium sulfate (Gold line (CP) CAS No. 7757-82-6, Associated Chemical Enterprises ACE) was used as a desiccant throughout the study, while silica gel (grade 634, of 100-200 mesh size (0.063-0.2 mm) purchased from Merck was used in preparation of both basic and acidic silica used for the clean-up of the extracts prior to analyses. Reagent grade sulfuric acid (specific gravity 1.84, Promark Chemicals) was used for acidification. All the glassware were baked in the oven at about 130 °C prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

4.2.3 Sampling and Sample Treatment

Soil and sediment samples were collected using the same sampling method. A total of seven soil and eight sediment samples were collected for winter and spring seasons respectively while a total of nine and ten samples were collected for sediment and soil in winter and spring seasons respectively. Bio-solids were collected as a sediment sample from the Darvill wastewater treatment plant. In addition, the point of discharge of treated wastewater back into the Msunduzi River was not accessible during the winter period due to major maintenance at that particular sampling site. Sediment samples were collected by scooping 0-10 cm of the sediment from the river bed with a stainless steel spade, while the soil samples were collected at a depth of 0-15 cm along the banks of the river close to the water using a grab sampler and stainless steel soil auger. The samples were stored in glass bottles. The lids of glass bottles were lined with acetone pre-washed aluminium foil to prevent sample reactions with phthalates possibly present in the plastic lining of the lid. Soil and sediment sample containers were kept cool under ice during transportation to the laboratory. Once in the laboratory, samples were kept at 4 °C prior to extraction to prevent break down and bio-degradation of the compounds of interest (Hilscherova *et al.*, 2003). Soil and sediment samples were air dried in the fume hood for five days; the dried samples were sieved with 75 µm, 300 µm, and 450 µm stainless steel sieves and stored prior to extraction.

Water samples were collected in 2.5 L amber reagent bottles, which were washed with phosphate-free soap (dDyna Chem), rinsed with tap water and distilled water prior to sampling. The bottles were also rinsed with HPLC grade acetone, and *n*-hexane to eliminate both polar and non-polar contaminants. Bottles were rinsed with the river water to be sampled before the water sample from the river was collected. Grab sampling technique was used to collect water samples from a depth of 1-2 cm below the water surface. A 1 mL aliquot of 50% sulfuric acid was added to each of the samples immediately after collection to prevent microbial degradation of the samples. Sample bottle lids were also lined with acetone pre-washed aluminium foil to prevent the possibility of migration of plasticizers (such as phthalates) from the plastic bottle lids into the sample (Derek and Sverko, 2006). Water samples were kept cool during transportation to the laboratory and stored at 4 °C prior to extraction. Glass and stainless steel was used throughout the sample preparation to prevent sample contamination with phthalates from plastic materials.

4.2.4 Sample extraction

Soil and sediment samples (20 g each) were dried, homogenized, and mixed with 10 g of anhydrous sodium sulfate to remove excess moisture from the sample. An ultrasonic bath (UMC 20, 90022112 Kenmare) was used for the extraction. Ultrasonication was the method of extraction, due to its efficiency for extracting organic pollutants as well as it requiring less solvent compared to the conventional soxhlet method, which requires much solvent and is time consuming (Adegbenro *et al.*, 2011). Soil and sediment samples were extracted with three times 20 mL DCM at a temperature of 30 °C for 30 minutes each. Extracts were combined, filtered and concentrated to 2 mL using rotary evaporation (Hei-Vap, Heidolph version, Germany).

Water extraction used liquid-liquid extraction because it offered better results (Fatoki and Awofolu, 2003; Sibali *et al.*, 2008) compared to the solid-phase extraction (SPE) method. SPE cartridges, during sample preparation, have been reported to introduce phthalate ester interferences, originating from the housing materials of the cartridges (Fatoki and Awofolu, 2003). A 500 mL aliquot of water was extracted with three times 40 mL of DCM in a separating funnel. The combined extract fractions were reduced to 2 mL using rotary evaporation. Only the water sample collected from the wastewater treatment plant was filtered through a vacuum glass funnel prior to extraction, to remove the solids and suspended particles due to its high turbidity.

4.2.5 Sample clean-up

All samples were subjected to clean-up after extraction. Clean-up is an important step after extraction, most especially for the removal of interferences from unwanted compounds and to prevent unambiguous results. Two major steps were needed to reduce interferences: lipids were removed by treating the extracts with concentrated sulfuric acid and elemental sulfur was removed by treating the extracts with activated copper powder set as a top layer on the silica column. In this study a multi-layer silica gel column was used as recommended by the United States Environmental Protection Agency (USEPA method 1668B 2008; Kumar *et al.*, 2013) for anthropogenic PCB pollutants. The column (Quickfit D1/11 England 50 mL) was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel; 2 g activated copper powder and 10 g anhydrous sodium sulfate (Na_2SO_4). The column was pre-eluted with 20 mL *n*-hexane before the extract was loaded; 50 mL of *n*-hexane:DCM:toluene solvent combinations were used for the elution in the ratio 2.5:1.5:1. The eluent was reduced to 2 mL using rotary evaporation and thereafter evaporated to dryness at room temperature. Samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45 μm acrodisc filter prior to GC-MS analysis.

4.2.6 Instrumental analyses and quality control

4.2.6.1 GC-MS Analysis

Samples were analysed using gas chromatography/mass spectrometry (GC/MS) (Shimadzu QP-2010 Ultra Japan), with a DB-5MS capillary column of length 30 m (0.25 μm internal diameter and 0.25 μm film thickness). Helium was the carrier gas with a flow rate of 0.72 mL/min and a total flow of 31.8 mL/sec, a linear velocity of 32.2 cm/s at purge flow of 3.0 mL/min using splitless injection mode. The injection and detector temperatures were set at 220 °C and 320 °C respectively. Oven temperature was set at 150 °C and held for 2 min, raised to 295 °C at 14 °C/min and held for a further 2 min. A 1 μL injection volume was used. All the quality control steps were followed. Laboratory blanks for both water and sediment were subjected to the same analytical procedures as applied to the original samples but did not show any significant peaks. Triplicate linear range values (R^2) for all the analytes were not less than 0.995 and LOD and LOQ values were determined for the analytes (Table 4.1). The method recoveries were calculated by analysing matrix spiked samples (USEPA method 1668B 2008). Sediment recoveries used the actual sediment samples that were then spiked and for water recoveries, tap water was spiked. Routine analysis of blanks with every

ten sample sets were carefully monitored to determine the possibility of any interferences from the column. Standards were run intermittently between samples to monitor changes in the instrument's sensitivity. Sample extracts were spiked with 80 µg/kg of the mixed PCB standards and their concentrations were determined. An external calibration method was used for the quantification of 8 PCB congeners based on the peak areas of the targeted compounds. Analytes were identified by comparing their retention times with those of the PCB standards.

Table 4.1 Percentage recoveries based on spiked sediment sampled from the agricultural area in winter and spring and spiked tap water, as well as limits of detection and quantification of PCB congeners in sediment and water.

PCB Congeners	Percentage recoveries		Limits of detection/Limits of quantification.				R ² Value (n=3)	Retention time (minutes)
	Water (%)	Sediment (%)	Sediment (ng/g)		Water (ng/mL)			
			LOD	LOQ	LOD	LOQ		
PCB 28	72.01	84.19	0.015	0.044	0.001	0.004	0.998	8.105
PCB 77	51.96	96.99	0.016	0.049	0.001	0.004	0.996	8.558
PCB 101	128.16	69.27	0.022	0.069	0.002	0.006	0.997	9.689
PCB 52	94.46	78.84	0.011	0.037	0.001	0.003	0.996	10.209
PCB 153	73.39	104.47	0.010	0.040	0.001	0.004	0.995	10.762
PCB 105	102.87	104.09	0.008	0.023	0.001	0.002	0.998	10.838
PCB 138	100.30	93.82	0.007	0.020	0.001	0.002	0.998	11.114
PCB 180	74.74	98.96	0.012	0.040	0.001	0.003	0.996	11.936

4.3 Results and Discussion.

4.3.1 Temperature and pH.

The pH, ambient and water temperatures were measured during the sampling seasons as shown in Table 4.2. The pH for all the sampling sites were shifted slightly towards acidic levels during the winter season except for the Du Toit sampling site which was within the neutral to slightly alkaline range. The pH values for all the sampling sites were within the alkaline range during the spring season but during the winter season, a low river flow rate was expected due to decreased rainfall which would result in higher accumulation of particulate matter in the water thus leading to low pH. Furthermore, during the spring period, the slightly higher temperature reduces the solubility of CO₂ which in turn leads to a more alkaline pH. Both water flow rate as well as current velocity affects adsorption and sediment transportation of pollutants (Yang *et al.*, 2009) which in turn affects the pH of the water. Pollutant dilution, and diffusion as well as distribution of organic pollutants in the surface sediments are greatly influenced by temperature as well as hydrodynamic conditions (Tang *et al.* 2000; Zhang *et al.* 2007).

Concentrations of PCBs were highest in sediment samples with 41.24% and 24.20% followed by soil samples with 15.80% and 17.00% in comparison to the water samples with 0.80% and 0.75% in winter and spring seasons respectively as shown below in Figure 4.3. The higher concentrations in the sediment and soil were expected because these pollutants are lipophilic and hydrophobic and tend to prefer to interact with organic surfaces and fatty tissues of organisms (WSPMP, 1996). Sediments and soils tend to be a 'sink' for these organic pollutants and are a measure of their concentrations over times (Aydrin and Yurdun, 1999).

Lower PCB concentrations were observed for the samples collected during the spring season as compared to the winter period for all matrices sampled. This is possibly due to the increase in temperature in spring, which would have caused snow, which fell during the winter season in high lying areas, to melt. This in turn leads to an increase in water flow, thereby increasing the dispersion and dilution of pollutants, resulting in lower detectable concentrations of PCB during the spring season. The increase in PCB concentration during the winter period could also possibly be due to low photochemical degradation, because of a decrease in temperature, shorter periods of available sunlight, and lower UV index values, which in turn could lead to high pollutant accumulation on particulate matter in the environmental media (Brunciak *et al.*, 2001; Yeo *et al.*, 2003; Cheng *et al.*, 2007).

Table 4.2 Sampling coordinates and physicochemical parameters of the Msunduzi River water during the winter and spring sampling seasons.

Site Name	Location		pH		Temperature °C (Winter)		Temperature °C (Spring)	
	Latitude	Longitude	Winter	Spring	Ambient	Water	Ambient	Water
HND	29° 38'51"	30° 17'32"	6.21	7.52	21	14	22	19
CMD	29° 36'47"	30° 22'36"	5.15	8.05	16	21	24	21
DUT	29° 35'52"	30° 24'01"	7.20	7.49	23	15	25	18
WWT 1	29° 36'15"	30° 25'52"	5.31	7.24	25	19	29	22
WWT 2	29° 36'15"	30° 25'52"	5.54	7.85	24	19	25	22
WWT 3	29° 36'15"	30° 25'52"	*	7.70	*	*	28	22
AGR	29° 36'40"	30° 33'32"	5.12	8.72	19	14	28	24
MST	29° 39'40"	30° 38'10"	4.77	8.92	20	15	24	26
NGD	29° 37'08"	30° 09'30"	5.56	8.87	18	15	22	21
UMJ	29° 37'16"	30° 40'46"	5.07	7.60	15	15	26	25

*= Samples were not collected due to major renovation at that particular sampling point during the sampling period. HND = Henley Dam Outlet; CMD = Camps Drift; DUT = Du Toit; WWT1 = Darvill Wastewater Treatment Plant 1 (inlet); WWT2 = Darvill Wastewater Treatment Plant 2 (after chlorination); WWT3 = Darvill Wastewater Treatment Plant 3 (discharge); AGA = Agricultural Area; MST = Msunduzi Town; NGD = Nagle Dam; UMJ = uMgeni, Msunduzi River joining point.

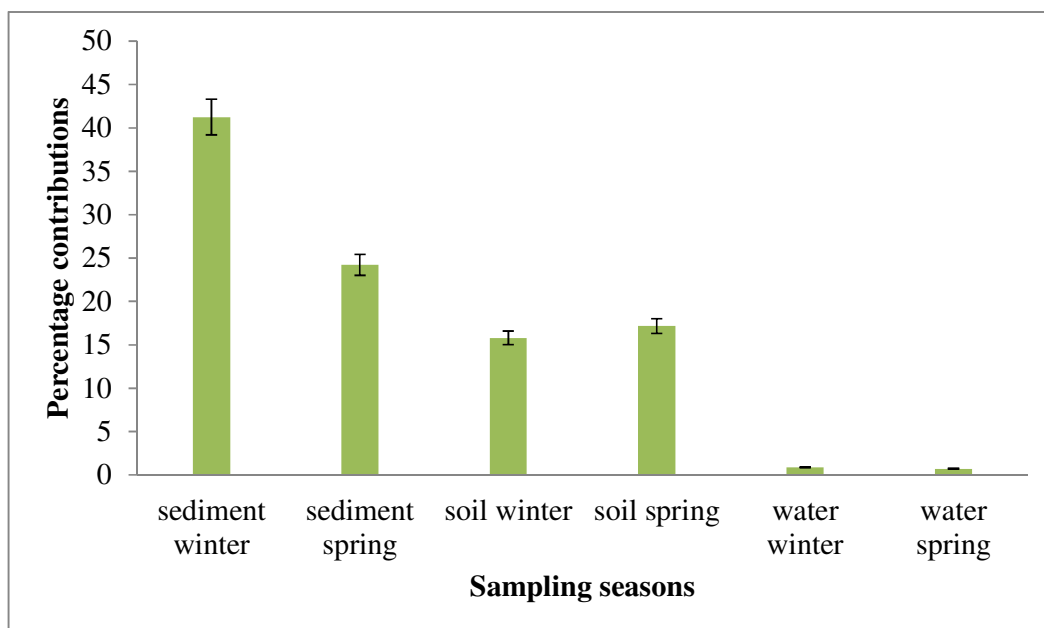


Figure 4.3 Percentage contribution of total PCB concentrations (%) of sediment, soil and water during winter and spring seasons.

Table 4.3 Total PCB concentrations and the percentage contribution of the analytes at sampling sites for sediment (ng/g), soil (ng/g) and water (ng/mL) during winter and spring seasons

SITE CODE	sediment		soil		water		Percentage (%)
	winter (ng/g)	spring (ng/g)	winter (ng/g)	spring (ng/g)	winter (ng/mL)	spring (ng/mL)	
HND	2972.79	1179.48	817.13	1063.75	51.3	22.87	12.74
CMD	2569.74	868.6	1191.78	991.83	48.88	15.57	11.86
DUT	3530.62	1255.5	1216.72	1161.37	45.34	16.31	15.07
WWT 1	3424.07	1734.27	Nil*	Nil*	78.71	129.32	11.19
WWT 2	669.18	1506.21	Nil*	Nil*	43.82	21.64	4.67
WWT 3	Nil	1468.05	Nil*	955.77	Nil*	25.84	5.11
AGA	644.63	808.81	1136.05	827.3	30.26	6.90	7.20
MST	1181.19	907.26	1427.22	1323.94	39.75	20.19	10.22
NGD	1603.83	1023.77	1365.54	634.35	64.94	74.4	9.94
UMJ	2874.84	673.71	1016.28	1142.21	44.39	8.74	12.01

*Sample not available

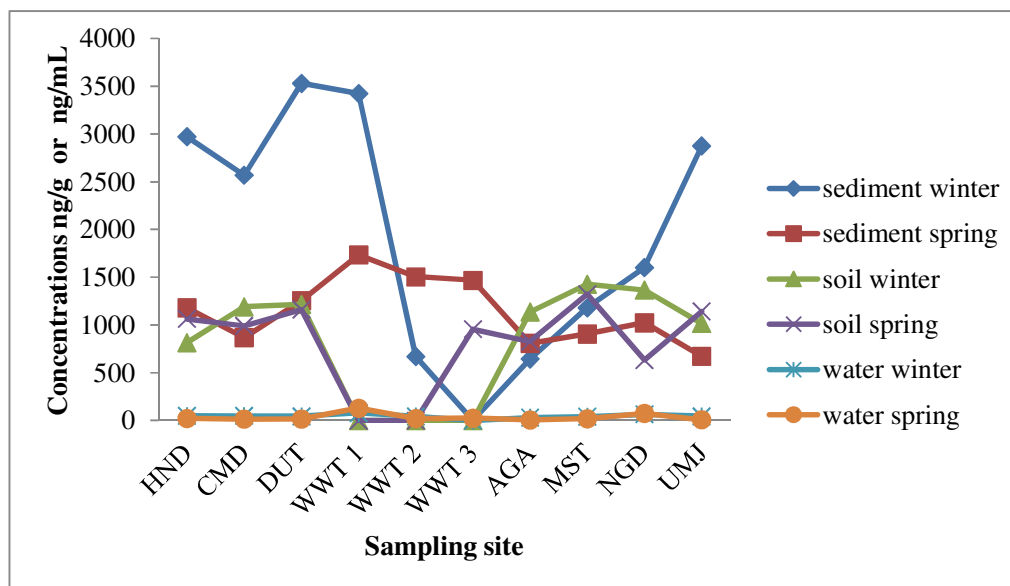


Figure 4.4 Variation of total PCB concentrations in sediment, soil and water along the Msunduzi River, during both winter and spring seasons.

Figure 4.4 and Table 4.3 show the total concentrations and percentage contribution of PCBs in the different matrices studied along the course of the river during the sampling seasons. The study area Du Toit (DUT) had the highest total PCB concentration for both sediment and soil during the winter season (3530.62 ng/g and 1216.72 ng/g respectively) with a total percentage of 15.31% followed by Henley dam outlet (HND) in all the sampling media with a percentage of 12.94%. Du Toit is located in the city centre of Pietermaritzburg, and high concentrations of PCBs found at this site are probably because it receives a high pollution load from its surrounding environment, such as open dumping and high vehicular activities (including heavy-duty vehicles, and the site is near an exit onto a national highway) as well as uncontrolled industrial effluents that could possibly seep into the river environment. Previous studies have shown that these activities lead to PCB contamination of the environment (Zhang *et al.*, 2003; Rissato *et al.*, 2006; Nasir *et al.*, 2014). Other sites that were shown to have high levels of the pollutants were the joining point of the Msunduzi tributary (UMJ) with the uMgeni River, Camps drift (CMD) as well as the wastewater treatment plant inlet (WWT1) with total PCB percentages of 12.20, 12.05 and 11.37% respectively. The UMJ sampling site is located within a rural area with various agricultural activities. The higher PCB concentrations in this area could be attributed to the unintentional release of agricultural by-products into the water body and uncontrolled burning in the area, because the main source of power for cooking is through burning of biomass. Higher levels of burning are also expected to occur in winter as a means of keeping homes warm. In

addition, this site might be receiving the accumulated pollutant load from the uMgeni River (upstream of the joining point), Nagle Dam, and the Msunduzi River passing through the Msunduzi town, which is only a few kilometres away. Thus there is an accumulated effect of PCBs that would contribute to this site's overall high PCB concentration. Camps drift (CMD) site was also determined to be relatively polluted. This area is known for its annual Dusi Canoe Race and is located in the city centre where vehicular activity is predominantly high. Since PCBs are trans boundary, there is a high tendency for them to be transported from the upper course of the river downstream.

The wastewater treatment plant collected its waste from different locations, such as domestic, industrial as well as from agricultural runoff. The total pollution level was therefore expected to be higher at this site due to the accumulation of various components of the waste from different locations, but it should be noted that soil samples were not available for this site and bio solids were collected as a representation of sediment samples.

Other areas with relatively high total PCB concentrations were the agricultural area (AGR), Nagle dam (NGD) and Msunduzi town (MST) with total PCB percentages of 10.38, 10.10 and 7.32% respectively. The AGR sampling site is located in a rural area with relatively low population density that has some small-scale to subsistence farming activity. High PCB levels in the area could be possibly due to open burning, most especially during the winter period, as preparation for the next planting season or to the use of sewage sludge, containing minor quantities of PCBs, applied to agricultural land (Gen and Berthouex, 1994). The presence of PCBs at the Nagle Dam (NGD) sampling site could be because the dam possibly serves as a 'sink' for the PCB pollutants received into the water ecosystem over long periods through water transportation from different locations. The presence of PCB concentrations at the Msunduzi town (MST) sampling site could probably be due to incineration of PCB-containing wastes (burning is a common practice in rural areas), improper dumping or spillage as well as deposition from vehicular emissions (MST sampling site was next to a taxi rank). The two sampling sites with the lowest PCB concentrations were the wastewater treatment after chlorination (WWT2) and the point of discharge back into the Msunduzi River (WWT3) with a total percentage of 4.75% and 5.19% respectively.

This suggests that the wastewater treatment process could possibly be removing substantial quantities of PCB containing pollutants before discharging the effluent back into the water ecosystem.

Table 4.4 a and b: PCB congener concentrations in sediment, soil (ng/g) and water (ng/mL) during the winter (a) and spring seasons (b) in the Msunduzi River, South Africa.

PCB Congeners	(a) WINTER SEASON								
	Sediment (n=9) ng/g			Soil (n=7) ng/g			Water (n=9) ng/mL		
	Min-Max	Mean	SD	Min-Max	Mean	SD	Min-Max	Mean	SD
PCB 28	21.93-549.19	209.36	208.55	86.33-165.54	140.25	27.44	3.90-12.97	8.24	2.97
PCB 77	130.80-438.18	295.08	108.55	36.78-200.66	132.72	56.90	1.45-5.80	3.40	1.50
PCB 101	8.87-611.92	216.60	252.63	90.88-397.75	209.52	96.24	6.86-21.77	14.55	4.89
PCB 52	38.86-422.55	214.13	146.84	46.82-343.44	275.20	103.37	2.84-22.37	9.19	6.16
PCB 153	15.05-656.86	196.21	207.84	49.18-190.80	157.17	48.48	0.20-19.33	5.22	5.92
PCB 105	11.92-683.77	264.58	256.79	54.67-110.14	88.14	18.31	0.09-5.73	2.21	2.37
PCB 138	127.75-933.34	447.59	266.50	25.64-111.42	62.07	27.08	0.50-9.00	3.04	2.86
PCB 180	6.52-745.88	319.89	280.17	42.73-134.51	101.87	29.52	1.66-5.54	3.85	1.56
ΣPCB	361.70-5041.69	2163.43	1727.36	433.03-1654.26	1167.25	407.64	17.56-102.51	49.71	28.24

SD = (Standard deviation).

PCB Congeners	(b) SPRING SEASON								
	Sediment (n=9) ng/g			Soil (n=7) ng/g			Water (n=9) ng/mL		
	Min-Max	Mean	SD	Min-Max	Mean	SD	Min-Max	Mean	SD
PCB 28	82.32-444.43	166.68	108.53	108.76-156.73	136.47	17.34	0.53-27.01	4.52	7.95
PCB 77	13.63-101.92	53.27	27.01	10.86-482.45	86.87	161.24	0.11-20.13	3.32	6.17
PCB 101	271.40-519.35	365.84	76.45	161.87-741.73	444.22	217.69	0.34-21.77	9.45	6.52
PCB 52	64.47-418.34	162.84	124.20	15.12-222.36	87.09	71.60	0.99-16.40	4.50	5.30
PCB 153	30.86-314.22	130.47	95.00	26.64-249.61	85.03	72.20	0.14-2.53	0.88	0.68
PCB 105	26.93-285.36	119.47	89.14	13.75-443.49	135.04	144.84	0.18-35.67	6.81	12.77
PCB 138	05.72-377.04	144.00	110.71	41.11-107.68	22.06	23.23	3.39-12.67	4.70	2.82
PCB 180	32.41-145.59	59.88	37.30	1.85-38.13	19.93	11.71	0.81-5.50	2.55	1.73
ΣPCB	528.24-2606.25	1202.45	668.34	379.96-2442.18	1076.69	719.84	6.49-141.68	36.73	43.93

Tables 4.4 a and b show the concentrations of each PCB congeners in the sediment, soil and water of the Msunduzi River during the winter and spring seasons. The percentage of each congener was evaluated as illustrated in Figure 4.5. The Σ PCB (sum of 8 congeners) concentrations (ng/g) in the winter and spring seasons of sediment samples at all the sampling sites were 361.70-5041.69 (mean 2163.43) and 528.24-2606.25 (mean 1202.45) respectively. While the corresponding concentrations (ng/g) of Σ PCB (sum of 8 congeners) in the soil samples for the two seasons was 433.03-1654.24 (mean 1167.25) and 379.96-2442.18 (mean 1076.69) respectively. However, the Σ PCBs (sum of 8 congeners) concentrations (ng/mL) in water samples for winter and spring seasons was 17.56-102.51 (mean 49.71) and 6.49-141.68 (mean 36.73) respectively. This study is in agreement with Zhou and co-workers and Zhang and co-workers, who suggested that less desorption of organic carbon from soil and sediment in water occurs in winter which may be attributed to the low temperature and low dilution rate of organic pollutants which largely depends on water flow (Zhou *et al.* 2006; Zhang *et al.* 2008). As a result there is a higher rate of sediment deposition in winter which leads to higher concentrations of pollutants. The trend of the PCB concentrations in the environmental media in this study also agreed with previous research carried out by Aydin and Yurdun, which showed that organic pollutants are more lipophilic and hydrophobic in nature and therefore bio-accumulate more in the organic matter than in surface water which is a possible reason for the high concentrations of pollutants observed in the sediment and soil than in the water (Aydin and Yurdun, 1999). Among the PCB congeners shown in Tables 4.4 a and b, and Figure 4.5, PCB 138 (hexa CB) was the dominant congener in the winter sediment followed by PCB 180 (hepta CB) and PCB 77. The lowest PCB congeners in winter sediment were PCB 153 and PCB 28 (hexa and tri CBs), while the dominant congeners in the winter soil and water were PCB 101 and PCB 52 (penta and tetra CB) respectively. However, in terms of individual PCB congeners across the river (Tables 4.4 a and b), the dominant congeners in both winter and spring seasons were PCB 101, PCB 138, PCB 52, PCB 28, and PCB 105. The PCB with the lowest concentration in the two seasons was PCB 180 which accounts for about 16.7% on an average of the total PCBs followed by PCB 77 and PCB 153 about 19.0% and 20.0% respectively. PCB 105 (penta CB) which is a dioxin type PCB was detected in the sediment samples having a concentration (ng/g) of 11.92-683.77 (mean 264.58) and 26.93-285.36 (mean 119.47) in both winter and spring respectively. The high total concentrations of PCB 28, PCB 52, PCB 101, PCB 105 (dioxin like) and PCB 138 could be attributed to fluids used in transformers, various electrical appliances, and paint industries (Barakat *et al.*, 2002)..

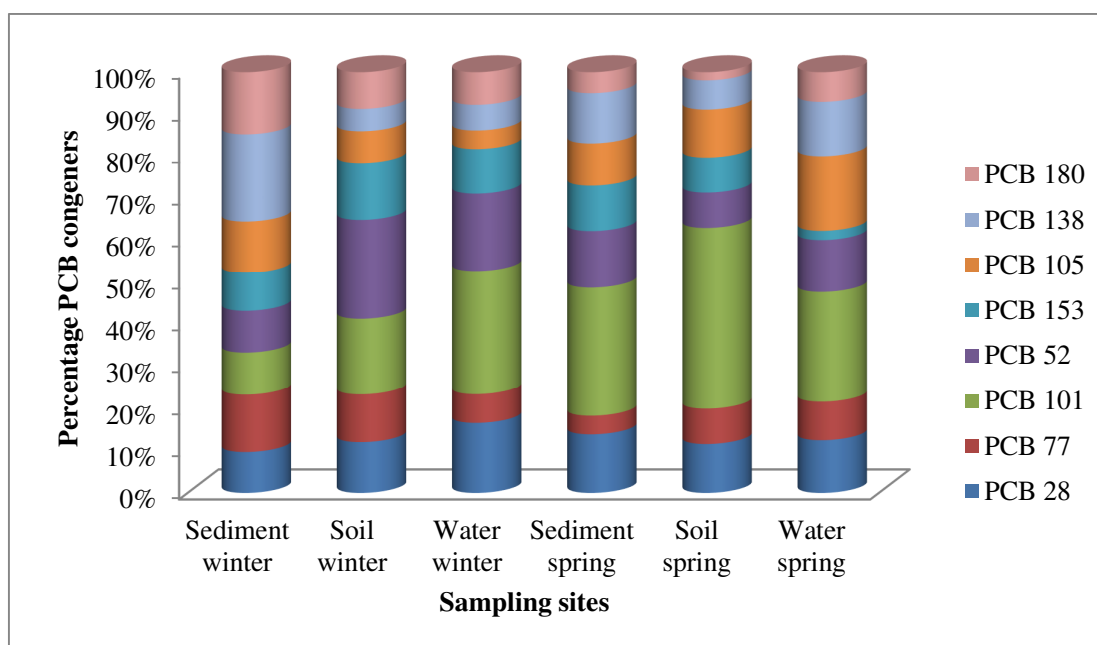


Figure 4.5 Percentage contribution of each PCB congener in the environmental media during winter and spring seasons of Msunduzi River, South Africa.

Table 4.5 Comparison of polychlorinated biphenyl concentrations in sediment (ng/g), soil (ng/g) and water (ng/mL) from different studies around the world.

Location			Σ PCBs	Sediment	Soil	Water	References
Msunduzi River Africa	South	Σ^8 PCBs	361.9-5041.7 ^a	433.0-1654.3 ^a	17.56-102.5 ^a	This study	
			528.2-2606.3 ^b	379.9-2442.7 ^b	6.49-141.7 ^b	This study	
Soil and sediment of central South Africa		Σ^{12} PCBs	1.2x10 ⁵ -1.8x10 ⁶	3x10 ⁵ - 4.7x10 ⁶		Nieuwoudt <i>et al.</i> (2009)	
Alexandria Harbour, Egypt		Σ^{96} PCBs	0.9-1211			Barakat <i>et al.</i> (2002)	
Bizerte lagoon, Tunisia		Σ^{10} PCBs	0.8-14.6			Barhoumi <i>et at.</i> (2013)	
Jinzhou Bay, China		Σ^{28} PCBs			0.2-3.2	Zhang <i>et al.</i> (2013)	
Minjiang River, China		Σ^{21} PCBs	15.1-57.9		0.2-2.5	Zhang <i>et al.</i> (2003)	
Northeastern , Brazil		Σ^7 PCBs		2x10 ⁻² -2.5x10 ⁻¹	2x10 ⁻⁵ -5x10 ⁻⁴	Rissato <i>et al.</i> (2006)	
Coast of Korea		2x Σ^{18} PCBs	0.2-371			Hong <i>et al.</i> (2006)	
Rhone Prodelta, France		Σ^{12} PCBs	38.3-228.5			Tolosa <i>et al.</i> (1995)	
Venice Lagoon, Italy		Σ^{18} PCBs	2x10 ⁻³ -2.1x10 ³			Bullucci <i>et al.</i> (2002)	
Coast, Spain		Σ^{18} PCBs	2.2x10 ⁻² -30.1			Eljarrat <i>et al.</i> (2005)	

a-winter, b- spring

The total PCB concentration obtained in this study was compared with the results reported by various authors from different parts of the world as shown in Table 4.5. Total PCB concentrations obtained in this work was higher compared to the results obtained in the study on Alexandria Harbour in Egypt, Bizerte lagoon in Tunisia and the Coast of Korea in 2002, 2013 and 2006 respectively (Barakat *et al.*, 2002; Hong *et al.*, 2006; Barhoumi *et al.*, 2013). The results obtained in this study for water were also higher than the results obtained by Zhang *et al.*, 2003 and 2013) on the Minjiang River and Jinzhou Bay in China. Overall, Table 4.5 shows that the results obtained in this study are higher than that obtained in most other similar studies undertaken on river environments around the world except results obtained on soil and sediment samples from central South Africa (Nieuwoudt *et al.*, 2009).

4.4 Conclusion

The concentrations of eight PCB congeners were determined during the winter and spring seasons along the Msunduzi River in Pietermaritzburg, South Africa. Pollutant dilution and distribution of particulates in the environmental matrices were dependent upon temperature and hydrodynamic conditions based on seasonal changes. Water contained a lower concentration of PCBs (winter: 0.68-22.37 ng/mL and spring: 2.53-35.69 ng/mL) compared to sediment (winter: 76.53-397.75 ng/g and spring: 20.84-443.49 ng/g) and the winter samples showed higher total concentrations of PCBs (214.21-610.45 ng/g) compared to the spring season (30.86-444.43 ng/g). The pollutant concentrations of the studied areas were found to be influenced by the anthropogenic activities at the different sampling sites. In all the sampling sites selected for this study, Du Toit was found to have the highest PCB concentration levels and the lowest was found to be after chlorination at the Darvill wastewater treatment plant. The results obtained for the total of eight PCB concentrations in this study were compared to that obtained from previous studies on the soil and sediment samples of Gauteng in Central South Africa, as well as to some studies done in other parts of the world. It could be possible that our studied area is more polluted with the selected PCB congeners as compared to other areas studied in previous studies. This finding suggests that the pollution sources needed to be investigated and urgent attention is needed to protect the aquatic life and health of the people consuming this water.

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CHAPTER 5: PAPER 2

Evaluation of Organochlorinated Pesticide (OCP) Residues in Soil, Sediment and Water during Winter and Spring Seasons from Msunduzi River, South Africa

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ABSTRACT

There is currently a lack of information available on the concentration levels and distribution pattern of organic pollutants within KwaZulu-Natal's rivers. Many studies done within this area have only focused on inorganic pollutants. However, organic pollutants such as organochlorine pesticides (OCPs) are just as toxic as inorganic pollutants. This lack of information has therefore prompted an investigation of the organic pollutants and in particular the organochlorinated pesticides in this river and the results and outcomes of this study serve as the first known study of OCPs found in the Msunduzi River. Organochlorinated pesticide concentrations were evaluated in sediment, soil and surface water of the Msunduzi River, South Africa using gas chromatography-mass spectrometry, after extraction by ultra-sonication with dichloromethane and clean up. The results showed that all 13 selected OCPs were detected at concentrations ranging between 1126.46-8974.69 (mean 3309.09) ng/g and 398.71-6159.03 (mean 1772.51) ng/g in sediment, 1346.71-5203.30 (mean 3143.80) ng/g and 796.76-5742.87 (mean 2746.24) in soil and 57.08-510.08 (mean 178.52) ng/mL and 22.48-262.30 (mean 110.48) ng/mL in surface water during winter and spring seasons respectively. Among the OCPs evaluated, DDT and its metabolites were predominant in all samples with total percentages of 60.68 and 55.47% in sediment, 57.96 and 58.65% in soil and 49.37 and 65.29% in water during the winter and spring seasons respectively. The indicative ratios and indicative indices for DDT revealed the possibility of aged long weathering and anaerobic degradation of DDT to DDD in water sediment over time. Mirex was found to be more prevalent in the environment despite its ban a long time ago. Dieldrin's concentration was higher compared to aldrin, heptachlor, endrin, HCB and HCH. In this study, the indicative ratios of aldrin/dieldrin revealed the possibilities of aldrin being converted to dieldrin resulting in higher concentrations of dieldrin. The results presented here are new and will provide knowledge and much needed information on the quality of water in the Msunduzi River.

Key words: *Organochlorinated pesticides, OCPs, Msunduzi River, gas chromatography-mass spectrometry, ultrasonication, DDT*

5.1 Introduction

Organochlorinated pesticides (OCPs) are important classes of POPs listed under the Stockholm convention's dirty dozen list which are a concern to the local and international communities (Covacia *et al.*, 2005; Wurl and Obbard, 2005). OCPs are predominantly used as pesticides, fungicides and insecticides for vector control (Eqani *et al.*, 2011). OCPs are fat soluble (lipophilic), have a tendency to accumulate in the fatty tissues of living organisms, and bioaccumulate and biomagnify through the food chain (Tanabe, 2002; Helberg, *et al.*, 2005; Chau *et al.*, 2005). Soil and sediment are the main reservoirs for OCPs accumulation over time (Nieuwoudt *et al.*, 2009). The health effects associated with OCPs range from acute to chronic such as reproductive disorders, birth defects and developmental disorders in children, immune suppression, endocrine disruption, neurological damage and even cancer, (Hileman, 1994; Van Den Berg *et al.*, 2006; Wang *et al.*, 2008). Due to their carcinogenic and toxic natures, their production and further usage was banned in the United States and in 1979 (Channa *et al.*, 2012) and South Africa's signing of the Stockholm Convention in 2004 confirmed its commitment to control the release of POPs into its environment (Bouwman, 2004; Burger and Nel, 2008). There is limited information on the levels and distributions of OCPs in South Africa most especially the rivers in KwaZulu-Natal. Previous studies have focused on inorganic pollutants and the few studies done on organic pollutants are outdated. Therefore there is a need for new research to be conducted on the presence of OCPs in this area and its entry into the Msunduzi River which is the main water source in this area. The objectives of the present study were to investigate the presence and concentration levels of selected OCP residues such as, hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), heptachlor, aldrin, *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT, *p,p*-DDT, dieldrin, endrin and mirex in sediment, soil and surface water of the Msunduzi River during winter and spring seasons. Figure 1.15 shows the structures of the selected OCPs investigated in this study.

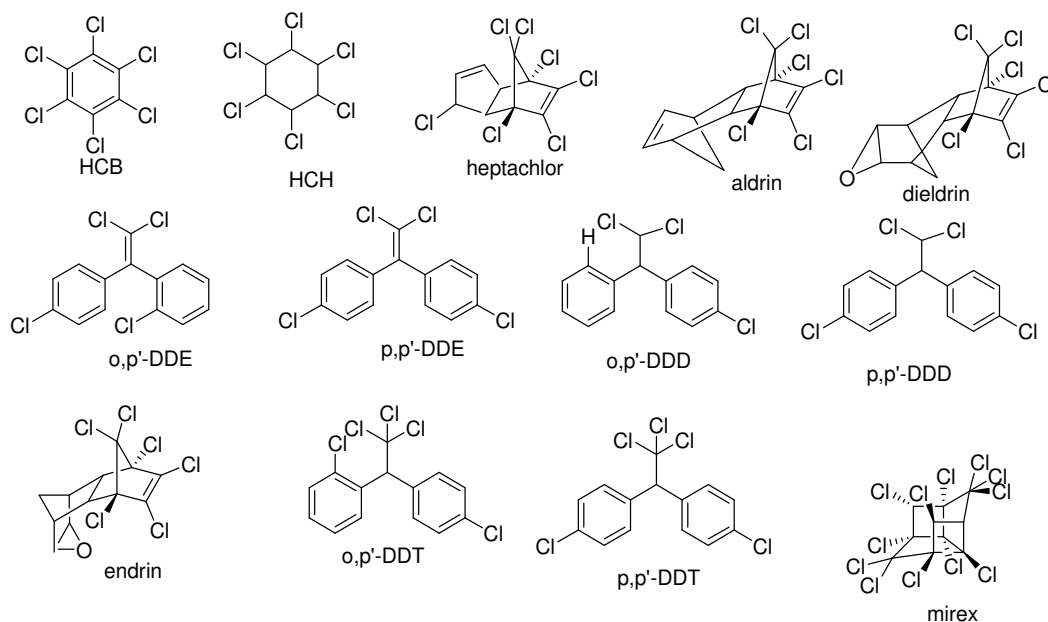


Figure 5.1 Structures of selected organochlorine pesticides.

5.2 Materials and methods

The study area for this research work was the Msunduzi River in the Pietermaritzburg catchment area, in KwaZulu-Natal, South Africa. Msunduzi River is popularly known by its anglicised name, the Dusi River, located in the uMgungundlovu district municipality and has a mean annual precipitation ranging from 684 to 1186 mm (Gericke *et al.*, 2004). The Msunduzi River was chosen for this study because it receives effluent from domestic households, untreated industrial waste, unmanaged municipal waste dumps as well as agricultural run-off which all contribute to the organic pollution levels in the river. A portion of the river is dammed for hosting the Dusi canoe marathon, the annual national water sport festival; where people could possibly be at risk of exposure to these toxic organic chemical pollutants. Samples were collected in July, and September, 2013 for winter and spring seasons respectively. Surface water, sediment and soil samples were selectively collected at different sites along the river, using the Global Positioning System (GPS) based on the site coordinates, as indicated in Figure 5.2 and Table 5.1



Figure 5.2 Map showing the sampling sites for this study along the Msunduzi River, South Africa.

Table 5.1 Sampling coordinates, physicochemical parameters and sampling site description.

Site Name	Location	Physicochemical parameters				Description of the sampling site
		pH		Temperature (°C)		
		Winter	Spring	Winter	Spring	
HND	29° 38'51"S	6.21	7.52	14	19	Domestic activities and surface runoff.
CMD	29° 36'47"S	5.15	8.05	21	21	Domestic and Commercial activities.
DUT	29° 35'52"S	7.20	7.49	15	18	Domestic and Commercial activities.
WWT 1	29° 36'15"S	5.31	7.24	19	22	Influent of various wastes from the city of Pietermaritzburg.
WWT 2	29° 36'15"S	5.54	7.85	19	22	Effluent of treated waste from the waste water treatment plant.
WWT 3	29° 36'15"S	-----	7.70	-----	22	Effluent of treated waste discharged and agricultural activities.
AGR	29° 36'40"S	5.12	8.72	14	24	Agricultural runoff and domestic activities.
MST	29° 39'40"S	4.77	8.92	15	26	Domestic and agricultural activities
NGD	29° 37'08"S	5.56	8.87	15	21	Dam for water supply and agricultural runoff.
UMJ	29° 37'16"S	5.07	7.60	15	25	Domestic, agricultural and surface water runoff.

HND = Henley Dam Outlet; CMD = Camps Drift; DUT = Du Toit; WWT1 = Darvill Wastewater Treatment Plant 1 (inlet); WWT2 = Darvill Wastewater Treatment Plant 2 (after chlorination); WWT3 = Darvill Wastewater Treatment Plant 3 (discharge); AGA = Agricultural Area; MST = Msunduzi Town; NGD = Nagle Dam; UMJ = uMgeni, Msunduzi River joining point.

5.2.1 Reagents and materials

All reagents and chemicals were of HPLC-grade, as well as the thirteen OCPs standards were purchased from Sigma-Aldrich South Africa. They were HCB, HCH, heptachlor, aldrin, *o,p*-DDE, *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT, *p,p*-DDT, dieldrin, endrin and mirex. Stock solutions of 200 mg/L of individual standards were prepared by dissolving 0.02 g of the individual OCP standards in 100 mL of dichloromethane and stored in the refrigerator at 4 °C. The OCPs lower working concentrations were prepared by appropriate dilution. High purity anhydrous sodium sulfate Gold line (CP) with CAS No. 7757-82-6 was obtained from Associated Chemical Enterprises (ACE) and used as a desiccant throughout the study, while silica gel, grade 634, of 100-200 mesh (0.063-0.2 mm) size, obtained from Merck, was used for both basic and acidic silica gel prepared in the laboratory for the clean-up of the extracts prior to analyses. Reagent grade sulfuric acid (specific gravity 1.84) obtained from Promark Chemicals was used for acidification. All the glass ware were baked in the oven at 130 °C, overnight prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

5.2.2 Sampling and sample treatment

5.2.2.1 Sample collection

Soil and sediment samples were collected using the same method as described paper 1, chapter 4.1.2.3. Briefly, sediment samples were collected by scooping 0-10 cm of the sediment from the river bed with a stainless steel spade, while the soil samples were collected at a depth of 0-15 cm on the banks of the river close to the water using a grab sampler and stainless steel auger and stored in glass bottles. Water samples were collected in 2.5 L amber reagent bottles, which were washed with phosphate free, soap (dDyna Chem), rinsed with tap water and distilled water and finally rinsed with HPLC grade acetone, and *n*-hexane to eliminate both polar and non-polar contaminants prior to sampling. Bottles were rinsed twice with the river water to be sampled, before the water sample was collected. A grab sampling technique was used to collect water samples from a depth of 1-2 cm from the water surface. A 1 mL aliquot of 50% sulfuric acid was added to each of the samples, immediately after collection, to prevent microbial degradation of the samples. The lids of the glass bottles were lined with acetone pre-washed aluminium foil to prevent possible sample contamination from phthalates which could leach from the plastic lining of the lid. Samples were kept cool under ice during transportation to the laboratory. Samples were kept at 4 °C prior to extraction to

prevent break down and bio-degradation of compounds of interest (Hilscherova *et al.*, 2003). Soil and sediment samples were air dried in the fume hood for five days; the dried samples were sieved with 75 µm, 300 µm, and 450 µm stainless steel sieves and stored in the fridge prior to extraction.

5.2.2.2 Sample extraction

Soil and sediment samples (20 g each) were dried and homogenized and then mixed with 10 g of anhydrous sodium sulfate to remove the excess moisture from the sample. An ultrasonic bath (UMC 20, 90022112 Kenmare) was used for the extraction due to its efficiency in extracting organic pollutants as well as the use of less solvent which makes it more environmentally acceptable compared to conventional soxhlet extraction (Adegbenro *et al.*, 2011). Soil and sediment samples were extracted with three times 20 mL dichloromethane (DCM), at 30 °C for 30 minutes each. Extracts were combined, filtered and concentrated to 2 mL using rotary evaporation.

Water extraction was carried out using a liquid-liquid extraction as described previously paper 1 (chapter 4.2.4). Liquid-liquid extraction has been reported to offer better results as compared to the solid-phase extraction (SPE) method (Fatoki and Awofolu, 2003; Sibali *et al.*, 2008) because it prevents the introduction of phthalate ester interferences that may originate from the housing materials of the cartridges (Fatoki and Awofolu, 2003). Briefly, a 500 mL aliquot of water was extracted with three times 40 mL DCM. The extract fractions were combined and concentrated to 2 mL using a rotary evaporator. The wastewater sample was filtered through a vacuum glass funnel, prior to the extraction, to remove suspended particles within the water sample.

5.2.2.3 Separation (Clean-up)

A multi-layer silica gel column was used in this study as recommended by the United States Environmental Protection Agency (USEPA method 1668B 2008) for anthropogenic pollutants. The details are provided in a previous paper 1 (chapter 4.1.2.5). The column was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel; 10 g anhydrous sodium sulfate (Na₂SO₄). The column was pre-eluted with 20 mL *n*-hexane, thereafter the extract was loaded and eluted with a total volume of 50 mL of *n*-hexane:DCM:toluene in the ratio 2.5:1.5:1. The fractions were combined and the volume reduced to 2 mL using rotary evaporation and finally air-dried.

Samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45 µm acrodisc filter prior to GC-MS analysis

5.2.2.4 GC-MS Analysis

Samples were analysed using gas chromatography/mass spectrometry (GC/MS Shimadzu QP-2010 Ultra Japan), using a DB-5MS capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness). Helium was used as the carrier gas with a flow rate of 0.72 mL/min and a total flow of 31.8 mL/sec, a linear velocity of 32.2 cm/s at purge flow of 3.0 mL/min using splitless mode. The injection and detector temperatures were set at 220 °C and 320 °C respectively. Oven temperature was set at 150 °C and held for 2 min, raised to 295 °C at 14 °C/min and held for a further 2 min. A 1 µL injection volume was used. All the quality control steps were followed. Laboratory blanks for both water and sediment that were subjected to the same analytical procedures as applied to the original samples did not show any significant peaks. Samples were analysed in triplicate. The linear range values (R^2) for all the analytes, LOD and LOQ values are shown in Table 5.2 Sediment recoveries were determined using the method adopted by McCarty and co-workers for matrix spiked data at 80 ng/g, while water recoveries were determined by spiking a 0.5 L tap water at 8 ng/mL (McCarty *et al.*, 2008). Method recoveries were evaluated based on the EPA standard method 1668B 2008. Average triplicate OCP recoveries for water and sediment ranged between 58.86-103.35% and 86.83-125.98% respectively as shown in Table 5.2 Routine analysis of blanks with every ten sample sets were carefully monitored to determine the possibility of any interferences from the column. Standards were run intermittently between samples to monitor changes in the instrument's sensitivity. Sediment and water sample extracts were spiked with the mixed OCPs standards at 0.50 ng/g and 0.25 ng/mL respectively, and their concentrations were determined. An external calibration method was used for the quantification of 7 OCPs together with 6 DDT metabolites based on the peak areas of the targeted compounds. Analytes were identified by comparing their retention times with those of the targeted OCP standards.

Table 5.2 Percentage recoveries based on spiked sediment sampled from the agricultural area during winter and spring and spiked tap water, R² values, limits of detection and quantification of OCPs in water and sediment.

OCPs	Percentage recovery		R ² value (n=3)	Limit of detection/ Limit of quantification.			
	Water	Sediment		Sediment/ (ng/g)			Water (ng/mL)
				LOD	LOQ	LOD	LOQ
HCB	83.23	125.98	0.9980	0.0073	0.0220	0.0006	0.0018
HCH	71.38	117.36	0.9962	0.0030	0.0092	0.0002	0.0007
Heptachlor	58.86	89.19	0.9948	0.0043	0.0131	0.0003	0.0010
Aldrin	67.83	97.47	0.9966	0.0042	0.0128	0.0003	0.0010
<i>o,p</i> - DDE	65.33	91.91	0.9918	0.0030	0.0090	0.0002	0.0007
<i>p,p</i> - DDE	66.56	104.95	0.9991	0.0021	0.0062	0.0002	0.0005
<i>o,p</i> - DDD	67.74	115.23	0.9930	0.0091	0.0275	0.0007	0.0022
Dieldrin	60.30	86.83	0.9981	0.0054	0.0163	0.0004	0.0013
Endrin	78.24	106.30	0.9935	0.0018	0.0055	0.0001	0.0004
<i>p,p</i> - DDD	67.08	122.19	0.9907	0.0070	0.0213	0.0006	0.0017
<i>o,p</i> - DDT	99.68	104.43	0.9982	0.0026	0.0080	0.0002	0.0006
<i>p,p</i> - DDT	78.24	109.48	0.9964	0.0080	0.0243	0.0006	0.0019
Mirex	103.35	91.82	0.9992	0.0015	0.0046	0.0001	0.0004

5.3 Results and discussion

The total and percentage OCP concentrations are summarised in Figure 5.3. Total OCP concentrations in sediment were found in the range of 464.65-3773.66 (mean 2290.91) ng/g and 605.29-3534.97 (mean 1670.20) ng/g and in soil in the range of 185.85-3576.91 (mean 1692.82) ng/g and 241.40-3460.71 (mean 1689.38) ng/g during the winter and spring seasons respectively. Water exhibited the lowest concentration levels in the range of 21.02-183.88 (mean 91.28) ng/mL and 21.55-277.07 (mean 84.99) ng/mL in both winter and spring seasons respectively. OCP concentrations during the winter period were slightly higher in sediment compared to that of the spring season, which could be as a result of lower temperature during the winter season. Concentrations of organic pollutants in environmental media are known to be dependent on adsorption and desorption from sediment based on temperature changes (Zhou *et al.*, 2006; Cheng *et al.*, 2007). Therefore in this study low water flow as well as low temperature during the winter season could be the major factor for the observed trends. Soil and sediment exhibited the highest OCP concentration during both seasons compared to surface water. The reason for this is that chlorinated pesticides have stronger carbon to chlorine bonds which results in them having a lower affinity for water (hydrophobic and highly lipophilic character) and higher tendency to bind to particulate matter and fatty tissue of organisms (WSPMP, 1995; Ritter *et al.*, 2005; Kumar *et al.*, 2013).

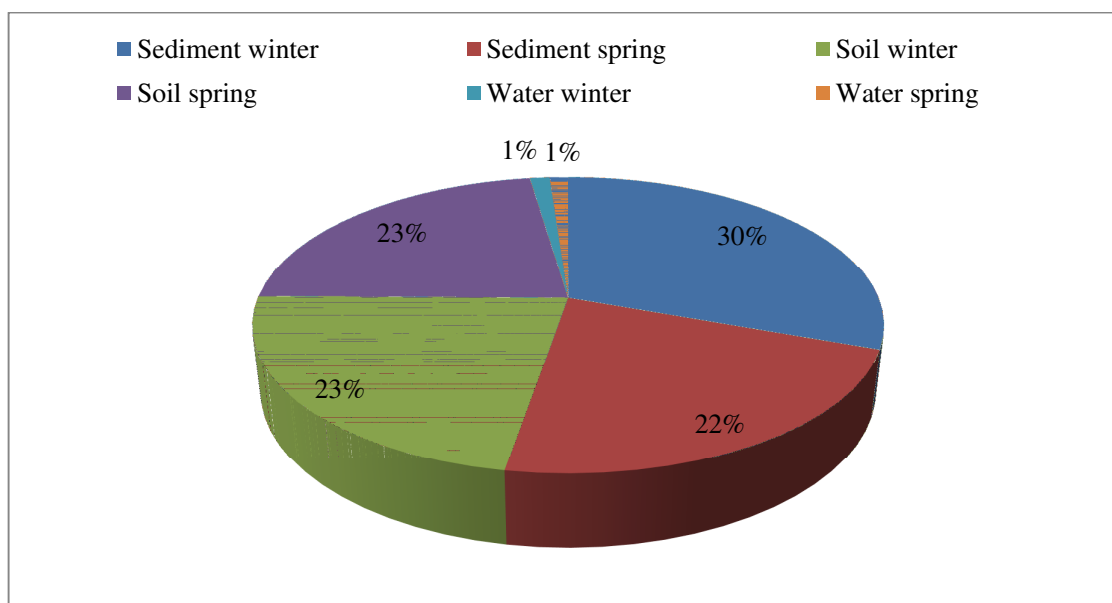


Figure 5.3 Percentage distribution level of total OCP residues in sediment, soil and water during winter and spring seasons.

Distributions and pollution levels of the OCPs in different media along the river are shown in the Figure 5.3 and Table 5.3. Among the studied sites, wastewater treatment plant 1 (influent) (WWT1) was the most polluted site for both sediment and water analyses during the winter and spring seasons. Soil samples were not available from the WWTP and the dried sludge was taken to represent the sediment sample at the site. The reasons for the higher OCP concentration at this site could be as a result of wastewater treatment plant (influent) receiving its pollution load from various sources such as industrial discharge and domestic waste. Previous studies have also shown high pollution load due to similar sources of effluent (Zhang *et al.*, 2003; Zhou *et al.*, 2006).

A high total concentration of OCP residues in all sample media for both seasons was recorded at the uMgeni Msunduzi joining point (UMJ) at 11965.53 ng/g (11.99%). The high concentration is probably due to the combined total pollutants received from both the uMgeni River and the Msunduzi River. In addition, there are also some rural farming activities close to this site which could be a point source for OCPs at this site. Msunduzi town (MST), Du Toit (DUT) and Henley dam outlet (HND) sampling sites also contained higher OCP concentrations at 11107.98 ng/g (11.14%), 10957.98 ng/g (10.98%) and 10489.33 ng/g (10.52%) respectively. There is no specific information available about the sources of these

pollutants in the area, but pollution rate at MST and HND sites could possibly be due to the runoff from agriculture because these sites are located in rural areas with agriculture as a major activity. The presence of OCPs at these sites could also be from previous use as vector controls prior to their banning. Similar studies by Minh and co-workers showed that OCPs are able to remain in the environment long after their use thus confirming their persistence (Minh *et al.*, 2004). Du Toit is located in the city centre of Pietermaritzburg and the high levels of pollutants in this area could possibly be as a result of various anthropogenic activities such as, accidental leakage from industrial effluents into the river, possibility of seepage from old domestic waste containing organochlorinated compounds. Other sites with relatively high concentrations of OCPs were the agricultural area (AGR), Nagle dam (NGD), WWT 2 and Camps drift (CMD) with total OCP percentages of 10.13%, 9.83%, 9.40% and 8.03% respectively. Site AGR is located in a rural area with a lot of farming activities where OCPs could possibly be entering into the river ecosystem through surface runoff from surrounding crops. Nagle dam is on the uMgeni River which is the main river in the province of KwaZulu-Natal. There are a number of tributaries passing by industrialized areas which eventually make their way to Nagle dam. There is also some minor farming activity in the surrounding area of Nagle dam which may contribute to run-offs into the dam. Wastewater treatment (WWT 2) refers to the effluent after chlorination from the Darvill wastewater treatment plant. This site was found to contain some level of OCP pollutants which could possibly be from insufficient removal of the selected organochlorinated pesticides from the treatment plant itself. Research has shown that water treatment plants generally do not remove pesticides (Fatoki and Awofolu, 2003). Camps drift is a popular site for the annual Dusi festival. The presence of the OCPs at this site could not be categorically ascertained, however because of trans boundary effects and long range of transportation OCPs could be transported from the upper course of the river to this sampling site (UNEP, 2005). WWT 3 had the lowest percentage concentration of 4.50% among the sampling sites.

Table 5.3 Total OCP concentrations in sediment, soil and water along the Msunduzi River during winter and spring seasons

OCP concentrations in winter season				OCP concentrations in spring season			Total OCP concentrations	Total OCPs Percentage (%)
SITE CODE	Sediment (ng/g)	Soil (ng/g)	Water (ng/mL)	Sediment (ng/g)	Soil (ng/g)	Water (ng/mL)		
HND	2171.95	4307.97	108.26	1909.81	1928.45	62.89	10489.33	10.52
CMD	3110.98	3127.73	135.07	786.01	826.35	26.05	8012.19	8.03
DUT	3135.84	3859.87	210.94	1619.08	2066.81	65.44	10957.98	10.98
WWT 1	7008.51	Nil*	211.48	3863.98	Nil*	362.30	11446.27	11.47
WWT 2	5771.14	Nil*	101.86	3397.4	Nil*	110.84	9381.24	9.40
WWT 3	Nil*	Nil*	Nil*	1769.56	2637.03	77.53	4484.12	4.50
AGA	2300.04	2461.35	85.58	1268.39	3934.07	52.86	10102.29	10.13
MST	2258.29	2943.34	81.38	3212.82	2474.14	138.01	11107.98	11.14
NGD	1819.29	2689.41	149.28	1607.19	3474.75	67.72	9807.64	9.83
UMJ	2205.79	2616.95	102.84	2278.39	4620.34	141.22	11965.53	11.99

Nil*= No soil samples were available for collection

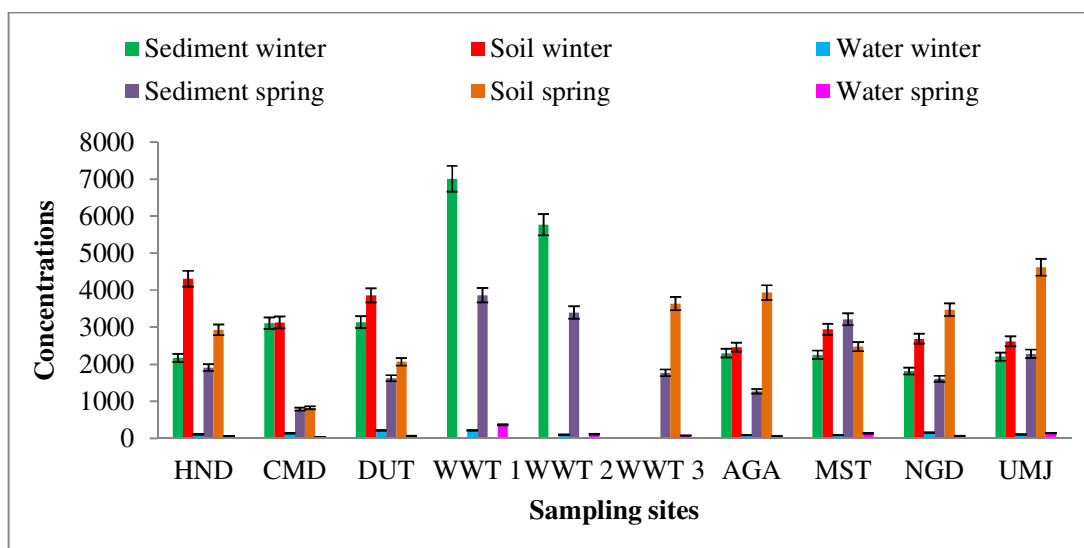


Figure 5.4 Variation of OCP residue concentrations along the Msunduzi River, during both winter and spring seasons.

Table 5.4 Range and mean OCP concentrations in sediment, soil (ng/g) and water (ng/mL) during the winter season.

OCPs	Winter Season								
	Sediment (n=9) ng/g			Soil (n=7) ng/g			Water (n=9) ng/mL		
	Min- Max	Mean	SD	Min-Max	Mean	SD	Min-Max	Mean	SD
HCb	1.39-154.49	67.72	53.65	11.60-83.43	46.10	28.41	0.30-6.34	2.34	1.88
HCH	1.85-442.36	81.95	141.91	21.08-348.72	139.98	115.11	6.67-291.39	66.18	98.18
Heptachlor	0.45-190.23	43.51	60.85	2.48-79.53	26.55	25.22	0.06-8.80	3.40	2.85
Aldrin	2.86-223.45	51.63	69.03	3.97-109.32	46.27	32.63	0.55-10.16	4.42	3.15
Dieldrin	128.2-1145.76	329.24	324.34	147.96-656.76	342.74	200.08	5.30-13.50	8.76	2.61
Endrin	19.20-1474.96	385.21	504.85	92.80-340.35	208.95	114.92	0.37-26.05	7.89	9.00
Mirex	105.82-846.96	341.87	223.00	117.29-790.30	510.99	252.14	10.97-37.00	20.43	8.60
<i>o,p</i> - DDE	75.05-376.23	165.70	98.54	117.57-269.26	193.13	57.01	5.56-14.04	8.71	2.77
<i>p,p</i> - DDE	236.58-954.21	419.48	217.58	130.13-515.52	358.01	149.47	10.89-27.50	15.67	5.08
<i>o,p</i> - DDD	243.66-701.87	383.30	136.98	348.79-681.09	427.43	120.65	11.46-16.36	14.57	1.54
<i>p,p</i> - DDD	90.49-1065.03	368.24	328.63	128.34-288.07	192.30	60.09	2.01-28.87	10.52	9.87
<i>o,p</i> - DDT	34.72-714.61	251.96	204.94	115.85-529.75	335.33	142.22	0.85-10.11	3.69	3.61
<i>p,p</i> - DDT	186.19-683.50	419.30	174.15	108.85-511.20	316.03	183.54	2.09-19.95	11.93	6.02
Σ DDTs	866.69-4495.45	2007.98	1160.81	949.53-2794.89	1822.23	712.97	32.86-116.83	65.10	28.90
Σ OCPs	1126.46-8974.69	3309.09	2538.43	1346.71-5203.30	3143.80	1481.49	57.08-510.07	178.52	155.17

Table 5.5 Range and mean OCP concentrations in sediment, soil (ng/g) and water (ng/mL) during spring.

OCPs	Spring Season								
	Sediment (n=9) ng/g			Soil (n=7) ng/g			Water (n=9) ng/mL		
	Min- Max	Mean	SD	Min-Max	Mean	SD	Min-Max	Mean	SD
HCB	3.90-169.55	82.84	52.82	1.88-375.66	70.81	129.65	0.05-8.14	2.155	2.81
HCH	7.50-210.26	74.11	59.46	1.98-57.46	30.18	18.13	1.97-16.08	4.701	4.21
Heptachlor	24.82-352.64	147.41	106.65	8.70-243.14	92.62	82.88	0.45-19.59	5.773	5.95
Aldrin	4.14-205.17	60.53	62.47	23.69-468.16	175.74	150.56	0.37-18.86	5.654	5.61
Dieldrin	8.94-432.84	162.65	138.22	40.39-511.14	186.88	154.38	0.42-18.99	6.328	6.31
Endrin	8.11-846.79	234.19	248.74	111.65-774.69	146.30	244.73	1.15-29.50	5.296	8.63
Mirex	35.90-361.99	205.12	86.07	194.75-684.02	432.59	199.75	1.69-47.23	8.438	13.75
<i>o,p</i>- DDE	16.98-271.29	105.81	94.25	18.22-453.32	263.90	180.38	0.27-14.68	4.319	4.26
<i>p,p</i>- DDE	136.58-603.96	350.71	146.59	79.14-640.47	337.44	206.29	7.49-40.47	27.707	9.63
<i>o,p</i>- DDD	6.17-358.03	119.25	107.18	2.22-102.94	42.91	40.27	0.94-14.75	6.745	5.24
<i>p,p</i>- DDD	126.53-1546.89	453.50	408.53	19.15-424.41	295.29	151.57	6.84-81.15	22.297	21.53
<i>o,p</i>- DDT	11.41-405.57	143.21	127.31	119.57-396.78	260.43	110.49	0.08-16.67	3.249	4.88
<i>p,p</i>- DDT	7.73-394.05	131.95	134.24	175.42-610.68	410.17	149.28	0.71-36.19	7.825	11.79
Σ DDTs	305.40-3579.79	1304.42	1018.08	413.72-2628.60	1610.13	838.28	16.33-203.91	72.14	57.32
Σ OCPs	398.71-6159.03	2271.26	1772.51	796.76-5742.87	2745.24	1818.38	22.43-262.30	110.48	104.60

Total OCP concentration levels in sediment, soil and surface water samples during winter and spring seasons are shown in Tables 5.4 and 5.5. The concentration of the 13 OCP residues in sediment ranged between 1126.46-8974.69 (mean 3309.09) ng/g and 398.71-6159.03 (mean 2271.26) ng/g in both winter and spring seasons and in soil between 1346.71-5203 (mean 3143.80) ng/g and 796.76-5742.87 (mean 2745.24) ng/g in winter and spring seasons respectively. Total concentrations in water ranged between 57.08-510.07 (mean 178.52) ng/mL and 22.43-263.30 (mean 110.49) ng/mL in winter and spring respectively. Among the OCPs evaluated DDT and its metabolites were predominant across the sampling sites in both seasons for sediment, soil and water samples as shown in Figures 5.5 a and b. Total percentage of DDT metabolites were 60.68 and 55.47% in sediment and 57.96 and 58.65% in soil, while in water they were 49.37 and 65.29% in both winter and spring seasons respectively. Technical DDT (DDT mixtures) in general contain 75% *p,p*-DDT, 15% *o,p*-DDT, 5% *p,p*-DDE, and < 5% others (Metcarf, 1973; Bopp *et al.*, 1982). Possible pollution sources of DDT can be assessed using relative total concentrations of DDTs together with its biological metabolites such as DDD and DDE which is an indicative index of pollution assessment. DDT is susceptible to degradation under aerobic conditions to DDE and under anaerobic condition to DDD (Bossi *et al.*, 1992). A ratio of DDE+DDD/DDTs > 0.5 indicates long term-weathering while a ratio of DDD/DDE > unity (1), indicates that the sediments were dominated by DDD which results from anaerobic degradation of DDT (Hitch and Day, 1992; Doong *et al.*, 2002a; Doong *et al.*, 2002b). The ratio of DDD/DDE was determined to be 1.28 and 1.04; 1.12 and 0.56 in sediment and soil for winter and spring seasons, respectively. They were greater than unity except for soil samples during the spring season, which indicated that both the sediment and soil of Msunduzi River are both dominated by *p,p*-DDD, a product of anaerobic degradation of *p,p*-DDT (Zhou *et al.*, 2006). The ratios of (DDE+DDD)/DDTs in both surface sediment and soil were 0.67 and 0.77, and 0.64 and 0.58 in both winter and spring season were also greater than 0.5. This result revealed that DDT metabolite contamination in soils and sediments of the Msunduzi River may be as a result of long term weathering of DDTs along river and retained by anaerobic conditions within the sediment and soil in the river. To assess the trend of DDT sources in water, the ratio of DDE/ Σ DDTs and DDD/ Σ DDTs were evaluated and values of 1.56 and 2.90, and 1.61 and 2.62 were obtained for both winter and spring seasons respectively. The values were greater than unity in water which is an indication that DDT metabolite contamination may be as a result of aged long weathering of DDT in the Msunduzi River. Mirex was also found to be more prevalent during both seasons with total percentages of 10.33 and 9.45% in sediment,

16.14 and 15.76% in soil and 15.50 and 7.64% in water during winter and spring seasons respectively. Mirex showed a significant difference in total percentage concentrations during winter and spring seasons in water compared to sediment and soil. This could be attributed to the fact that mirex is very insoluble in water and binds strongly to the aquatic soil and sediment. Mirex has no natural origin but historically it has been used in South Africa as a termite control and produced industrially through catalytic processes of dimerization of hexachlorocyclopentadiene, and majorly used as an insecticide, flame retardant in plastics, paper and electrical appliances (ATSDR, 1995, Ritter, *et al.*, 2005). Its production has since been banned, but the residues of this compound may still remain in the environment due to its long half-life, historical use, and accidental spillages, open dumping and burning and leaching from old materials. Both endrin and dieldrin (half-life of approximately 5 years in temperate soil for dieldrin) were also found in appreciable concentrations in the environmental media in both seasons and their source could possibly be traced to extensive usage in agriculture for the control of soil insect vectors of diseases before they were banned. Aldrin and heptachlor as well as HCH concentrations were lower compared to others, however the lower concentration of aldrin could possibly be due to its instability in the environment as aldrin is readily and rapidly converted to dieldrin (UNEP, 2001; Ritter, 2005). In this study, the indicative ratios of aldrin/dieldrin were 0.16, 0.37 and 0.14 in sediment, soil and water in winter and 0.94, 0.51, and 0.89 in the three matrices during spring which confirms aldrin's degradation to dieldrin.

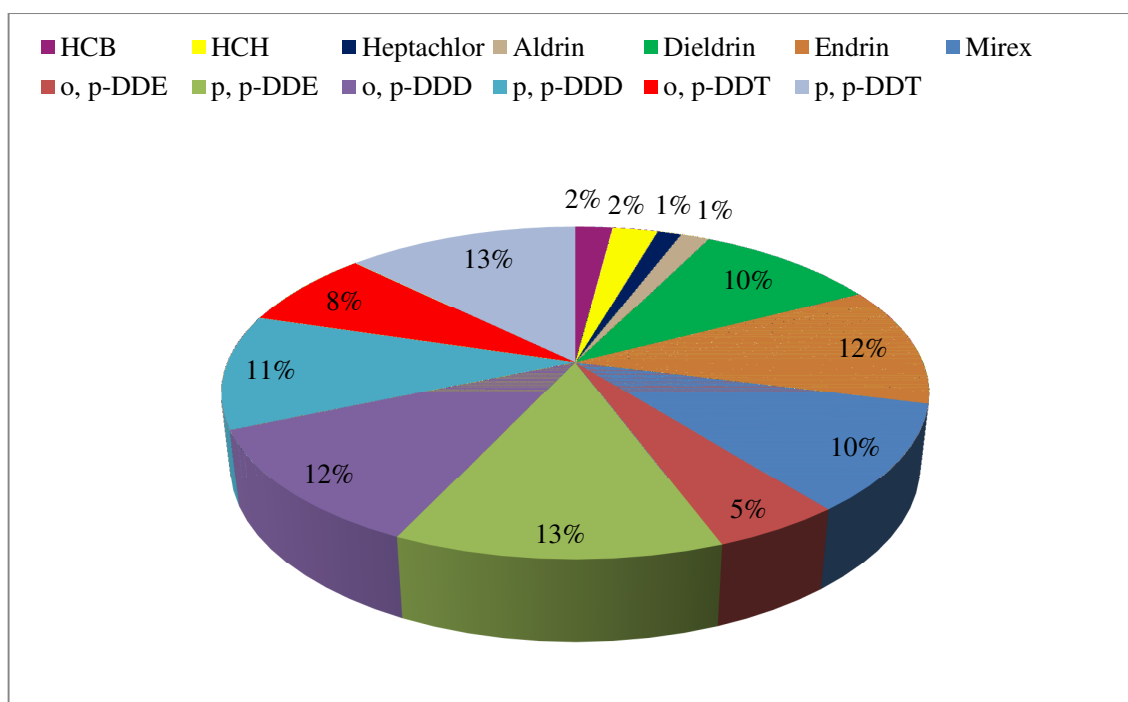
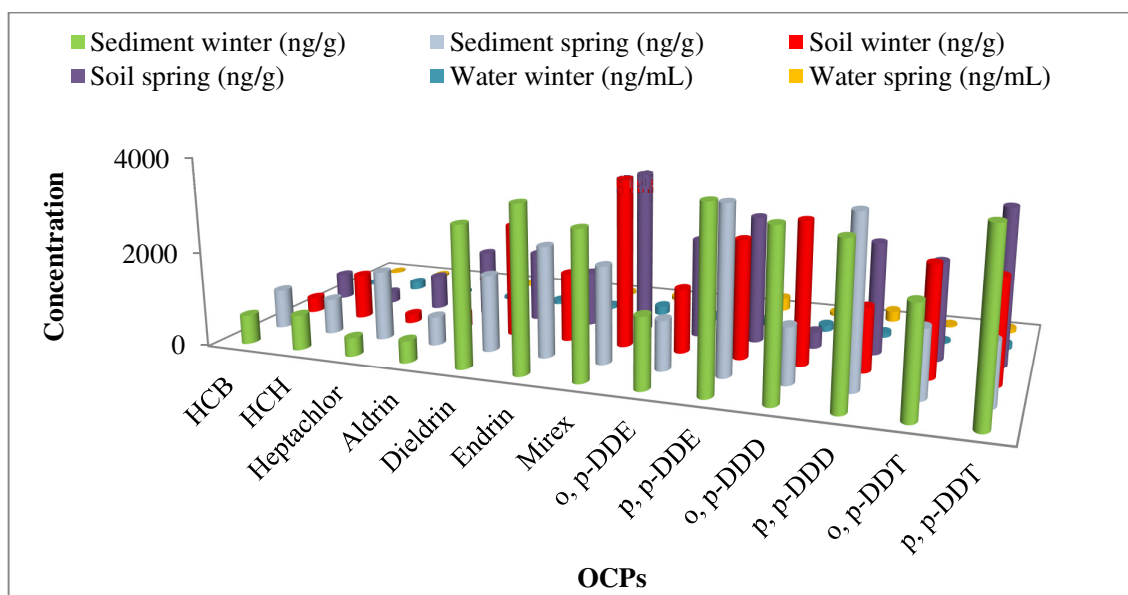


Figure 5.5 a and b Total and percentage concentrations of OCPs in environmental media during the winter and spring seasons.

Table 5.6 Comparison of OCP concentration levels in sediment (ng/g), soil (ng/g) and water (ng/mL) with other studies.

Location	Σ OCPs	Sediment (ng/g)	Soil (ng/g)	Water (ng/mL)	References
Msunduzi River, South Africa	Σ^{13} OCPs	464.65-3773.66 ^a 605.29-3534.97 ^b	185.85-3576.91 ^a 241.40-3460.71 ^b	21.02-183.88 ^a 21.55-277.07 ^b	This study This study
Jujskei River, South Africa	Σ^{13} OCPs	4.26-22914		1.07-15400	Sibali <i>et al.</i> (2008)
Cocoa producing area, Ondo State, Nigeria	Σ^{15} OCPs	10-57400		1.07-15400	Okoya <i>et al.</i> (2013)
Qiantang River, China	Σ^{13} OCPs	23.11-316.50			Zhou <i>et al.</i> (2006)
Tasman, Waikato Auckland, New Zealand	Σ^6 OCPs	30.0-34500			Gaw, <i>et al.</i> (2006)
Agricultural Soils, India	Σ^{13} OCPs		3.59-160.30		Kumar <i>et al.</i> (2013)

a = Winter, b = Spring.

The result of the present study in both river sediment and water was lower compared to the studies done by Sibali and co-workers, on the Jujskie River catchment area in Gauteng, South Africa (Sibali *et al.*, 2008) and compared to sediment and water of a cocoa producing area in the Ondo State in Nigeria (Okoya *et al.*, 2013). The study done by Gaw and co-workers on OCPs in sediments of Tasman Waikato Auckland, New Zealand was higher compared to the results obtained in this study even though they had only investigated 6 OCPs (Gaw *et al.*, 2006). This study indicated that this particular river in South African is less polluted compared to some other parts of the world but is relatively contaminated compared to the study on the Qiantang River in China (Zhou *et al.*, 2006) and the agricultural soils investigated in India (Kumar *et al.*, 2013).

5.4 Conclusion

The concentrations of chlorinated pollutants were evaluated in sediment, soil and surface water samples during winter and spring seasons, from the Msunduzi River, South Africa. The pesticide concentrations were influenced by temperature during the studied seasons in the

environmental media as well as the anthropogenic activities at the various sites. The winter season samples had higher concentrations of OCPs ranging from 1126.46-8974.69 (mean 3309.09) ng/g in sediment, 1346.71-5203.30 (mean 3143.80) ng/g in soil and 57.08-510.08 (mean 178.52) ng/mL in surface water. The spring season samples had concentrations ranging from 398.71-6159.03 (mean 1772.51) ng/g in sediment, 796.76-5742.87 (mean 2746.24) g/g in soil and 22.48-262.30 (mean 110.48) ng/mL in surface water. Among the sites sampled, apart from Darvill wastewater treatment plant influent with the highest OCP concentration, the uMgeni Msunduzi joining point and Du-Toit sites were also found to have higher concentrations of the selected pesticides. The results indicated that DDT and its metabolites were found to be more prevalent among the OCPs studied. This could probably be due to aged long weathering and anaerobic degradation of DDT isomers into their metabolites. The higher lipophilicity and particle affinity of DDT to sediments (low water solubility, high stability and semi-volatility) may also be a possible reason for the higher total concentrations of DDT obtained in this study despite their long time ban in South Africa. Total OCP concentrations in this present study were lower compared to that obtained in the Jukskei River catchment area in Gauteng, South Africa and generally higher than the tolerable level of 0.1 µg/kg guideline for aquatic ecosystems as recommended by the European Union (EU). Therefore urgent attention and increased monitoring is required to protect the water ecosystem and health of people consuming this water.

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CHAPTER 6: PAPER 3

Assessment of Selected Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs) in Sediment, Soil and Surface Water During Autumn Season from Msunduzi River, KwaZulu-Natal, South Africa

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ABSTRACT

The increase in industrial activities and urban development in the Pietermaritzburg area has prompted our investigation into the presence of polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) in the surface water, sediment and soil of one of the main rivers passing through this area. Currently there is limited information on the levels and distribution of PCBs and OCPs in the river water of KwaZulu-Natal and previous studies had mainly focused on inorganic pollutants. This study is therefore the first to investigate the concentration patterns of eight PCBs as well as thirteen OCPs present in sediment, soil and surface water during the autumn season from the Msunduzi River in KwaZulu-Natal, South Africa. Soil, sediment and water samples were collected at 10 different sites along the river. Soil and sediment samples were extracted using an ultrasonic bath with dichloromethane, and water samples were subjected to liquid-liquid extraction using dichloromethane. Sample extracts were cleaned up using multi-layered acidic/basic silica gel. Concentrations of the PCB congeners and OCPs were determined by gas chromatography-mass spectrometry (GC-MS). Percentage recoveries ranged between 55.09-99.97% and 60.45-84.05% in water for both PCBs and OCPs; and in sediment the percentage recoveries were 77.96-101.23% and 80.42-114.91% for PCBs and OCPs respectively. A point of discharge of treated wastewater back into the Msunduzi River (W 3) exhibited the highest PCB and OCP concentrations, with total concentrations of 1288.83 ng/g and 1609.37 ng/g in sediment and 1108.46 ng/g and 1370.91 ng/g in soil respectively. Among the PCB congeners investigated in this study, PCB 180 exhibited the highest concentration. Of the OCPs studied, DDT and its isomers were found to have higher concentrations in almost all the sampling sites in sediment, soil and water compared to other OCPs except endrin which

was also found at higher concentrations along the sampling sites. The concentrations of individual PCB congeners at different sites were found to be higher than the lowest limit set by the US EPA and most of the OCP concentrations in water, river sediment and soil were also found to be higher than the maximum permissible levels (MPL) in the environment.

Keywords: *Polychlorinated biphenyls, organochlorinated pesticides, GC-MS, sediment, surface water, Msunduzi River.*

6.1 Introduction

Polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) belong to the group of organochlorines (OCs) that have posed a serious environmental threat due to their toxicity to both human health and the aquatic ecosystem. These compounds are generated through anthropogenic activities (man-made chemicals) and are released into the environment through human activities. Most of these persistent organic pollutants (POPs) are very insoluble in water but readily soluble in most organic solvents (HSDB, 20010). They are resistant to acids and bases; are non-flammable, have a high dielectric constant as well as a high resistance to thermal degradation. Due to these properties OCs have been widely used in a number of different industrial, domestic and agricultural applications, such as dielectrics in transformers and capacitors, as heat exchange fluids, paint additives, used in carbonless copy paper, flame-retardants, as insecticides and fungicides as well as for the prevention and control of various pests in agricultural crops and malarial vectors in most mosquito endemic areas (UNEP, 1990; WHO, 2003; Ritter *et al.*, 2005). Generally, water solubility, environmental degradation and vapour pressure of OCs is largely dependent on the number, and the degree of chlorination as well as the isomeric substitution pattern of chlorines in most of the OC molecules. These properties are highly influenced by the *n*-octanol water partition coefficient (K_{ow}), soil adsorption coefficient (K_{oc}/K_d), vapour pressure (V_p) as well as Henry's law constant (K_h). OCs is lipophilic and poorly soluble in water and therefore, in the environment, they are more associated with the organic particulate matter of soils, sediments, and biological tissues or with dissolved organic matter in aquatic systems (Ritter *et al.*, 2005). OCs tends to bioaccumulate in living organisms both by uptake from the environment over time and along the food chain (biomagnification) (Chau, 2005). OCs also tends to be transported on air currents from warmer regions of the globe towards colder Polar Regions. Hence they are global contaminants due to their extensive release and long range of transport

which enables them to attain high levels in remote regions, such as the Arctic (Wania and Mackey, 1993; Iwata *et al.*, 1994; Michelle and Bea, 2000). Health associated effects of exposure include skin conditions in adults, neurobehavioral and immunological changes as well as behavioural and learning disturbances in children. In animals, exposure to OCs has been linked to reproductive dysfunction and immune suppression. OCs is also known to be a risk factor for cancer related cases in animals (IARC, 1987; Lemesh, 1992; Kimbrough, 1995; ATSDR, 2001). There has been no historical production of PCBs and OCPs in South Africa but their release into the environment could be traced to various previous industrial, domestic and agricultural applications, such as coolant fluids in electrical appliances like transformers and capacitors, heat exchange fluids, flame retardants, prevention and control of pests in crops as well as malarial vector controls (Carey *et al.*, 1998; Whyllie *et al.*, 2003; Awofolu and Fatoki, 2003; Bouwman, 2004). Due to the persistent and toxic nature of PCBs and OCPs in the environment, routine monitoring in the environment is necessary. However, there is limited information on the levels and distribution of PCBs and OCPs in the river water of KwaZulu-Natal and previous studies had mostly focused on inorganic pollutants. This study therefore investigated the presence and levels of 8 PCB congeners and 7 OCPs including six isomers of DDT during the autumn season to determine if the results are affected by changes in the seasons. The analytes investigated include PCB 28, PCB 52, PCB 77, PCB 101, PCB 105, PCB 138, PCB 153 and PCB 180, HCB, HCH (lindane), heptachlor, aldrin, dieldrin, endrine, mirex, *o,p*-DDE *p,p*-DDE, *o,p*-DDD, *p,p*-DDD, *o,p*-DDT and *p,p*-DDT in the sediment, soil and surface water during the autumn season along the Msunduzi River.

6.2 Materials and methods

6.2.1 Sampling site

Sediment, soil and surface water samples were collected from ten different sites along the river course in May, 2013 (autumn season). The sampling map is shown in Figure 6.1 and the sampling coordinates as well as physicochemical parameters are shown in Table 6.1.



Figure 6.1 Map showing the sampling sites for this study along the Msunduzi River, South Africa.

6.2.2 Reagents and materials

All reagents and chemicals were of HPLC-grade, all PCBs and OCP standards were purchased from Sigma-Aldrich® (South Africa). The stock solutions of 1000 mg/L of PCB and OCP standards were prepared separately by dissolving 0.10 g of the individual PCB and OCP standards in a 100 mL volumetric flask with dichloromethane and stored in the refrigerator at 4 °C. Details of the chemicals and reagents used are reported in the previous chapters (Chapters 4.2.1 and 5.2.1). All glass ware were baked in the oven at about 130 °C overnight, prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

6.2.3 Sampling and Sample Treatment

Sediment, soil and surface water samples were collected during the autumn season. Dried sludge was collected as a sediment sample from the Darvill wastewater treatment plant 1 (W 1 influent). Detailed sampling procedures and sample treatment are reported in chapters 4.2.2 and 5.2.2

6.2.3.1 Sample extraction

Briefly, soil and sediment samples (20 g) were dried, homogenized and mixed with 10 g of anhydrous sodium sulfate to remove excess moisture from the sample. An ultrasonic bath (UMC 20, 90022112 Kenmare) was used for the extraction as recommended by US EPA 3550B 1996 due to its efficiency over the soxhlet method of extraction. Sediment and soil samples were extracted with three times 30 mL DCM at a temperature of 30 °C for 30 minutes each. Extracts were combined, filtered and concentrated to 2 mL using rotary evaporation (Hei-Vap, Heidolph version, Germany). Water samples were extracted using liquid-liquid extraction with DCM. The extractions were repeated three times and the extracts were combined, filtered through 10 g anhydrous Na₂SO₄ and thereafter concentrated to 2 mL using rotary evaporation.

6.2.3.2 Sample clean-up

The soil, sediment and water extracts were subjected to a multi-layer silica gel column clean-up as recommended by the United States Environmental Protection Agency (USEPA method 1668B 2008) for anthropogenic OC pollutants. The column (Quickfit D1/11 England 50 mL) was packed from bottom to top with 2.5 g silica gel, 1.5 g basic silica gel, 2.5 g silica gel, 5.0 g acidic silica gel, 2.5 g silica gel; 2 g activated copper powder and 10 g anhydrous sodium sulfate (Na₂SO₄). The column was pre-eluted with 20 mL *n*-hexane before the extract was loaded and thereafter 50 mL of *n*-

hexane:DCM:toluene solvent combinations were used for the elution in the ratio 2.5:1.5:1. The eluent was reduced to 2 mL using rotary evaporation and thereafter evaporated to dryness at room temperature. Samples were reconstituted to 2 mL with *n*-hexane and filtered through a 0.45 µm acrodisc filter prior to GC-MS analysis.

6.2.4 Instrumental analyses and quality control

6.2.4.1 GC-MS Analysis

Both PCB and OCP congeners were separated and detected using an Agilent gas chromatography/mass spectrometry (GC/MS) (GC-6890-MS-5973 series Germany), with a ZB-5MS fused-silica capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness). Helium was used as a carrier gas with a flow rate of 1.0 mL/min, a total flow of 43.8 mL/sec and a linear velocity of 28 cm/s using splitless injection mode. The injection and detector temperatures were set at 250 °C and 325 °C respectively. Oven temperature was set at 125 °C and held for 1 min, raised to 295 °C at 15 °C/min and held for a further 2 min. A 1 µL injection volume was used. All the quality control steps were followed. Laboratory blanks for both water and sediment were subjected to the same analytical procedures as applied to the original samples but did not show any significant peaks. Triplicate linear range values (R^2) for all the analytes were not less than 0.9950. LOD and LOQ values were determined for the analytes using three times standard deviation of the response over the slope of the calibration curve while ten times the standard deviation of the response over the slope of the calibration curve was used to determine the LOQ values (Shrivastava and Gupta, 2011) (Table 6.1). The recovery was determined using a matrix spiked method. Routine analysis of blanks with every ten sample sets were carefully monitored to determine the possibility of any interferences from the column. Instrument sensitivity was carefully monitored by running standards intermittently between samples. Sample extracts were spiked with 2 mg/L using 250 µL of the mixed PCB and OCP standards and their concentrations were determined. An external calibration method (USEPA method 608) was used for the quantification of PCBs and OCPs based on the peak areas of the targeted compounds. The analytes were identified by comparing their retention times with those of the PCB and OCP standards as well as their corresponding mass spectra.

Table 6.1 Percentage recoveries based on spiked sediment sampled from Du Toit sampling site during autumn, and spiked tap water, limits of detection and quantification, R² values and retention times of OCPs and PCBs in water and sediment.

Analytes	Recoveries (%)		Limit of Detection and Quantification				R ² Values	Retention Times (mins)
	Water	Sediment	Sediment (ng/g)		Water (ng/mL)			
			LOD	LOQ	LOD	LOQ		
HCB	75.01	95.22	0.016	0.051	0.0007	0.002	0.9995	6.898
HCH	79.02	101.04	0.046	0.051	0.0018	0.0021	0.9980	7.309
Heptachlor	66.31	80.42	0.002	0.023	0.0001	0.0001	0.9920	8.818
Aldrin	72.81	94.7	0.012	0.037	0.0005	0.0015	0.9971	9.639
<i>o,p</i> -DDE	64.13	88.23	0.007	0.022	0.0003	0.0086	0.9980	10.058
<i>p,p</i> - DDE	66.15	98.22	0.008	0.025	0.0002	0.0008	0.9993	10.159
<i>o,p</i> -DDD+Dieldrin	68.3	106.24	0.006	0.021	0.0002	0.0009	0.9982	10.435
Endrin	67.24	100.13	0.020	0.065	0.0008	0.0026	0.9954	10.620
<i>p,p</i> -DDD	60.45	114.91	0.005	0.016	0.0002	0.0006	0.9956	11.925
<i>o,p</i> -DDT	84.05	96.01	0.004	0.04	0.0005	0.0016	0.9997	11.726
<i>p,p</i> -DDT	68.52	88.86	0.003	0.011	0.0004	0.0004	0.9992	12.137
Mirex	78.48	92.11	0.006	0.021	0.0003	0.0008	0.9995	12.531
PCB 28	65.21	94.43	0.009	0.027	0.0005	0.0014	0.9962	8.105
PCB 77	55.09	84.87	0.005	0.014	0.0002	0.0007	0.9934	8.558
PCB 101	72.01	85.66	0.002	0.005	0.0001	0.0003	0.9980	9.689
PCB 52	67.74	88.03	0.015	0.005	0.0001	0.0002	0.9974	10.209
PCB 153	71.37	77.96	0.014	0.041	0.0007	0.0021	0.9980	10.762
PCB 105	99.97	101.23	0.004	0.013	0.0002	0.0007	0.9996	10.838
PCB 138	87.78	90.4	0.003	0.01	0.0002	0.0005	0.9984	11.114
PCB 180	68.57	81.24	0.008	0.003	0.0001	0.0002	0.9962	11.936

6.3 Results and Discussion

Table 6.1 indicated a water temperature range between 13.80 and 22.80 °C during the autumn sampling season. The lower temperature during this season has a significant effect on the pollutant concentration as the vapour pressure is expected to be lower as temperature decreases thereby discouraging the desorption of pollutants from soil particulate matter. High temperatures tend to encourage volatilization of the pollutants from sediment and soil to water and into air (Zhang *et al.*, 2008) consequently leading to reduced pollutant concentrations in sediment, soil and particulate matter. Table 6.1 also indicated that the pH at all the sampling sites were within the slightly acidic levels which suggests that the geological characteristic of the soil, sediment and water at the sampling sites is the presence of carbonates which is the principal component regulating ion for pH in natural waters (Apha, 1995). The high pH is also an indication of a high organic content which results because microorganisms break down organic material to form CO₂ as the by product which then will dissolve and equilibrate with the water forming carbonic acid (H₂CO₃) and bicarbonates (HCO₃) (Sujitha *et al.*, 2011). Higher conductivities of 51-421 µs/cm and total dissolved solids (TDS) of 11-244 mg/L were recorded during the autumn sampling season. These higher values may be as a result of low hydrological conditions such as low water flowrates which could lead to a higher rate of sediment deposition during this season.

Table 6.2 Sampling coordinates and physicochemical parameters of the Msunduzi River water during the autumn season.

Site Name	Location		Physicochemical parameters			
	Latitude	Longitude	pH	Temperature (°C)	Conductivity (µs/cm)	TDS (mg/L)
M 1	29° 38'51"	30° 17'32"	5.51	13.8	192.90	112.00
M 2	29° 36'47"	30° 22'36"	6.36	15.1	390.00	226.00
M 3	29° 35'52"	30° 24'01"	6.01	15.3	421.00	244.10
W 1	29° 36'15"	30° 25'52"	5.77	21.8	118.50	69.00
W 2	29° 36'15"	30° 25'52"	5.95	20.7	148.00	86.00
W 3	29° 36'15"	30° 25'52"	6.16	17.1	81.40	47.00
M 4	29° 36'40"	30° 33'32"	5.50	14.2	51.00	30.00
M 5	29° 39'40"	30° 38'10"	5.75	15.1	55.90	33.00
M 6	29° 37'08"	30° 09'30"	6.07	22.8	51.70	30.00
M 7	29° 37'16"	30° 40'46"	6.70	19.8	18.80	11.00

M 1 = Henley Dam Outlet; M 2 = Camps Drift; M 3 = Du Toit; W 1 = Darvill Wastewater Treatment Plant 1 (inlet); W 2 = Darvill Wastewater Treatment Plant 2 (after chlorination); W 3 = Darvill Wastewater Treatment Plant 3 (discharge); M 4 = Agricultural Area; M 5 = Msunduzi Town; M 6 = Nagle Dam; M 7 = uMgeni, Msunduzi River joining point.

**TDS = Total dissolved Oxygen.

Table 6.3 a, b and c: PCB concentrations in sediment (ng/g), soil (ng/g) and water (ng/mL) across the sampling sites during the autumn season.

PCBs	a: Mean concentrations (ng/g dry wt \pm RSE) of PCBs in sediment collected during autumn season									
	M 1	M 2	M 3	W 1	W 2	W 3	M 4	M 5	M 6	M 7
PCB 28	70.68 \pm 1.27	41.32 \pm 0.13	99.33 \pm 0.25	62.25 \pm 1.45	75.66 \pm 2.47	257.34 \pm 0.47	38.48 \pm 0.69	132.91 \pm 1.13	79.91 \pm 1.00	69.9 \pm 1.10
PCB 77	46.18 \pm 1.20	34.12 \pm 2.28	53.33 \pm 1.54	41.54 \pm 0.47	42.52 \pm 2.30	157.62 \pm 0.04	29.85 \pm 1.48	110.78 \pm 0.45	68.62 \pm 1.87	49.08 \pm 0.77
PCB 101	42.41 \pm 2.02	37.99 \pm 0.46	54.44 \pm 1.35	62.77 \pm 0.17	25.69 \pm 0.04	164.39 \pm 0.15	34.16 \pm 0.23	156.73 \pm 0.09	62.83 \pm 2.37	52.07 \pm 0.06
PCB 52	30.91 \pm 1.40	24.26 \pm 0.16	61.45 \pm 1.73	30.75 \pm 0.05	27.93 \pm 0.45	165.46 \pm 0.41	17.85 \pm 0.22	111.19 \pm 0.07	28.03 \pm 1.30	72.77 \pm 1.15
PCB 153	56.4 \pm 0.58	26.3 \pm 1.68	47.41 \pm 1.74	34.9 \pm 1.48	44.65 \pm 0.03	129.81 \pm 0.10	24.78 \pm 0.42	121.5 \pm 1.29	43.65 \pm 2.47	38.79 \pm 1.49
PCB 105	31.84 \pm 1.19	37.13 \pm 0.19	66.55 \pm 0.76	55.04 \pm 2.08	64.61 \pm 0.05	137.92 \pm 0.33	19.32 \pm 5.20	88.28 \pm 0.91	37.12 \pm 2.33	46.95 \pm 0.99
PCB 138	28.27 \pm 0.39	15.08 \pm 1.07	30.89 \pm 0.59	30.69 \pm 0.69	43.19 \pm 0.31	128.57 \pm 0.49	10.69 \pm 1.17	60.04 \pm 1.68	56.74 \pm 1.50	5.31 \pm 0.39
PCB 180	46.06 \pm 1.85	84.56 \pm 0.92	185.09 \pm 0.48	208.85 \pm 0.73	101.16 \pm 1.50	147.45 \pm 0.29	60.83 \pm 0.82	92.04 \pm 0.15	76.17 \pm 0.52	106.01 \pm 0.32
Σ PCB	334.36 \pm 0.10	300.76 \pm 0.14	598.49 \pm 0.16	526.79 \pm 0.22	426.02 \pm 0.12	1288.83 \pm 0.06	235.85 \pm 0.13	874.09 \pm 0.07	452.93 \pm 0.08	440.91 \pm 0.13

PCBs	b: Mean concentrations (ng/g dry wt \pm RSE) of PCBs in soil collected during autumn period.							
	M 1	M 2	M 3	W 3	M 4	M 5	M 6	M 7
PCB 28	94.48 \pm 0.09	120.62 \pm 0.14	163.78 \pm 0.85	151.98 \pm 0.03	112.88 \pm 0.54	44.75 \pm 1.41	85.1 \pm 1.01	133.31 \pm 0.90
PCB 77	82.96 \pm 0.03	121.66 \pm 0.32	93.8 \pm 0.44	149.63 \pm 0.03	44.8 \pm 0.24	20.99 \pm 1.60	56.39 \pm 1.18	101.45 \pm 0.81
PCB 101	137.94 \pm 1.73	117.99 \pm 0.56	76.03 \pm 0.21	147.61 \pm 0.35	71.16 \pm 0.47	41.21 \pm 1.56	72.08 \pm 0.61	95.72 \pm 1.51
PCB 52	23.37 \pm 0.12	59.24 \pm 1.08	56.06 \pm 1.11	59.66 \pm 0.70	37.11 \pm 1.91	33.42 \pm 0.25	41.6 \pm 1.44	42.46 \pm 2.72
PCB 153	83.87 \pm 0.41	98.15 \pm 0.47	81.74 \pm 0.18	145.54 \pm 0.57	35.97 \pm 1.17	13.25 \pm 0.87	23.46 \pm 1.60	74.62 \pm 1.41
PCB 105	26.33 \pm 0.28	55.52 \pm 2.32	62.44 \pm 0.02	87.08 \pm 0.80	45.3 \pm 0.18	4.14 \pm 1.26	12.11 \pm 0.64	59.5 \pm 0.61
PCB 138	18.24 \pm 0.28	30.45 \pm 0.16	43.67 \pm 0.27	69.01 \pm 1.17	14.31 \pm 2.04	36.73 \pm 0.33	14.49 \pm 0.30	58.8 \pm 0.21
PCB 180	178.09 \pm 0.20	259.67 \pm 0.18	255.1 \pm 0.12	297.95 \pm 0.15	30.61 \pm 0.33	24.9 \pm 2.26	10.53 \pm 1.45	36.37 \pm 1.75
Σ PCB	645.28 \pm 0.17	863.3 \pm 0.16	832.62 \pm 0.17	1108.46 \pm 0.13	392.14 \pm 0.15	219.39 \pm 0.13	315.76 \pm 0.18	602.23 \pm 0.11

PCBs	c: Mean concentrations (ng/mL \pm RSE) of PCBs in water collected during autumn period.									
	M 1	M 2	M 3	W 1	W 2	W 3	M 4	M 5	M 6	M 7
PCB 28	10.05 \pm 0.03	4.73 \pm 1.02	5.96 \pm 0.83	6.31 \pm 0.04	7.51 \pm 0.39	4.83 \pm 1.03	4.86 \pm 2.18	2.6 \pm 0.31	4.7 \pm 0.25	6.2 \pm 0.02
PCB 77	8.4 \pm 0.31	3.73 \pm 2.28	4.11 \pm 0.91	5.27 \pm 0.04	3.39 \pm 0.10	2.29 \pm 0.33	4.41 \pm 2.29	2.23 \pm 0.70	2.73 \pm 0.45	6.15 \pm 0.00
PCB 101	6.89 \pm 0.11	4.15 \pm 1.39	3.35 \pm 1.75	5.98 \pm 0.46	6.62 \pm 0.34	2.23 \pm 2.23	5.55 \pm 0.71	1.85 \pm 0.95	3.22 \pm 0.03	5.18 \pm 0.22
PCB 52	5.78 \pm 0.67	4.92 \pm 0.71	4.22 \pm 0.03	4.3 \pm 0.29	4.74 \pm 0.18	1.55 \pm 1.75	4.69 \pm 0.53	0.95 \pm 0.28	1.35 \pm 0.71	4.74 \pm 0.00
PCB 153	5.44 \pm 0.39	2.27 \pm 2.04	3.36 \pm 1.00	4.41 \pm 0.60	3.7 \pm 1.17	1.47 \pm 1.76	1.92 \pm 4.97	1.6 \pm 1.11	2.03 \pm 0.13	4.44 \pm 0.03
PCB 105	4.95 \pm 0.24	3.26 \pm 0.28	2.47 \pm 2.67	3.27 \pm 0.75	3.46 \pm 0.95	2.53 \pm 0.11	4.13 \pm 0.02	2.21 \pm 0.34	1.13 \pm 1.52	4.53 \pm 0.03
PCB 138	3.92 \pm 0.50	2.67 \pm 0.03	1.48 \pm 2.32	3.39 \pm 0.31	2.71 \pm 0.88	1.54 \pm 0.10	2.17 \pm 2.05	1.51 \pm 0.61	0.69 \pm 0.28	3.29 \pm 0.05
PCB 180	8.65 \pm 0.50	4.91 \pm 0.88	7.55 \pm 0.87	9.47 \pm 0.59	11.45 \pm 0.66	6.41 \pm 1.33	9.58 \pm 0.55	10.18 \pm 0.10	10.24 \pm 0.41	21.41 \pm 0.12
Σ PCB	54.08 \pm 0.08	30.64 \pm 0.07	32.5 \pm 0.12	42.4 \pm 0.09	43.58 \pm 0.13	22.85 \pm 0.15	35.7 \pm 0.15	23.13 \pm 0.25	26.09 \pm 0.23	55.94 \pm 0.21

Tables 6.3 a, b and c, as well as Figure 6.2 show the concentrations of PCB congeners at different sites in sediment, soil and surface water during the autumn season. Among the sampling sites the wastewater point of discharge into the Msunduzi River (W 3) showed the highest PCB concentration level in the range of 128.57-295.45 ng/g and 59.66-297.95 (ng/g) in both sediment and soil respectively. This site receives waste discharge from the treatment plant as well as upstream pollutants from the river which could be a possible reason for the higher concentration of the PCBs at this site. Furthermore, the results obtained in this work suggest that the concentrations of PCBs and OCPs in the wastewater treatment plant varies considerably depending on the type of effluent passing through the plant at any point in time on any given day. The high results at the discharge point also suggest that the wastewater treatment plant could be a possible point source for PCBs into the Msunduzi River (Figure 6.2). High PCB concentrations were also detected at the wastewater treatment plant influent and effluent (W 1 and W 2) with concentrations ranging between 30.69-208.85 (ng/g) and 25.69-155.16 (ng/g) in sediment; and 3.27-9.47 (ng/mL) and 2.71-11.45 (ng/mL) in water respectively. Site W 1 receives its wastewater from industrial, domestic as well as possible agricultural runoffs along the course of the river which could all contribute to higher PCB concentrations at this site. W 2 is a point just after the chlorination process in the treatment plant and has similar or slightly lower levels of PCBs compared to W 1 which suggest that the treatment plant process up to the chlorination step does not remove much PCBs. Along the river, the Msunduzi joining point (M 7) had concentrations ranging between 5.31-279.01 (ng/g) and 3.29-21.41 (ng/mL) in sediment and water samples respectively. The higher concentrations at this site could be due to the higher accumulation of pollutant loads received from both the uMgeni River and the Msunduzi River as this point is already on the uMgeni river where the Msunduzi tributary joins the uMgeni River. The Du Toit (M 3) sampling point is located within the city centre of Pietermaritzburg and was found to have concentrations of 30.89-185.09 (ng/g) 43.67-255.10 (ng/g) and 1.48-7.55 (ng/mL) in sediment, soil and water respectively. This site is characterized by various anthropogenic activities such as industrial drainage, possible municipal and domestic leaching into the river ecosystem which may be point and non-point sources of PCB pollutants at this site. High concentrations of PCBs at this site could also be as a result of high vehicular activities (including heavy duty vehicles) which were noted during sampling. Studies have shown that these activities lead to high contamination of PCBs in the environment (Zhang *et al.*, 2003; Nasir *et al.*, 2014). Other sites with some level of PCB concentrations are Henley dam outlet (M 1), Msunduzi town (M 5), Nagle dam (M 6) and the agricultural sampling site (M 4). The concentrations were 28.27-70.68 (ng/g), 18.24-178.09 (ng/g) and 3.92-10.05 (ng/mL) in sediment, soil and water for M 1 and 60.04-170.04 (ng/g), 4.14-44.75 (ng/g) and 0.95-10.18 (ng/mL) in sediment soil and water for M 5 respectively. M 1 and M 5 are

both located in semi-rural and rural areas and the presence of PCBs could possibly be resulting from burning and incineration of PCB containing waste such as PCB treated wood used for cooking and heating of homes. Although PCBs have been banned a long time ago, its presence in the environment could also be due to previous usage in the environment since they are persistent and degrade very slowly in the environment and settle within the particulate matter of sediment and soil.

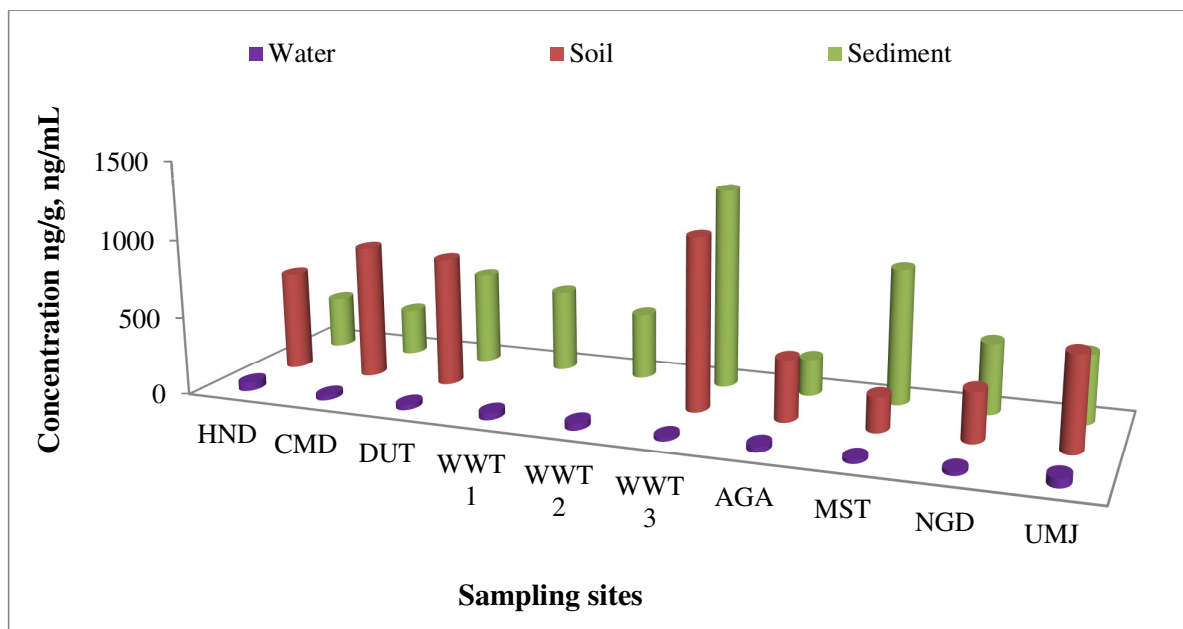


Figure 6.2 Total PCB concentrations (ng/g, ng/mL) in sediment, soil and water samples across all sampling sites during the autumn season.

Total concentrations of targeted PCB congeners in sediment, soil and water during the autumn season are presented in Figure 6.3. Among the congeners, PCB 180 was found to be dominant in all sample media during the autumn season. Generally, an increasing number of chlorine substituents decreases biodegradation of PCBs in the environmental media. The most highly chlorinated congeners (with 7-10 chlorine atoms) tend to bind tightly to sediment, soil and organic particulate matter in the environment which could result in accumulation over time and could be a possible reason for the higher concentrations of PCB 180 obtained in this study. Also PCB 101, PCB 105 and PCB 153 are all penta- and hexa-chlorobiphenyls respectively which were also found to have high concentrations except PCB 138 with a relatively lower concentration compared to others. These classes of PCBs (penta-, hexa- and hepta- PCBs) are known to be both bioavailable and resistant to degradation in sediment, soil and in organisms (Koslowski *et al.*, 1994; Willman *et al.*, 1997). The

concentrations of tri- and tetra- CBs which were PCB 28, PCB 77 and PCB 52 were also found to be high in this study. Previous studies have shown that highly polychlorinated biphenyls are extremely resistant to aerobic transformation but undergo anaerobic reductive de-chlorination yielding lower levels of tri- and tetra- as well as higher dichloro- and monochloro-biphenyls (Fiedler *et al.*, 1994). Also the high concentrations of tri- and tetra- CBs detected could be as a result of aged long anaerobic degradation of more highly chlorinated PCBs that are still persistent in the environment. Some studies done on sediment, soil and water in other countries were compared with the present study. Lead and co-workers, found total concentrations of 6.1-52 ng/g (d.w) for 6 PCBs in rural and semi-rural soil in Norway in 1995 (Lead *et al.*, 1997). Holoubek and co-workers found levels of PCBs to be 469-543 ng/g (d.w) and 0.048-0.221 ng/mL in both sediment and water respectively in the soil and sediment of Rozmítal and water of Morava and Oder (Baltic sea) in the Czech Republic (Holoubek *et al.*, 2003a). Zhang and co-workers reported some low concentrations of 0.78-8.74 ng/g (d.w) of 12 PCBs in the sediment of Tonghui River, China (Zhang *et al.*, 2004b). A study carried out by Sapozhnikova and co-workers on the sediment of the Salton Sea, California, USA revealed concentrations of 116-304 ng/g (d.w) for aroclor and kenechlor PCB mixtures (Sapozhnikova *et al.*, 2004). Generally, the concentrations of individual PCB congeners at different sites in this study were found to be higher than the lowest limit of 0.014 ng/mL set by the US EPA guideline for surface water which is considered to pose no hazard to the aquatic and human health. The results in this study are also higher than the maximum allowable concentration for underground waters of 0.01 ng/mL set by the European Union.

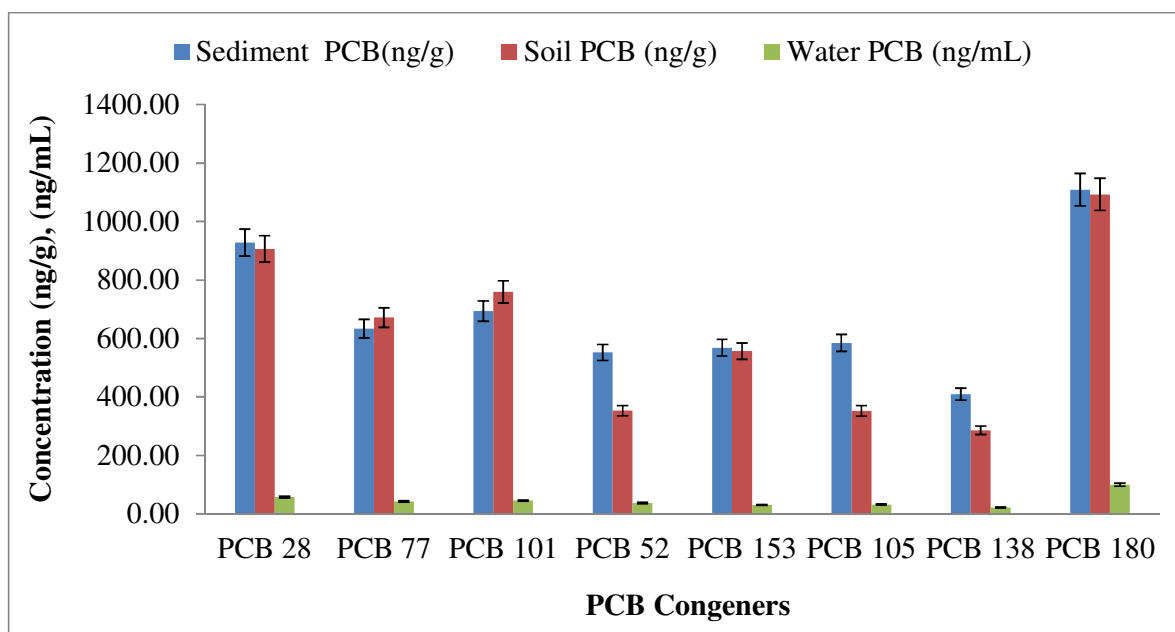


Figure 6.3 Total concentrations of PCB congeners in sediment (ng/g), soil (ng/g) and water (ng/mL) during the autumn season.

Table 6.4 a, b and c: OCP concentrations in sediment (ng/g), soil (ng/g) and water (ng/mL) during the autumn season.

	a: Mean concentrations (ng/g dry wt \pmRSE) of OCPs in sediment collected during autumn season.									
OCPs	M 1	M 2	M 3	W 1	W 2	W 3	M 4	M 5	M 6	M 7
HCB	63.65 \pm 0.37	20.77 \pm 0.12	65.88 \pm 0.13	38.69 \pm 0.4	19.7 \pm 1.66	150.22 \pm 0.28	70.89 \pm 0.95	17.98 \pm 0.32	5 \pm 0.57	25.93 \pm 0.01
HCH	95.28 \pm 0.2	40.86 \pm 2.15	99.8 \pm 0.47	49.97 \pm 0.74	28.78 \pm 0.1	109.75 \pm 0.92	80.75 \pm 0.89	7.78 \pm 2.02	46.12 \pm 0.91	19.66 \pm 0.62
Heptachlor	114.55 \pm 0.37	96.61 \pm 0.04	105.87 \pm 0.4	69.23 \pm 0.47	61.25 \pm 0.37	142.57 \pm 0.25	121.61 \pm 0.22	24.51 \pm 1.82	86.21 \pm 0.21	52.12 \pm 0.00
Aldrin	100.1 \pm 0.54	42.37 \pm 2.15	70.1 \pm 0.33	27.77 \pm 0.79	31.7 \pm 0.42	11.15 \pm 0.17	85.61 \pm 0.42	10.66 \pm 0.05	51.27 \pm 0.97	32.81 \pm 0.03
Endrin	240.79 \pm 0.73	128 \pm 1.61	252.88 \pm 0.71	198.31 \pm 0.10	69.94 \pm 0.77	258.12 \pm 2.05	183.17 \pm 0.41	62.52 \pm 0.58	187.74 \pm 0.34	176.67 \pm 0.02
Mirex	36.88 \pm 0.98	12.4 \pm 0.18	50.01 \pm 1.01	11.53 \pm 0.39	8.35 \pm 1.36	46.54 \pm 1.92	27.1 \pm 1.17	7.27 \pm 2.45	19.01 \pm 0.48	10.8 \pm 0.09
<i>o,p</i>-DDE	120 \pm 0.74	81.32 \pm 1.57	91.19 \pm 1.7	94.94 \pm 0.53	116.91 \pm 0.7	175.18 \pm 0.65	176.18 \pm 0.63	39.1 \pm 1.42	109.1 \pm 0.54	59.57 \pm 0.77
<i>p,p</i>- DDE	108.17 \pm 0.49	39 \pm 2.65	106.65 \pm 0.54	47.92 \pm 0.86	25.19 \pm 2.36	170.36 \pm 0.00	85.22 \pm 0.42	11.4 \pm 0.81	56.69 \pm 0.86	16.11 \pm 2.65
<i>o,p</i>-DDD+Dieldrin	194.07 \pm 0.02	153.86 \pm 0.41	247.13 \pm 0.01	82.14 \pm 1.39	73.34 \pm 2.58	224.23 \pm 1.63	220 \pm 0.02	100.98 \pm 1.71	143.75 \pm 0.56	67.72 \pm 0.16
<i>p,p</i>-DDD	54.85 \pm 0.5	6.28 \pm 2.03	44.36 \pm 0.33	21.59 \pm 0.69	6.39 \pm 2.59	78.62 \pm 1.38	42.07 \pm 0.72	0.53 \pm 2.73	16.62 \pm 2.30	4.46 \pm 1.50
<i>o,p</i>-DDT	104.38 \pm 0.7	62.07 \pm 0.05	106.56 \pm 0.52	25.01 \pm 0.31	22.89 \pm 0.08	97.93 \pm 1.55	105.25 \pm 0.04	6.41 \pm 0.02	17.77 \pm 1.62	51.3 \pm 0.37
<i>p,p</i>-DDT	83.97 \pm 0.77	164.12 \pm 0.89	87.52 \pm 1.09	53.66 \pm 1.30	53.63 \pm 0.11	144.7 \pm 1.43	140.82 \pm 0.01	8.02 \pm 2.16	95 \pm 0.73	29.44 \pm 1.68
Σ DDT	665.44\pm0.14	506.65\pm0.19	683.41\pm0.20	325.26\pm0.09	298.35\pm0.12	891.02\pm0.16	769.54\pm0.19	166.44\pm0.11	438.93\pm0.13	228.6\pm0.07
ΣOTHER OCPs	651.25\pm0.21	341.01\pm0.13	644.54\pm0.22	395.5\pm0.20	219.72\pm0.07	718.35\pm0.26	569.13\pm0.16	130.72\pm0.06	395.35\pm0.19	317.99\pm0.18
Σ OCPs	1316.69\pm0.08	847.66\pm0.13	1327.95\pm0.10	720.76\pm0.14	518.07\pm0.12	1609.37\pm0.09	1338.67\pm0.09	297.16\pm0.20	834.28\pm0.13	546.59\pm0.16

OCPs	b: Mean concentrations (ng/g dry wt \pm RSE) of OCPs in soil collected during autumn period.							
	M 1	M 2	M 3	W 3	M 4	M 5	M 6	M 7
HCB	63.87 \pm 2.15	16.65 \pm 0.06	84.84 \pm 0.29	336.53 \pm 0.04	35.66 \pm 0.83	1 \pm 2.43	7.76 \pm 0.72	63.65 \pm 0.03
HCH	67.29 \pm 0.29	87.41 \pm 0.04	58.36 \pm 0.20	110.57 \pm 0.05	3.35 \pm 0.18	1.12 \pm 0.96	1.03 \pm 2.15	5.16 \pm 0.57
Heptachlor	51.88 \pm 0.7	66.91 \pm 0.49	35.41 \pm 1.54	232.54 \pm 0.04	36.34 \pm 2.06	7.61 \pm 1.39	20.77 \pm 0.95	48.91 \pm 0.52
Aldrin	82.78 \pm 0.76	52.89 \pm 0.09	48.09 \pm 1.06	120.33 \pm 2.00	17.29 \pm 2.77	11.4 \pm 0.32	6.64 \pm 0.84	33.54 \pm 0.02
Endrin	219.96 \pm 0.54	278.68 \pm 0.06	302.75 \pm 0.13	360.25 \pm 0.02	60.32 \pm 0.33	40.2 \pm 0.06	40.95 \pm 0.38	102.65 \pm 0.78
Mirex	41.44 \pm 0.44	19.22 \pm 0.93	11.7 \pm 0.04	210.69 \pm 0.82	48.91 \pm 1.20	16.21 \pm 1.08	24.28 \pm 0.17	51.24 \pm 0.00
<i>o,p</i> -DDE	122.87 \pm 0.73	104.9 \pm 0.24	178.43 \pm 1.19	248.52 \pm 0.07	77.26 \pm 0.65	28.85 \pm 1.20	45.68 \pm 0.00	80.79 \pm 0.21
<i>p,p</i> -DDE	126.84 \pm 1.20	106.49 \pm 0.12	149.64 \pm 2.06	314.99 \pm 0.48	32.67 \pm 2.19	7.76 \pm 0.31	1.85 \pm 0.04	31.89 \pm 0.73
<i>o,p</i> -DDD+Dieldrin	196.86 \pm 0.52	238.44 \pm 0.05	204.4 \pm 0.07	372.65 \pm 0.1	243.84 \pm 0.01	46.22 \pm 0.00	69.46 \pm 0.61	117.74 \pm 2.50
<i>p,p</i> -DDD	67.56 \pm 1.29	47.54 \pm 0.12	25.18 \pm 0.22	129.1 \pm 0.09	35.38 \pm 0.01	39.19 \pm 0.01	39.31 \pm 0.15	57.06 \pm 0.00
<i>o,p</i> -DDT	131.5 \pm 1.55	101.03 \pm 0.01	24.31 \pm 2.01	330.08 \pm 0.08	66.94 \pm 1.15	3.88 \pm 2.16	21.91 \pm 1.78	42.38 \pm 2.72
<i>p,p</i> -DDT	169.96 \pm 0.77	148.72 \pm 0.09	76.46 \pm 0.20	196.08 \pm 0.12	118.85 \pm 0.52	76.33 \pm 0.10	71.12 \pm 0.19	176.49 \pm 0.11
Σ DDT	815.59 \pm 0.11	747.12 \pm 0.17	658.42 \pm 0.23	1591.42 \pm 0.11	574.94 \pm 0.27	202.23 \pm 0.26	249.33 \pm 0.21	506.35 \pm 0.21
Σ OTHER OCPs	527.22 \pm 0.25	521.76 \pm 0.38	541.15 \pm 0.39	1370.91 \pm 0.15	201.87 \pm 0.20	77.54 \pm 0.37	101.43 \pm 0.29	305.15 \pm 0.21
Σ OCPs	1342.81 \pm 0.09	1268.88 \pm 0.13	1199.57 \pm 0.15	2962.33 \pm 0.06	776.81 \pm 0.16	279.77 \pm 0.16	350.76 \pm 0.14	811.5 \pm 0.11

OCPs	c: Mean concentrations (ng/mL ±RSE) of OCPs in water collected in autumn period.									
	M 1	M 2	M 3	W 1	W 2	W 3	M 4	M 5	M 6	M 7
HCB	0.53±0.17	1.12±0.19	0.82±1.15	1±2.26	1.39±0.55	0.43±0.82	0.65±2.03	3.41±0.82	1.19±0.01	0.24±0.14
HCH	0.61±0.17	4.78±0.41	2.9±0.45	4.07±1.21	3.78±0.77	2.04±0.12	3.8±0.2	4.98±1.09	3.69±0.02	1.23±1.13
Heptachlor	1.58±0.09	1.53±0.79	0.84±0.39	1.48±2.63	1.72±0.63	1.55±0.13	0.96±0.66	3.79±0.74	0.83±0.32	1.17±0.47
Aldrin	1.12±0.16	1.43±0.02	1.4±0.42	1.19±2.45	2.56±0.18	1.53±0.59	1.08±0.49	4.24±1.06	1.59±0.20	0.6±0.32
Endrin	3.61±0.43	2.76±0.77	1.46±2.47	17.63±0.71	9.61±0.01	4.61±0.04	4.45±0.21	7.06±0.71	2.66±0.27	3.28±0.13
Mirex	0.93±1.28	1.35±0.93	2.77±0.67	2.39±0.68	3.18±0.53	1.81±1.08	3.03±1.80	4.04±0.52	2.92±0.28	1.87±0.20
<i>o,p</i> -DDE	2.79±0.02	4.64±0.15	4.04±0.40	4.56±0.60	3.51±0.08	3.14±0.11	3.14±0.43	5.93±0.64	4.78±0.02	2.62±0.57
<i>p,p</i> - DDE	0.67±0.91	1.71±0.18	0.47±0.93	2.15±0.44	1.77±0.22	2±0.81	0.16±2.35	3.55±1.11	1.55±0.43	0.26±0.12
<i>o,p</i> -DDD+Dieldrin	2.79±0.2	2.36±1.14	2.74±1.60	9.06±1.33	0.43±0.71	1.68±0.06	2.42±0.62	4.96±1.76	4.12±0.60	8.32±0.03
<i>p,p</i> -DDD	0.4±0.49	0.86±0.47	1.21±1.3	1.54±2.61	0.81±0.00	0.17±1.36	1.09±0.00	1.31±2.01	1.62±0.07	0.36±1.03
<i>o,p</i> -DDT	1.58±1.44	3.87±1.51	4.96±0.16	3.78±0.65	2.11±1.03	2.76±0.63	1.51±0.00	3.46±0.39	2.65±1.62	2.61±0.08
<i>p,p</i> -DDT	4.51±0.02	4.52±0.00	4.74±0.03	7.41±0.09	4.88±0.20	13.29±0.06	6.83±0.25	5.23±0.63	6.39±0.12	6.68±0.05
Σ DDT	12.74±0.18	17.96±0.15	18.15±0.10	28.5±0.44	13.51±0.44	23.04±0.12	15.15±0.21	24.44±0.11	21.11±0.10	20.85±0.10
ΣOTHER OCPs	8.38±0.11	12.97±0.09	10.19±0.06	27.76±0.23	22.24±0.17	11.97±0.08	13.97±0.11	27.52±0.05	12.88±0.06	8.4±0.07
Σ OCPs	21.12±0.13	30.93±0.09	28.34±0.11	56.26±0.17	35.75±0.13	35.01±0.19	29.12±0.13	51.96±0.05	33.99±0.10	29.25±0.17

6.3.1 Distributions of OCPs along the sampling site

OCP concentrations in sediment, soil and water are presented in Tables 6.4 a, b and c respectively and also in Figure 6.3. The concentration levels and distribution of OCPs along the river in sediment, soil and water varies and is dependent on the anthropogenic activities at each sampling site. Among the sampling sites investigated, the point of discharge of wastewater (W 3) had the highest OCP concentration levels which showed the same trend with that of PCB concentrations as noted earlier. The reason for this occurrence could be due to the wastewater treatment plant not adequately removing the OCPs in its treatment process and thereby can be considered a point source of entry for OCPs as well into this river. Sites M 1 and M 4 are both located in rural settlements and the relatively high OCP concentrations determined at these sites could be as a result of illegal usage of pesticide-related chemicals among the local farmers to control crop pests where rural agriculture is prevalent. Camps drift (M 2) and Du Toit (M 3) showed higher OCP concentrations during this season. The sources of high OCP concentrations at these sites could not be explained since no agricultural activities take place at these sites. These pollutants are also persistent enough such that their presence could be a result of age long usage in the area or trans boundary effects. These sites were found to show the highest conductivities of 421 $\mu\text{S}/\text{cm}$ and 244 $\mu\text{S}/\text{cm}$ as well as total dissolved solid (TDS) 390 and 226 mg/L respectively. Research has shown that high TDS values in the river sediment, soil and river water indicate that there could be an extraneous pollution source which may be the reason for the high OCP concentrations observed (Kataria, *et al.*, 1996). The reasons for the high OCP concentration levels found at the Msunduzi/uMgeni joining point (M 7) and the wastewater treatment plant (W 1 and W 2) could be due to the higher accumulation of pollutant loads received from both the uMgeni River and the Msunduzi River at the joining point (M 7), and W 1 receives its waste from both industrial and domestic as well as agricultural runoffs which could all be contributing factors for higher OCP concentrations at this site. W 2 is a point just after the chlorination process of the treatment plant where high OCP residues suggest that the treatment plant process up to the chlorination step does not remove much OCPs.

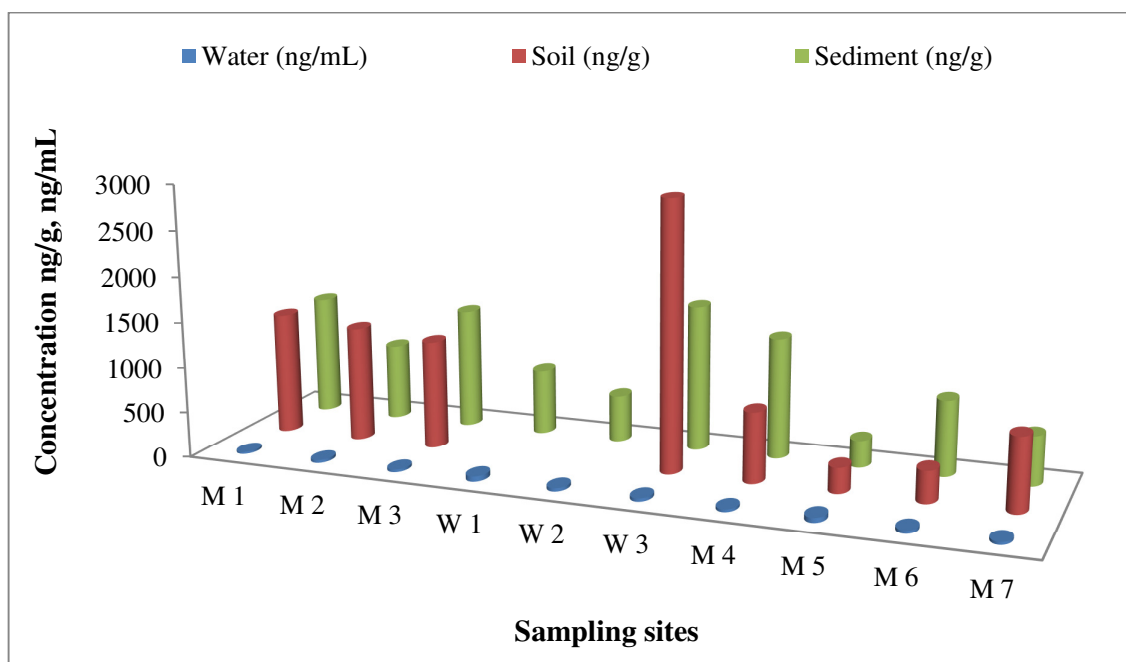


Figure 6.4 Total OCP concentrations in sediment, soil and water (ng/g, ng/mL) across all sampling sites for autumn.

Figure 6.4 shows the total OCP concentrations in sediment, soil and surface water during the autumn season. DDT and its metabolites were most frequently detected with DDE being the most predominate among the DDT isomers in river sediment, soil and water samples with the total concentrations of (*o,p*-DDE + *p,p*-DDE) found to be 1730.20 ng/g, 1659.43 ng/g and 53.44 ng/mL in sediment, soil and water respectively. Previous studies have shown that DDT can be converted to DDE and DDD *via* anaerobic conditions (Bossi *et al.*, 1992). The predominance of DDE could possibly indicate that there is aged long degradation of DDT and no recent input of DDT in the Msunduzi River. The relatively high concentrations of DDT and its metabolites in the samples collected could also possibly be as a result of its persistence from applications in the past, prior to its banning. A comparison of OCP concentrations obtained in this study with other studies shows that the levels of DDE in the Msunduzi River is slightly lower compared to the levels found in Okavango Delta, Botswana having concentrations of 2.4-61.40 ng/mL in water (Mmualefe *et al.*, 2009). In the present study, apart from total DDTs, endrin was also found in high concentrations ranging between 62.52 and 258.12 ng/g in sediment, 40.20-360.25 ng/g in soil and 1.46-17.63 ng/mL in water samples respectively. Endrin has been used previously as an insecticide on field crops such as

cotton and grains. Its production and usage in the environment has been stopped some time ago but its presence is still detectable in the environment because of its high stability, semi-volatility and long-range transport. Levels of endrin in water in this study were higher than the maximum contaminant level (MCL) for endrin in drinking water of 0.2 µg/L as recommended by the EPA (FSTRAC, 1990). The levels of OCPs in water were higher than the USEPA guidelines for water quality to protect aquatic ecosystems at 0.00059 ng/mL, 0.00083 ng/mL, 0.00021 ng/mL, and 0.018 ng/mL for *p,p*-DDT, *p,p*-DDT, heptachlor and lindane respectively (USEPA, 1995). The level of DDT and metabolites recommended guideline is 1 µg/L set by the Food and Agriculture Organization of the United Nations and World Health Organization to protect human health in drinking-water (FAO/WHO, 2001). Total *o,p*-DDD and dieldrin were evaluated in this study as one due to its co-elution. Dieldrin is known to be more stable than aldrin and aldrin is known to convert to dieldrin however, the mechanism could not be totally ascertained in this study because of the difficulty in separating the dieldrin peak from *o,p*-DDD to determine the actual concentration of dieldrin.

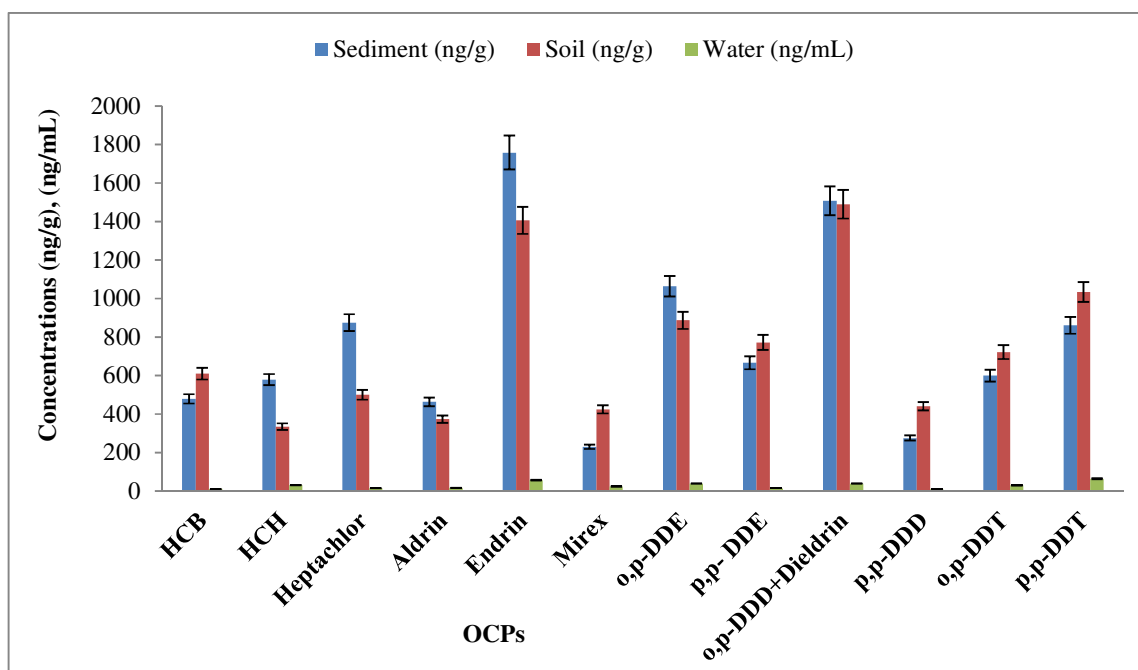


Figure 6.5 Total concentrations of OCPs in sediment (ng/g), soil (ng/g) and water (ng/mL) during the autumn season.

6.3.2 General trend of pollutants distributions in sediment, soil and water

Figures 6.4 and 6.5 shows the distribution pattern of the PCB and OCP pollutants in sediment, soil and water respectively. The concentrations of the pollutants were found to be higher in sediment and soil compared to the corresponding water samples during the autumn season. Their higher concentrations in sediment and soil confirm their more hydrophobic interactions and lipophilicity, thereby preferring to stay within the organic particulate matter of soil and sediment. Thus sediment and soil serve as a 'sink' for organic pollutants (Aydin and Yurdun, 1999; Chee *et al.*, 1996). The results in this study are further confirmed by the high K_{ow} values for these pollutants which mean a lower solubility in water and greater adsorption onto the sediment and soil. The K_d value is used to evaluate how tightly the organic pollutants will bind or stick to soil particles. The greater the K_d value, the less likely a chemical will leach or contribute to the runoff. Majority of these pollutants have high K_d values, such as, PCB 28 and PCB 180 with K_d values of 5.28 and 5.78-6.90 as well as endrin, *o,p*-DDT and *p,p*-DDT with K_d values of 4.53, 5.35 and 5.18 respectively (ATSDR, 2000; HSDB, 2010). This further confirms their preference for organic interactions over water, and hence is one of the reasons for their high concentrations in soil and sediment compared to water.

6.4 Conclusion

The results obtained in this study show that both PCB and OCP residues are still present in the studied area despite their banning a long time ago. Their presence may be attributed to their persistence and long half-lives in the environmental media. The concentrations and distributions of PCBs and OCPs in the environment are influenced by anthropogenic activities as well as climatic changes. The PCB and OCP concentrations in water were generally lower than that in the corresponding sediment and soil samples, because of their hydrophobic interactions. The sampling point where treated wastewater re-enters the Msunduzi River had the highest PCB and OCP concentrations in soil and sediment. The total concentrations for PCB and OCP were 1288.83 ng/g and 1609.37 ng/g in sediment and 1108.46 ng/g and 1370.91 ng/g in soil respectively. PCB 180 and DDT and its metabolites were found to be the contaminants in highest concentration in almost all sediment, soil and water samples. The concentrations of PCBs in water during the autumn season in this study were found to be higher than allowable concentrations of 10 ng/L set by the European Union (EU) and 14 ng/L of United State Environmental Protection (USEPA) standard for surface water. The Msunduzi River was also found to have higher levels of DDT and its metabolites than that set by the Food and Agriculture Organization of the United Nations and World Health Organization. The Msunduzi River is therefore considered to be highly polluted with PCBs and OCPs and it is recommended that proper and stricter measures be put in place to protect the human, animal and aquatic lives consuming this water or using it for recreational purposes.

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CHAPTER 7: PAPER 4

Spatial Distribution of Selected Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs) in Sediment, Soil and Surface Water During Summer Season from Msunduzi River, KwaZulu-Natal, South Africa

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ABSTRACT

The spatial distribution of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) were determined in sediment, soil and water of the Msunduzi River, South Africa during the summer season. Generally the wastewater treatment plant influent and effluent (W 1 and W 2) were found to have the highest individual PCB concentrations in the range of 11.53 to 124.84 ng/g and 9.65 to 217.73 ng/g in sediment and 7.05 to 13.40 ng/mL and 6.34 to 18.20 ng/mL in water samples during this season. OCP concentrations for the same two sites ranged between not detectable (ND) to 612.56 ng/g and ND to 519.86 ng/g in sediment and 0.41 to 24.39 ng/mL and 1.01 to 11.83 ng/mL in water samples. The Du Toit (M 3) site was also found with relatively high concentrations for OCPs in sediment, soil and water samples in the range of 4.83 to 123.69 ng/g, 8.12 to 140.96 ng/g and 0.70 to 4.57 ng/mL respectively. Nagel dam was found to exhibit the lowest individual PCB concentrations among the sites with concentration ranges of 9.43 to 56.53 ng/g, 1.42 to 40.25 ng/g and 0.12 to 5.69 ng/mL in sediment, soil and water respectively. The concentration of PCBs at Camps drift (M 2) was in the range of 5.91 to 98.71 ng/g, 2.06 to 43.72 ng/g and 0.77 to 4.51 ng/mL in sediment, soil and water respectively. Similar trends were also observed for concentrations of OCP in sediment and soil samples where Nagel dam exhibited the lowest concentration of 35.36 to 186.12 ng/g and 34.73 to 82.60 ng/g respectively. Among the PCB congeners; PCB 180, PCB 52 and PCB 28 (hepta-CB, tetra-CBs and tri-CB) were predominant. Concentrations of DDT were generally found to be the highest OCPs along the sampling sites in sediment, soil and water samples. The indicative indices were used to highlight the potential input contribution of DDT contaminations in the environment. The results showed that there is no possible current input of DDT but rather historical degradation of DDT through aerobic oxidative dehydrochlorination to DDE and reductive dechlorination of DDT *via* anaerobic degradation to DDD in most of the sampling sites. Concentrations of the pollutants were

found to be dependent on the anthropogenic contributions at each site along the river. This is the first such research on the spatial distribution of PCBs and OCPs in the Msunduzi River during the summer season. The results presented are the new and provide knowledge on the distribution of PCBs and OCPs from source to mouth as well as the effect of summer rains on the distribution of these organic pollutants.

Keywords: *Spatial distribution, polychlorinated biphenyls, organochlorine pesticides, Msunduzi River.*

7.1 Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) such as hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), heptachlor, aldrin, dieldrin, mirex, 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT) and its metabolites comprises eight of the twelve major groups of chemicals known as persistent organic pollutants (POPs) listed under the Stockholm Convention on POPs. These groups of chemicals are known as dirty dozen with serious environmental impacts which have led to its stoppage in production and usage and final ban in the environment (UNEP, 2001). Possible reported harmful effects of POPs on experimental animals include behavioural and developmental problems, neurotoxic to teratogenic effects, carcinogenic and endocrine disruptive effects among others (USEPA, 2007). Residues of these chemicals are still present in the environment, despite its banning some time ago, due to its lipophilic properties, slow degradation and long range transportation which enables its wider distribution and bioaccumulation (Wolska and Namiesnik, 2002; Buccini, 2003). The behaviour and spatial distribution of organic contaminants in environmental media is mostly controlled by factors such as mineral and organic matter content, as well as physico-chemical properties of the pollutants such as aqueous solubility, polarity, hydrophobicity, lipophilicity (octanol-water partition coefficient K_{ow} , soil adsorption coefficient K_{oc}/K_d) as well as molecular structures of the organic pollutants (Zacharia, 2011). Their distribution in the environmental media are also influenced by climatic factors such as temperature, vapour pressure and precipitation rate as well as the hydrodynamics of the river (Reid *et al.*, 2000; Zhou *et al.*, 2006). All these may be used as an indicator to evaluate the contaminant status as well as pollution sources in the river ecosystem. In addition, pollutants are more likely to come into contact with soil and sediment

particulate matter during the process of sediment transportation and deposition and prefer to associate more with suspended particulate matter due to their non-polar and low water solubility (Vigano *et al.*, 2003). In this investigation the spatial distribution of 8 PCB congeners as well as 7 OCPs together with DDT metabolites were investigated in sediment, soil and water samples of Msunduzi River KwaZulu-Natal South Africa during the summer season. This is the first such research on the spatial distribution of PCBs and OCPs in the Msunduzi River during the summer season. The results presented are the new and provide knowledge on the distribution of PCBs and OCPs from source to mouth as well as the effect of summer rains on the distribution of these organic pollutants.

7.2 Material and Methods

Sampling sites were carefully selected as discussed earlier in Chapter 3, 4, 5 and 6 (papers 1-3). The sampling sites have different anthropogenic interferences with varying degrees of exposure to organic pollutants. The pH of the sampling sites during the summer season ranged between 6.10 to 7.95 while the average water temperature was between 24.30 to 30.90 °C. The sampling coordinates as well as the sampling map has being shown in chapters 3 as well as in papers 1 - 3.

7.2.1 Sampling and analyses

A total of nine sediment samples approximately 0-10 cm from the surface of the river bed and seven soil samples from a depth of 0-15 cm on the banks of the river close to the water were collected using a grab sampler and stainless steel soil auger. The nine surface water samples were collected using a grab sampling technique (1-2 cm) from the water surface during the summer sampling season in February, 2014. The integrity of the samples was maintained during and after collection as suggested by Moody and co-workers and Derek and Seveko (Moody and Lindstorm, 1977; Derek and Sverko, 2006). Samples were stored prior to extraction using conditions described by Hilscherova and co-workers (Hilscherova *et al.*, 2003). Details of sediment and soil pre-extraction processes have been previously reported in Chapters 3 and papers 1-3. Soil and sediment samples were extracted using an ultrasonic bath with dichloromethane as solvent, while water samples were subjected to liquid-liquid extraction using dichloromethane (Fatoki and Awofolu, 2003; Zhou *et al.*, 2006). The final extracted samples were cleaned-up using multi-layered silica gel as described previously in

chapters 3 and 4. The cleaned extracts were air-dried and stored in the fridge prior to gas chromatography/mass spectrometry (GC-MS) analyses. Sample extracts were reconstituted with 2 mL *n*-hexane, spiked with equal volumes of PCB and OCP standard mixtures and subjected to GC-MS analyses. The GC-MS (GC-6890-MS-5973 series Germany) with a ZB-5MS fused-silica capillary column of length 30 m (0.25 µm internal diameter and 0.25 µm film thickness), helium carrier gas (constant flow rate of 1.0 mL/min) a total flow of 43.8 mL/sec and a linear velocity of 28 cm/s using splitless injection mode was used. The injection and detector temperatures were set at 250 °C and 325 °C respectively. Oven temperature was set at 125 °C and held for 1 min, raised to 295 °C at 15 °C /min and held for a further 2 min. A 1 µL injection volume was used. All the quality control steps were observed as described in chapter 3 and papers 1-3. Percentage recoveries ranged between 68.64-109.26% and 88.42-115.91% in water and sediment for PCB while OCPs had recoveries in the range of 85.3-109.22% and 64.21-100.72% in sediment and water respectively. Limits of detection (LOD) for PCBs in water and sediment were found in the range of 0.0001- 0.0005 µg/mL and 0.001-0.008 µg/g and limits of quantification (LOQ) were in the range of 0.0003-0.002 µg/mL and 0.004-0.022 µg/g in both water and sediment respectively. Also, LOQ and LOQ for OCP ranged between 0.0015-0.0120 µg/g, 0.0001-0.0008 µg/mL and 0.0051-0.0398 µg/g and 0.0004-0.0025 µg/mL in sediment and water respectively. Quantitative data for PCBs and OCPs were obtained by an external calibration method. An eight point calibration curve between the range of 0.250 to 10.00 µg/mL for each PCB and OCP standards were prepared. All the reagents and chemicals used were of HPLC-grade, as well as PCB and OCP standards were purchased from Sigma-Aldrich® (South Africa). All detail about the chemicals and reagents used in this study has being reported earlier in papers 1-3 in chapter 4. All the glass ware were baked in the oven at about 130 °C, overnight prior to use and the cotton wool was soaked in acetone and activated in the oven over night at 130 °C prior to use.

7.3 Results and Discussion

7.3.1 Spatial distribution of PCB concentrations in sediment, soil and water during the summer season:

The spatial distribution of PCB concentrations in sediment, soil and water samples during the summer season in the Msunduzi River KwaZulu-Natal, South Africa are presented in Figures 7.1, 7.2 and 7.3 respectively. Among the sampling sites studied, the wastewater treatment

plant influent and effluent (W 1 and W 2) were found to have the highest PCB concentrations in the range of 11.53-124.84 ng/g and 9.65-217.73 ng/g in sediment, and 7.05-13.40 ng/mL and 6.34-18.20 ng/mL in water samples during the summer season. The high concentrations at these 2 sites could be attributed to the possibility of the waste treatment plant receiving its waste from various anthropogenic sources such as industrial and domestic and could also probably be due to the higher runoff based on the high hydrodynamic volume as well as high depositional rates of pollutants into the water ecosystem during the summer season as reported by Zhou and co-workers on organochlorine pollutants in the surface water and sediment from the Qiantang River, East China (Zhou *et al.*, 2006). Du Toit (M 3), Henley dam outlet (M 1), the joining point of the Msunduzi and uMgeni Rivers (M 7) as well as Msunduzi town (M 5) were also found to have concentration ranges between 4.83-123.69 ng/g, 8.12-140.96 ng/g and 0.70-4.57 ng/mL for site M 3; 5.75-96.06 ng/g, 14.05-94.20 ng/g and 0.01-4.30 ng/mL for site M 1 and 15.57-51.41 ng/g, 14.87-67.72 ng/g and 0.41-4.77 ng/mL for site M 7 and for M 5 a concentration range of 14.24-76.02 ng/g, 10.62-98.71 ng/g and 0.53-6.21 ng/mL in sediment, soil and water samples respectively. The possible sources of PCB contamination at M 7 could be attributed to the higher accumulation of pollutant loads received from both the uMgeni River as well as the Msunduzi River. The high concentrations obtained at the other sites which are mostly rural and semi-rural sites could be due to the burning and incineration of PCB treated wood used for cooking and heating of homes as earlier reported in chapters 4.1.3 and 4.3.3. Other sites such as the agricultural area (M 4), Camps drift (M 3) and Nagle dam (M 6) had slightly lower PCB concentrations relative to other sampling sites. Site M 3 is located in an area known for the annual Dusi-festival where there is no known historical use of PCBs or source of PCBs except through inputs of PCB due to atmospheric deposition and urban runoff or trans boundary origins. A similar phenomenon was observed by Zhou and co-workers who studied the seasonal distribution of dissolved pesticides in the Humber Estuary and Humber Coastal Zone in China (Zhou *et al.*, 1996). There is also a possibility of pollutant mobility between the sampling sites along the river, particularly during the summer sampling season when there is a significantly higher volume of river water that is able to transport pollutants along the river.

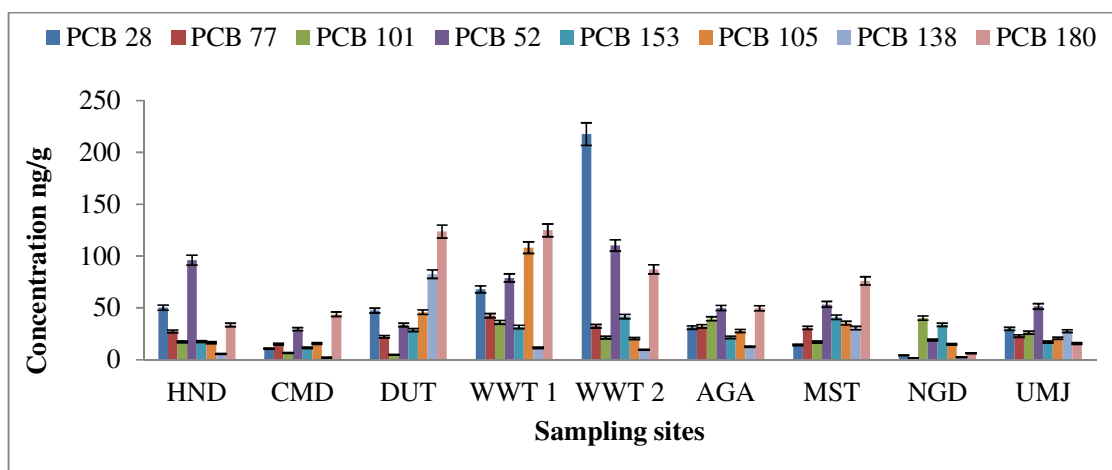


Figure 7.1 Distribution of PCB concentrations in sediment samples during the summer season along the Msunduzi River, South Africa.

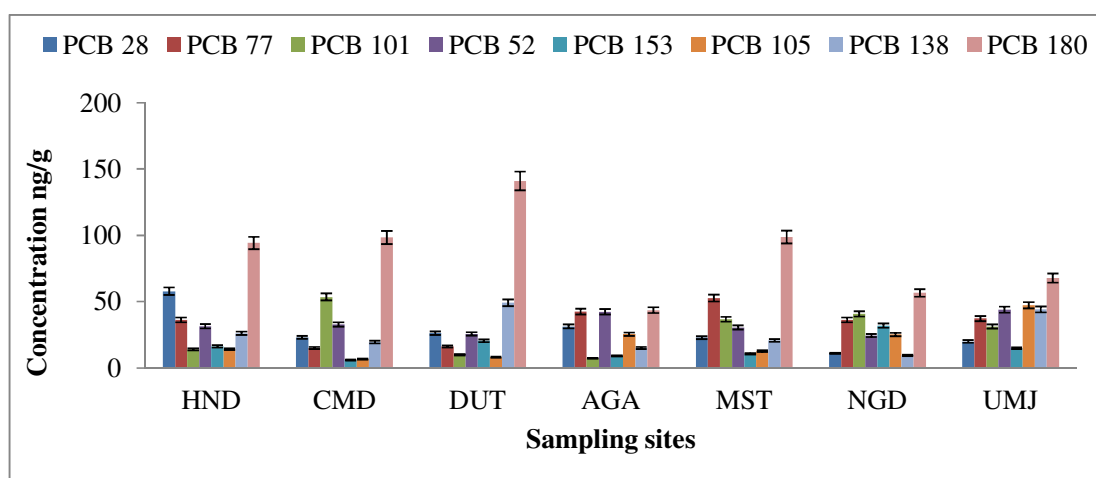


Figure 7.2 Distribution of PCB concentrations in soil samples during the summer season along the Msunduzi River, South Africa.

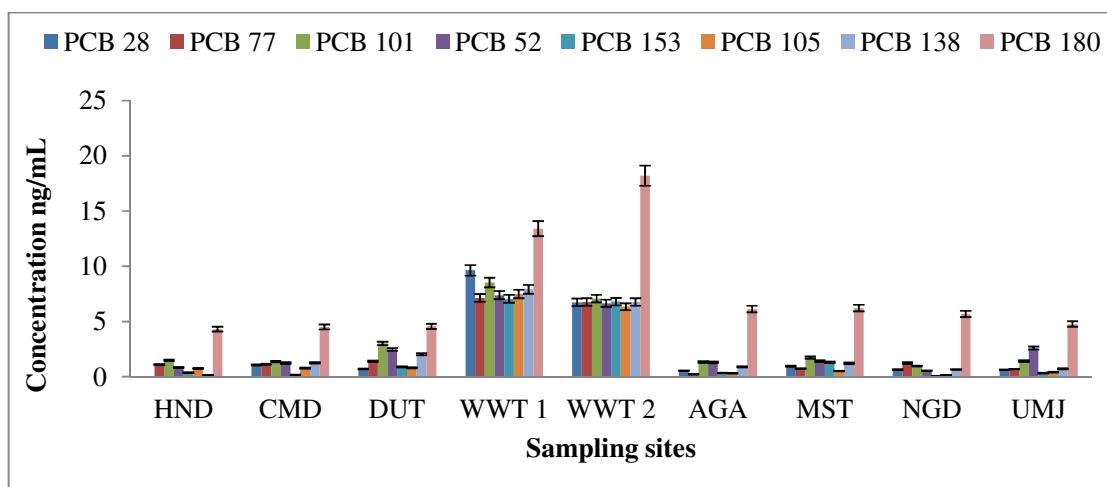


Figure 7.3 Distribution of PCB concentrations in water samples during the summer season along the Msunduzi River, South Africa.

There is a general increase in concentrations of hepta-CB, and tetra-CBs as well as tri-CBs (PCB 180, PCB 52 and PCB 28) in sediment, soil and water during this season compared to other PCB congeners. This could probably be due to the higher chlorinated PCB such as hexa- and penta-chlorobiphenyls undergoing anaerobic reductive de-chlorination to lower chlorinated tri- and tetra-biphenyls (Fiedler *et al.*, 1994). A similar trend was also observed during the autumn season as discussed in chapter 6.3. The distribution pattern of PCB congeners between the different matrices analysed in this study is consistent with the results reported by Zhang *et al* and Yang *et al* on fate and assessment of persistent organic pollutants in water and sediment from the Minjian River Estuary in Southeast China and occurrence and possible sources of polychlorinated biphenyls in surface sediments from Wuhan city (Zhang, *et al.*, 2003; Yang *et al.*, 2009). PCB concentrations were found to be higher than the USEPA guideline (14 ng/L) set for surface water to be considered not hazardous to aquatic or human health and the European Union maximum acceptable level of 100 ng/L except for PCB 28 at Henley dam outlet (10 ng/L at M 1) which is below these guidelines.

The Toxic Equivalent (WHO₂₀₀₅-TEQ) of dioxin-like PCBs (PCB 77 and PCB 105) was evaluated in sediment and soil sample using the Toxic Equivalent Factor (WHO₂₀₀₅-TEF). The sum of the TEQ values were in the range of 0.59-7.50 ng/kg WHO₂₀₀₅-TEQ and 1.68–5.63 ng/kg WHO₂₀₀₅-TEQ in sediment and soil samples respectively which are relatively high considering that these values are for only two dioxins compared to the guideline of 5-10

ng/kg WHO₂₀₀₅-TEQ for Canada and Germany and 10 ng/kg WHO₂₀₀₅-TEQ for USA which is for a total of 11 dioxin-like compounds (ASTDR, 1998, BMU, 1999, CCME, 2002). See Appendix C for the calculations.

7.3.2 Spatial distributions of OCP concentrations in sediment, soil and water during the summer season.

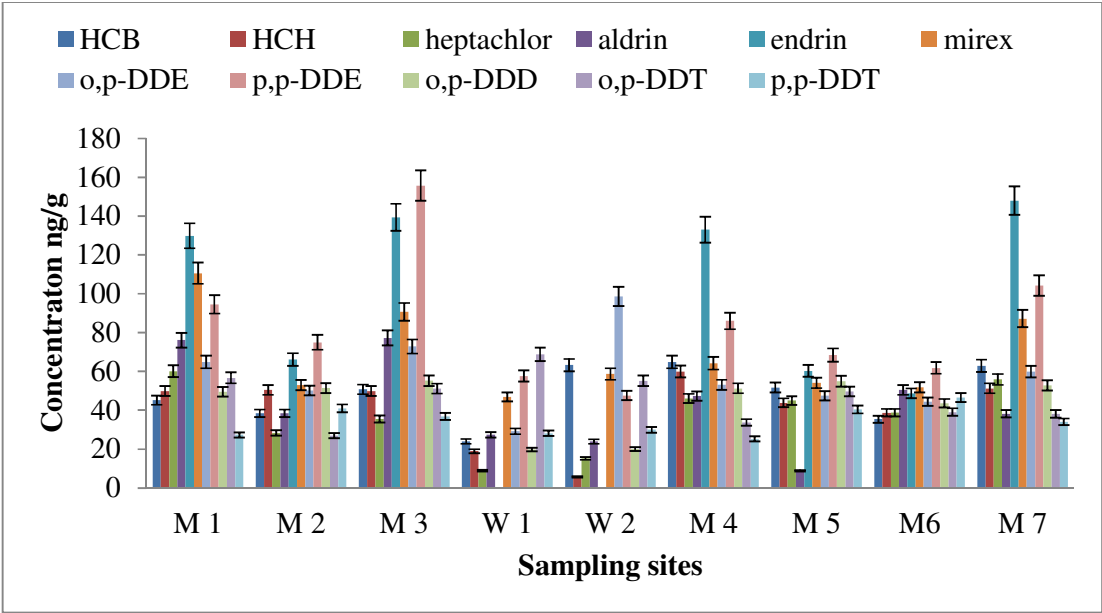


Figure 7.4 Distribution of OCP concentrations in sediment samples during the summer season along the Msunduzi River, South Africa.

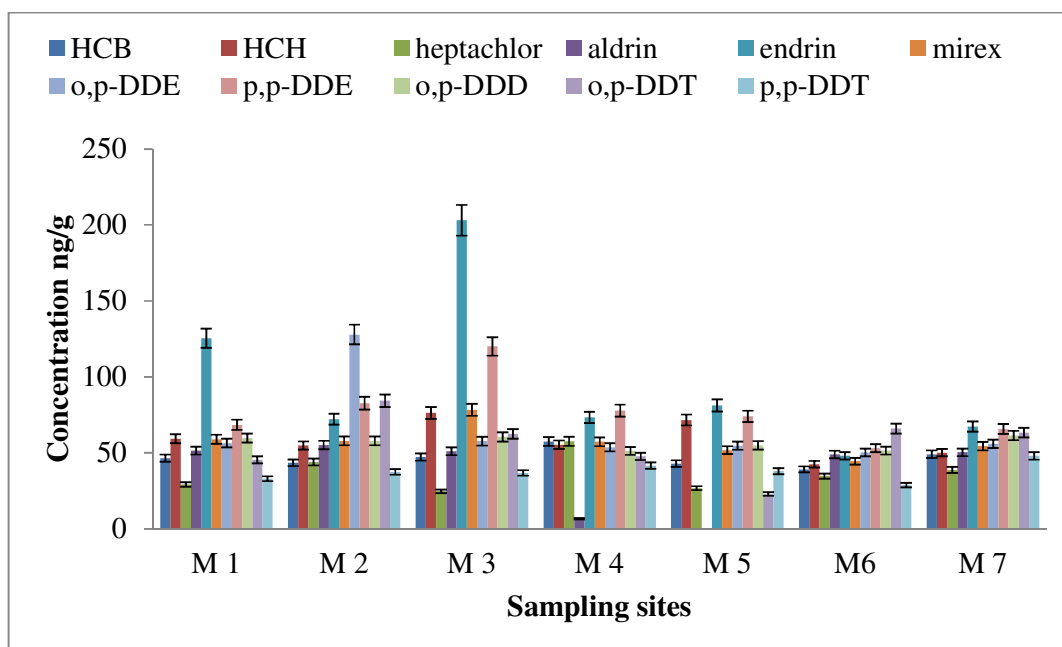


Figure 7.5 Distribution of OCP concentrations soil samples during the summer season along the Msunduzi River, South Africa.

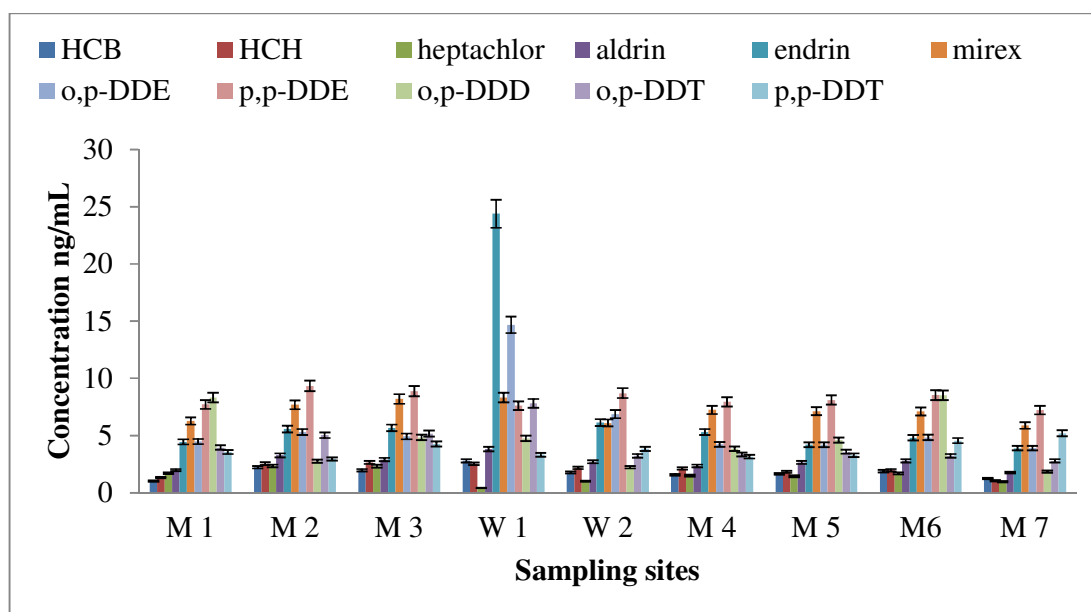


Figure 7.6 Distribution of OCP concentrations in water samples during the summer season along the Msunduzi River, South Africa.

Concentrations of OCP in sediment, soil and water are presented in Figures 7.4, 7.5 and 7.6 respectively. OCP concentrations were found from ND-155.69 ng/g, ND-298.59 ng/g and 0.41-26.55 ng/mL in sediment, soil and water along the river sampling sites during the summer season. Pesticide distribution across the sites was influenced by anthropogenic activities of each studied sampling site during the season. The wastewater treatment plant (W 1), Du Toit (M 3), Henley dam (M 1) and the agricultural area (M 4) were found to be more prevalent with the studied pesticides. Pesticide concentrations at W 1 could possibly be as a result of high pollution load it receives from both industrial and domestic waste during the summer season. The source of pollution at M 1 and M 4 could be emanating from illegal applications of these pesticides by the local farmers during the planting season. M 1 and M 4 are in a semi-rural and agricultural area which may be receiving runoff from the nearby farming areas during the summer season that is known to have high rainfall. Although these chemicals are no longer sold to the general public, their presence can be attributed to their extensive usage prior to their banning (Van Dyk *et al.*, 1982). The results of this study showed higher DDT and its metabolite concentrations generally across all the sites followed by endrin. The presence of these chemicals in the environment could also be due to their persistent nature. In order to determine the input point of these chemicals especially DDT and its metabolites, the environment indicative indices were used to evaluate the pollution sources of the relative concentrations of the parent DDT compound and its metabolites either through current or historical input. DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions in the environment (Aislabie *et al.*, 1997). This largely depends on certain environmental conditions such as temperature as well as the nature of the soil and therefore predominance of DDE over DDD in the environment suggests an oxidizing environment (Aislabie *et al.*, 1997). The ratio of $DDE/\sum DDT$ and $DDD/\sum DDT > 1$ (unity) was used to assess if current DDT contamination occurred in the environment along the studied sites as shown in Table 7.1. Along the sampling sites all the values obtained were greater than unity which suggests degradation of DDT to DDE as well as no current input of DDT in any of our studied sites. DDT contamination is therefore most probably due to the historical application in the areas (Guenzi and Beard, 1976; Hitch and Day, 1992). Also, the ratios of DDD/DDE were found to be between 0.25 to 0.95 which were below unity suggesting the dominance of DDE over DDD indicating long-term weathering and aerobic degradation of DDTs into DDE. Figure 7.7 further confirms the relationship between DDE, DDD and DDT showing degradation of DDT to its metabolites. Apart from total DDTs, endrin and mirex were also found in relatively high concentrations compared to other

pesticides along the sampling sites which are consistent with the trend observed in the previous results of winter, spring and autumn results as reported in chapters 5.3 and 6.3. The level of endrin detected in this study could be as a result of its previous application as insecticides to control field crops (Smith, 1991). Heptachlor was found with the lowest concentration among the OCPs. The levels of OCPs detected could be attributed to their persistence in the environment since they are no longer used in South Africa but they are ubiquitously distributed in the environment due to trans boundary effects and long range of transportation.

Table 7.1 Ratio of DDD/DDT and DDE/DDT to evaluate DDT contamination along the sampling sites during summer

Sampling code	DDD/DDTs	DDE/DDTs
M 1	1.18	1.90
M 2	1.46	2.34
M 3	1.13	1.81
W 1	1.02	1.64
W 2	1.16	1.87
M 4	1.68	2.70
M 5	1.10	1.77
M6	1.16	1.86
M 7	1.37	2.21

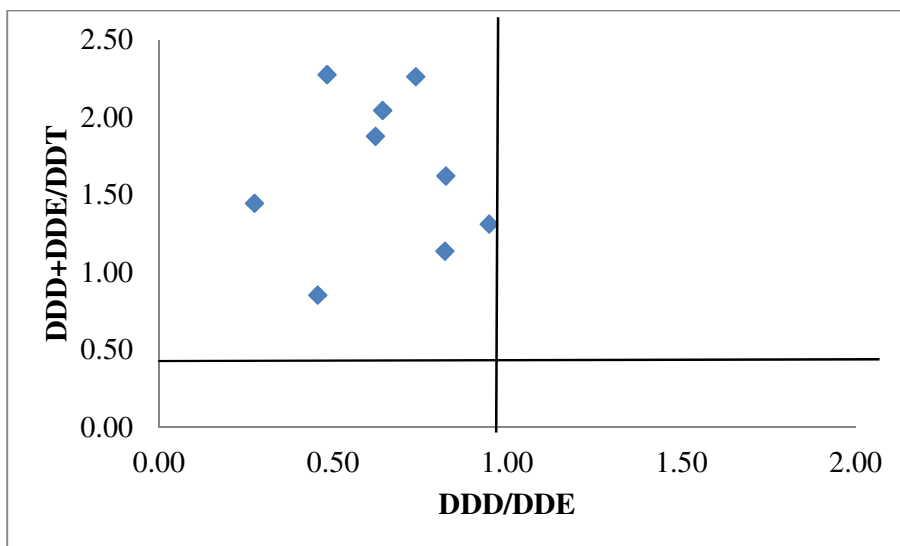


Figure 7.7 Relationship between (DDE+DDD)/DDT and DDD/DDE in surface sediments collected from Msunduzi River, South Africa during the summer season.

7.4 Conclusion

The spatial distribution of PCBs and OCPs in sediment, soil and water samples of the Msunduzi River revealed that runoff could be one of the main contributors of organic pollutants in the river during the summer season particularly because of the high rainfalls experienced during this season. Input point sources of pollutants was the common pattern of contamination generally observed which were primarily dependent on anthropogenic activities such as industrial, domestic and local economic activities as well as historical usage along the river. The concentrations of PCB and OCP during the summer sampling season were found to be generally lower compared to previous sampling seasons of winter, spring and autumn as reported in chapters 4, 5 and 6 respectively. This could be due to higher dilution as a result of the increase in the volume of water from the higher rainfalls as well as higher temperatures that could probably aid in volatilization of pollutants during the summer sampling season. The wastewater treatment plant influent and effluent samples contained the highest concentrations of PCBs and OCPs. PCB concentrations were in the range of 11.53 to 124.84 ng/g and 9.65 to 217.73 ng/g in sediment and 7.05 to 13.40 ng/mL and 6.34 to 18.20 ng/mL in surface water. OCP concentrations were in the range of ND to 612.56 ng/g and ND to 519.86 ng/g in sediment and 0.41 to 24.39 ng/mL and 1.01 to 11.83 ng/mL in water samples. The lowest concentrations of PCBs and OCPs were found at Nagel Dam (PCB

concentration: 9.43 to 56.53 ng/g in sediment, 1.42 to 40.25 ng/g in soil and 0.12 to 5.69 ng/mL in surface water; OCP concentration: 35.36 to 186.12 ng/g in sediment and 34.73 to 82.60 ng/g in soil). Generally, concentrations of PCBs in water samples were found to be greater than the USEPA maximum guideline of 0.014 ng/mL and OCP concentrations in water samples along the river were all found to be higher than the maximum acceptable concentration limit set by the European Union (EU) 0.01 ng/mL. Therefore, further investigation of the pollutant source is required as well as immediate action needs to be taken on the state of water in this river to protect the lives of primary users consuming this water.

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CHAPTER 8

GENERAL CONCLUSION AND RECOMMENDATION

The presence, quantification and distribution as well as seasonal and spatial variation and distribution patterns of eight PCB congeners and seven OCPs together with six DDT metabolite concentrations were quantitatively investigated in sediment, soil and surface water during autumn, winter, spring and summer seasons from the Msunduzi River in KwaZulu-Natal, South Africa. The results revealed the presence of the selected pollutants in varying concentrations where sediment and soil exhibited the highest concentrations among the selected priority POPs while water samples were found to contain the lowest concentrations of all the analytes investigated. This could be attributed to the fact that soil and sediment serve as a 'sink' for the pollutants due to the lipophilic and hydrophobic nature of the organic pollutants. Generally, the results for the winter sampling season was found to be higher followed by spring and autumn seasons while the summer season showed the lowest concentration of all the selected PCBs and OCPs investigated. This could be due to the higher dilution during the summer season as a result of the increase in rainfall leading to higher volumes of water in the river as well as higher temperatures that could probably aid volatilization of pollutants. Distribution of the pollutants was also found to be dependent on the anthropogenic, local economic activities as well as historical applications of the pollutants in the areas investigated. The wastewater treatment plant was found to be a possible input point source of PCBs and OCPs back into the Msunduzi River. Point of discharge back into the Msunduzi River (W 3) was found to be the most polluted sampling site with PCBs and OCPs during the autumn season. Apart from the wastewater treatment plant (W 1 and 2), Du Toit (M 3) and the joining point (M 7) were also found to be more polluted with Camps drift and Nagle dam (M 2 and M 6) being the least polluted with PCBs and OCPs in general. PCB 180, PCB 105, PCB 52 and PCB 28 which is hepta-, hexa-, tetra- and tri-chlorobiphenyls were found in the highest concentrations with PCB 138 having the lowest concentration among the congeners in this study. PCB concentrations were found to be dependent on the degree of chlorination and how susceptible they are to microbial degradation and volatilization. The PCBs and OCPs have being banned a long time ago but their residues were still detectable in the environment in this study even though there is no proof of possible current inputs of the pollutants in the environment. Therefore their presence could be

attributed to historical applications in the environment. Among the OCPs investigated, DDT and its metabolites were the most predominant compared to others and the presence of DDT metabolites could be attributed to the aged long degradation of the parent DDT to its metabolites by aerobic oxidative dehydrochlorination into DDE and anaerobic reductive dechlorination of DDT to DDD. Many of the PCB congeners and OCP concentration levels determined in this study were found to be higher compared to studies done in other parts of the World. The concentrations of the OCs detected in water samples were also higher than the lowest limit of 0.014 ng/mL set by the United State Environmental Protection Agency (USEPA) guideline for surface water which is considered to pose no hazard to the aquatic and human health. The results in this study are also higher than the maximum allowable concentration for underground waters of 0.01 ng/mL set by the European Union (EU). However, most of the pollutants were found to be higher than targeted South African Water Quality Guidelines to protect aquatic ecosystems such as DDTs 1.5 ng/L, aldrin 10 ng/L, dieldrin 5 ng/L, endrin 2 ng/L and heptachlor 5 ng/L (DWAF, 1996).

RECOMMENDATIONS

These pollutants were found to still be present despite their banning a long time ago in the selected studied area at high concentrations in sediment, soil and water of Msunduzi River KwaZulu-Natal, South Africa. However, most of the pollutants were found to be higher than targeted South African Water Quality Guidelines to protect aquatic ecosystems such as DDTs 1.5 ng/L, aldrin 10 ng/L, dieldrin 5 ng/L, endrin 2 ng/L and heptachlor 5 ng/L. The following are recommended for further investigation:

- ✓ More detailed studies are needed to determine the the point and non-point sources of these pollutants most especially organochlorine pesticides.
- ✓ More detailed soil characteristics such as soil particle size and total organic carbon content of soil and sediment is recommended to further understand the interactions between the soil and the pollutants.
- ✓ Only two dioxin-like PCBs were investigated in this study, further study is needed on the remaining dioxins in order to properly evaluate the toxic equivalence (TEQ) and understand the pollution status of these classes of pollutants in the environment.

- ✓ Generally, further investigations on ecotoxicological effects of these organic pollutants in river sediment and soil are highly recommended to assess the risk of these pollutants on the aquatic organisms and human health.
- ✓ Continued monitoring is required in order to safe guard the lives of the primary consumers of this water.

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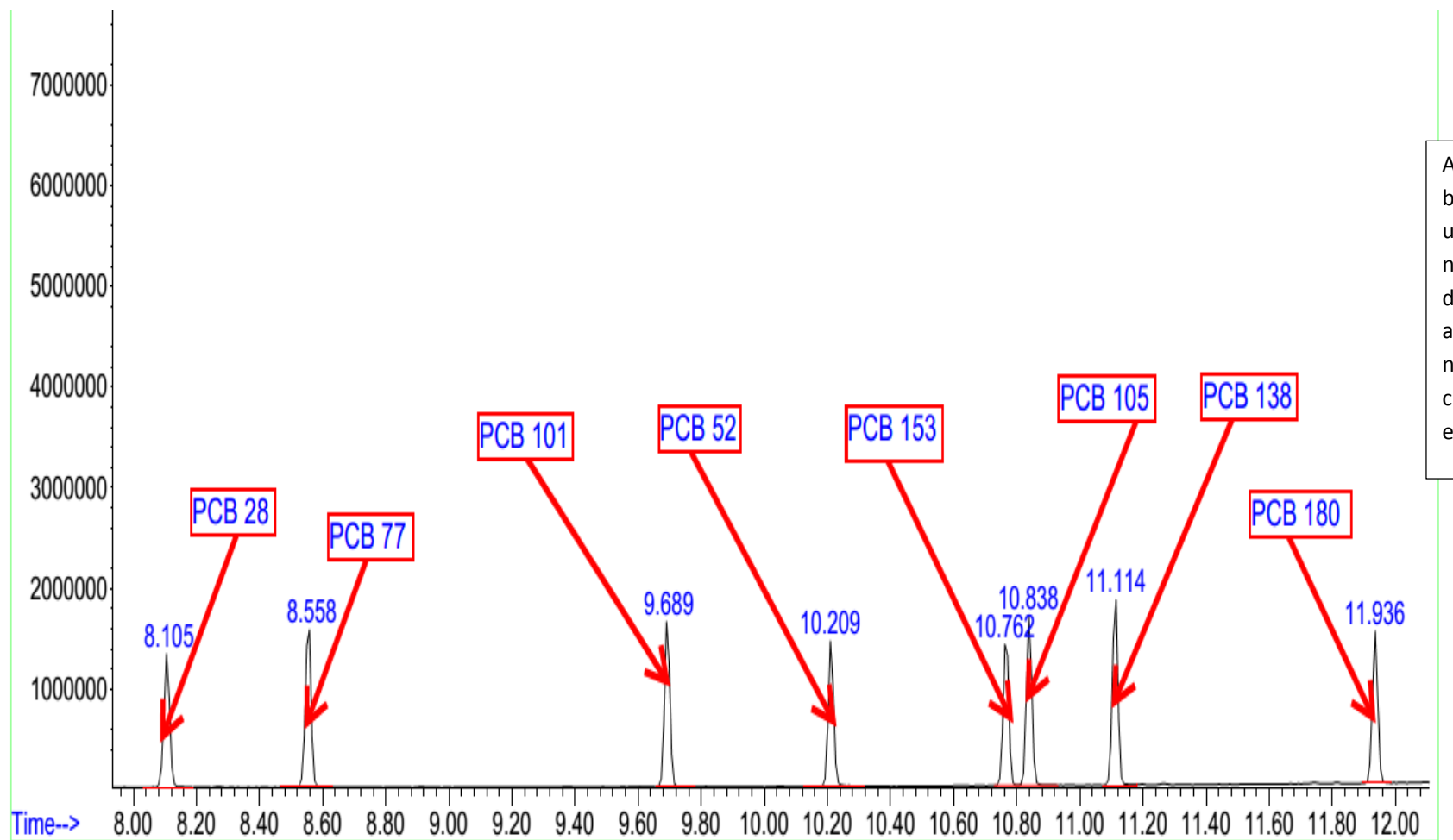
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APPENDICES

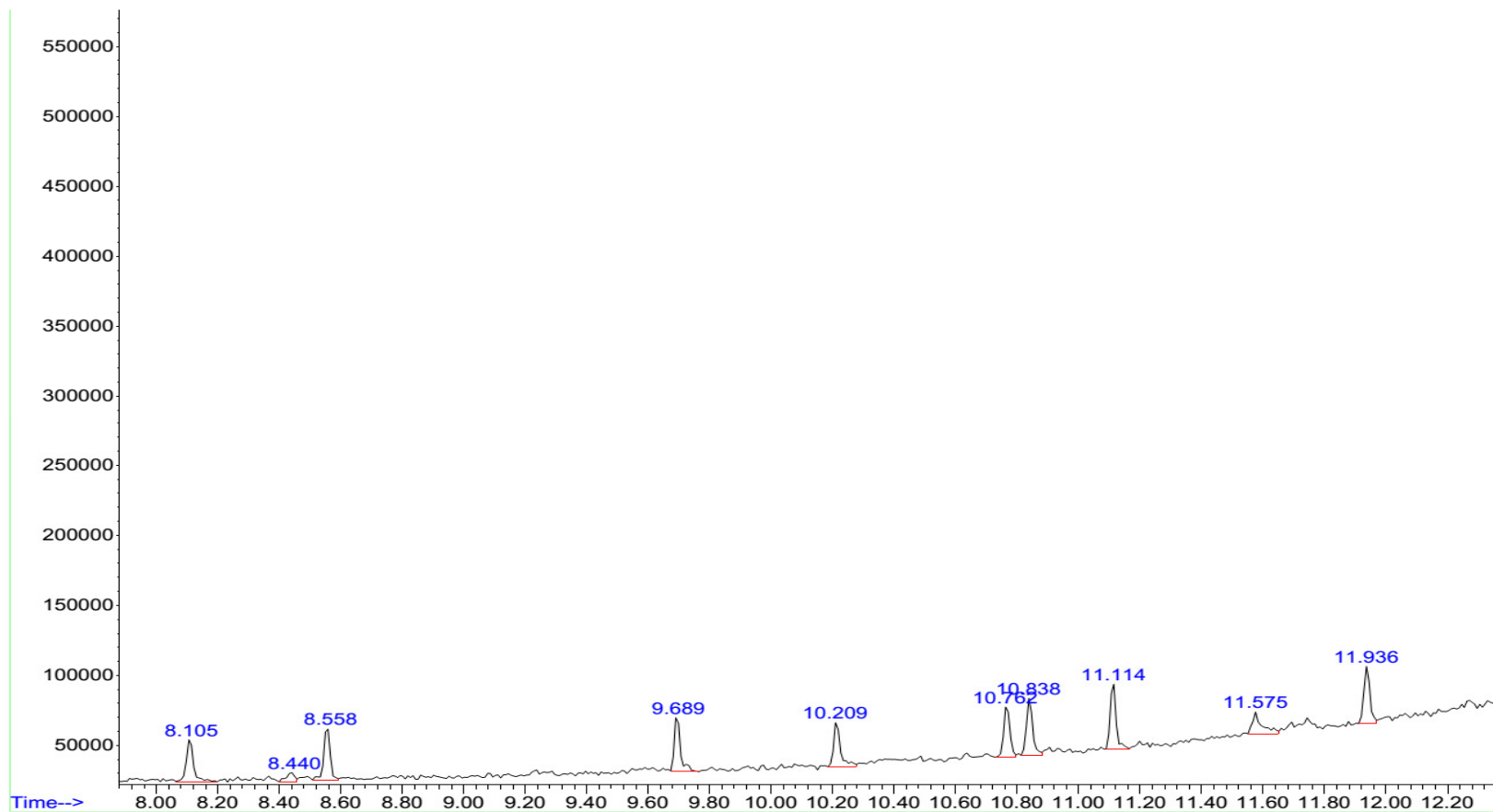
Appendix A:

Representative chromatograms for PCBs and OCPs standards in sediment, soil and water samples.

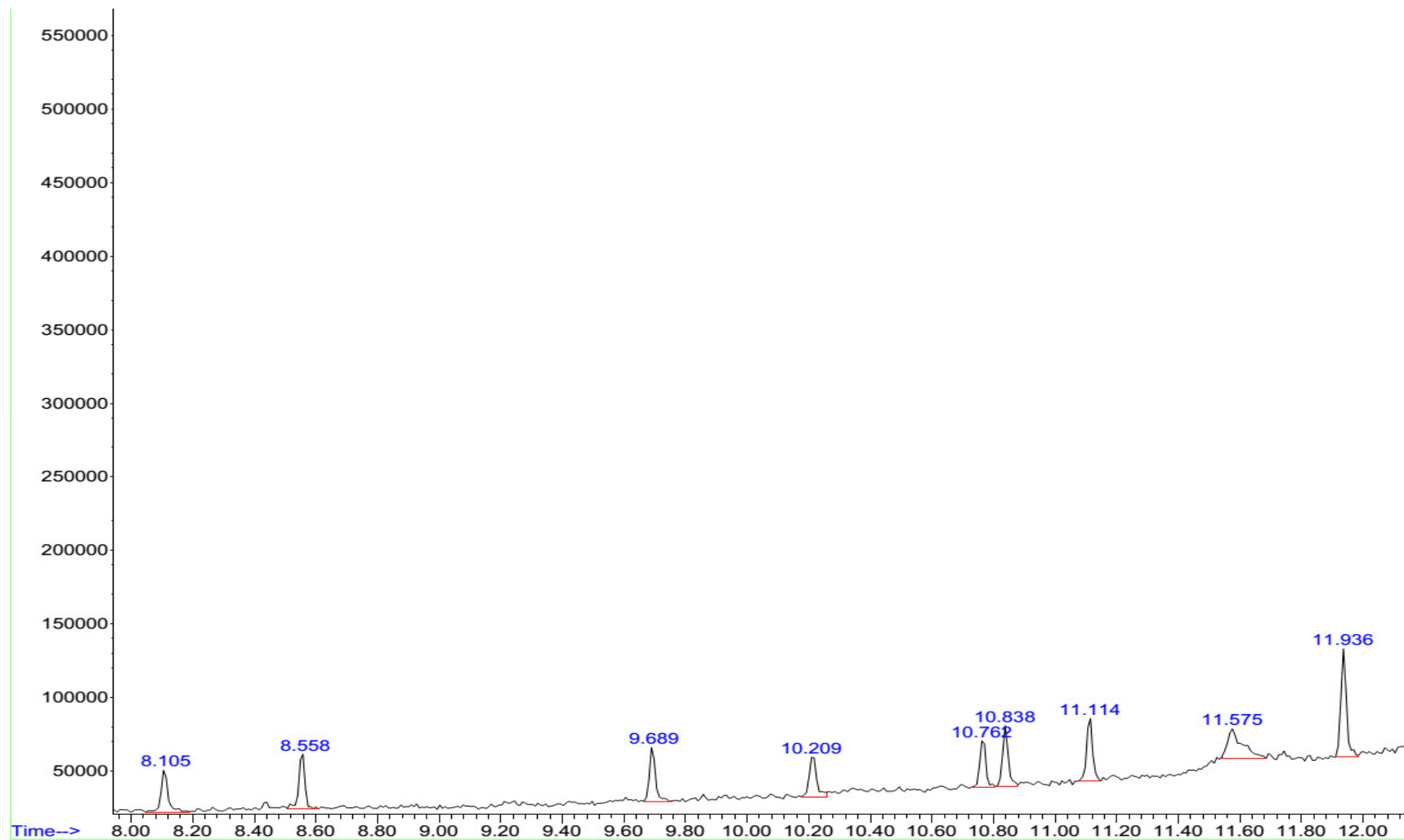
Appendix A 1 – GC-MS chromatogram of 8 PCB congeners



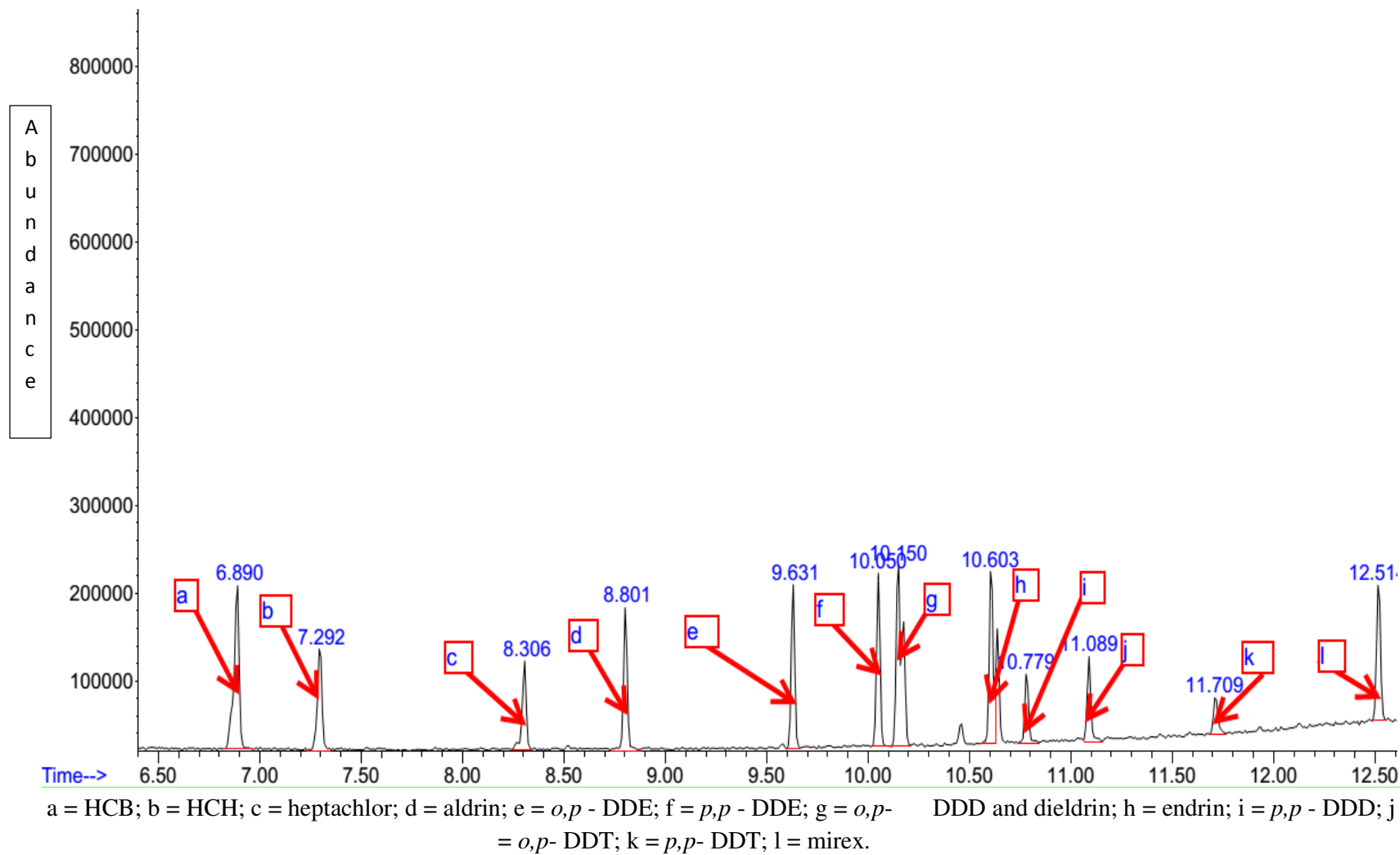
Appendix A 1.0 – GC-MS chromatogram of 8 PCB congener's standards.



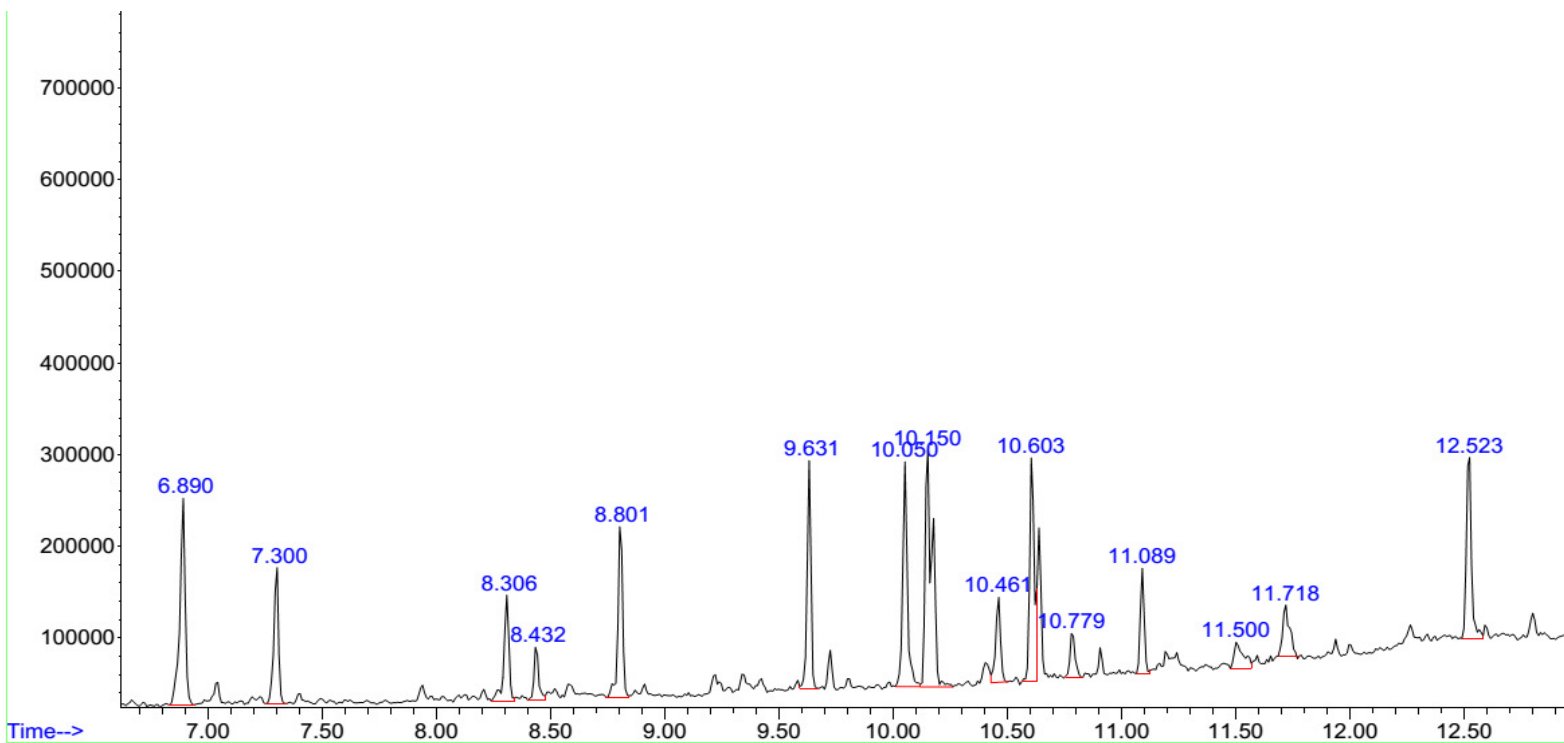
Appendix A 1.1 – GC-MS chromatogram of 8 PCB congeners in cleaned sediment sample.



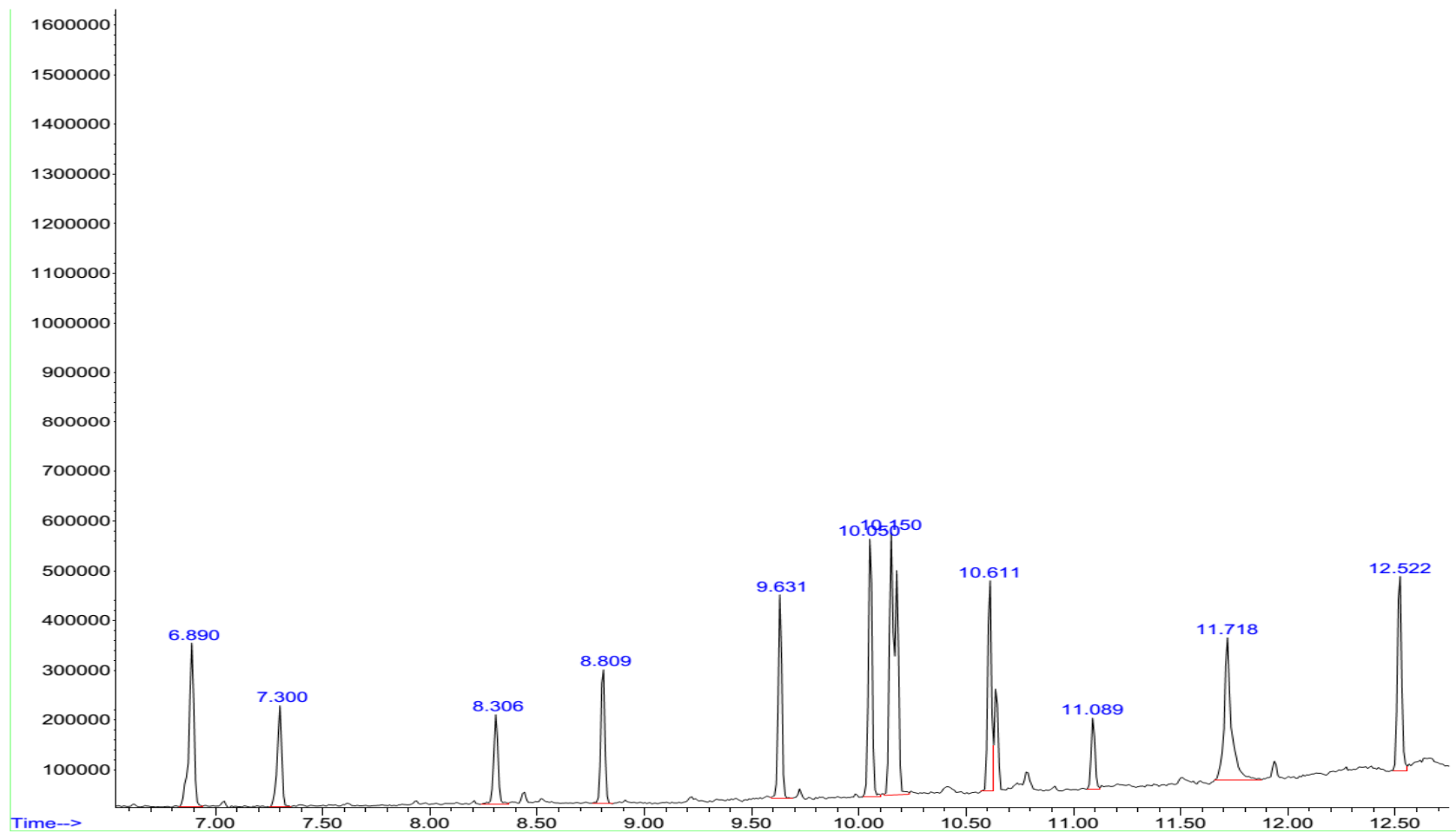
Appendix A 1.2 – GC-MS chromatogram of 8 PCB congeners in cleaned water sample.



Appendix A 2.0 – GC-MS chromatogram of OCP standards.



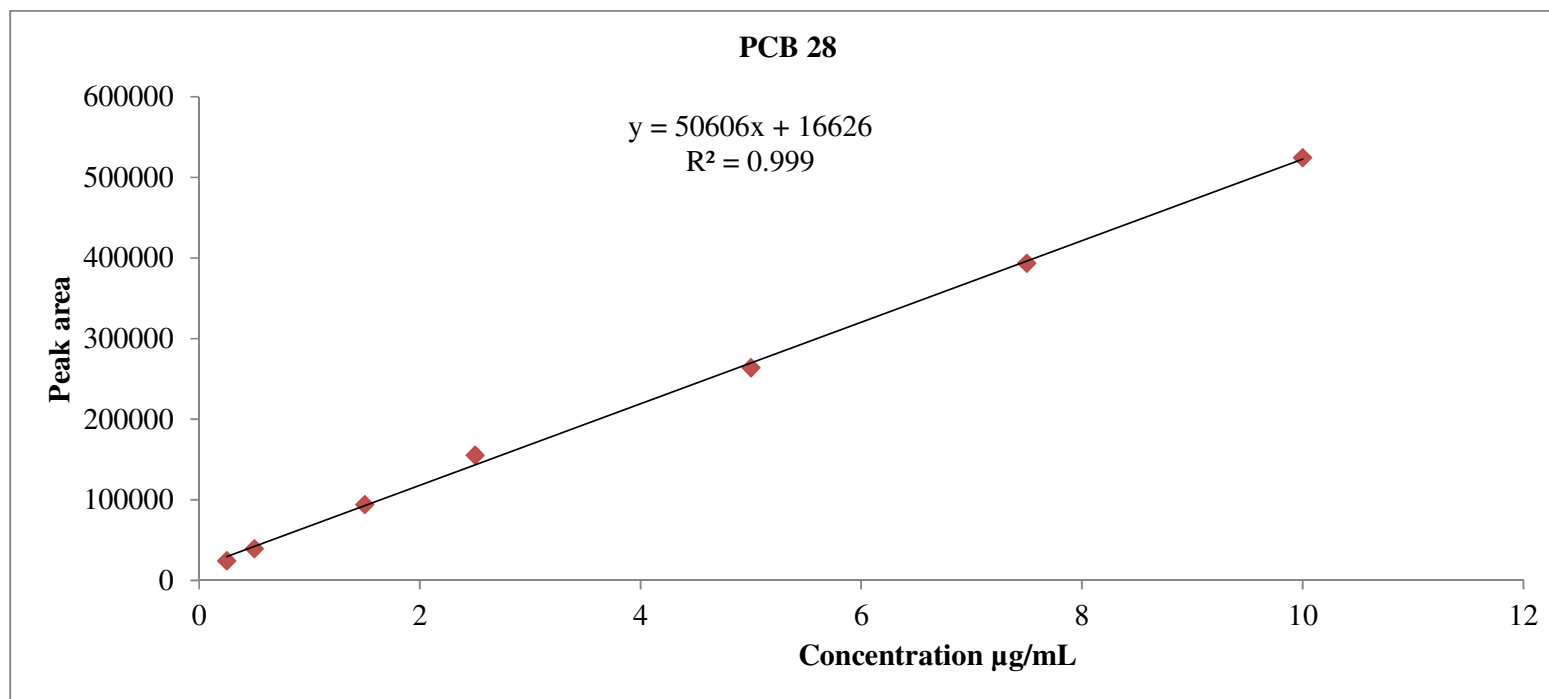
Appendix A 2.1 – GC-MS chromatogram of OCPs in sediment sample.



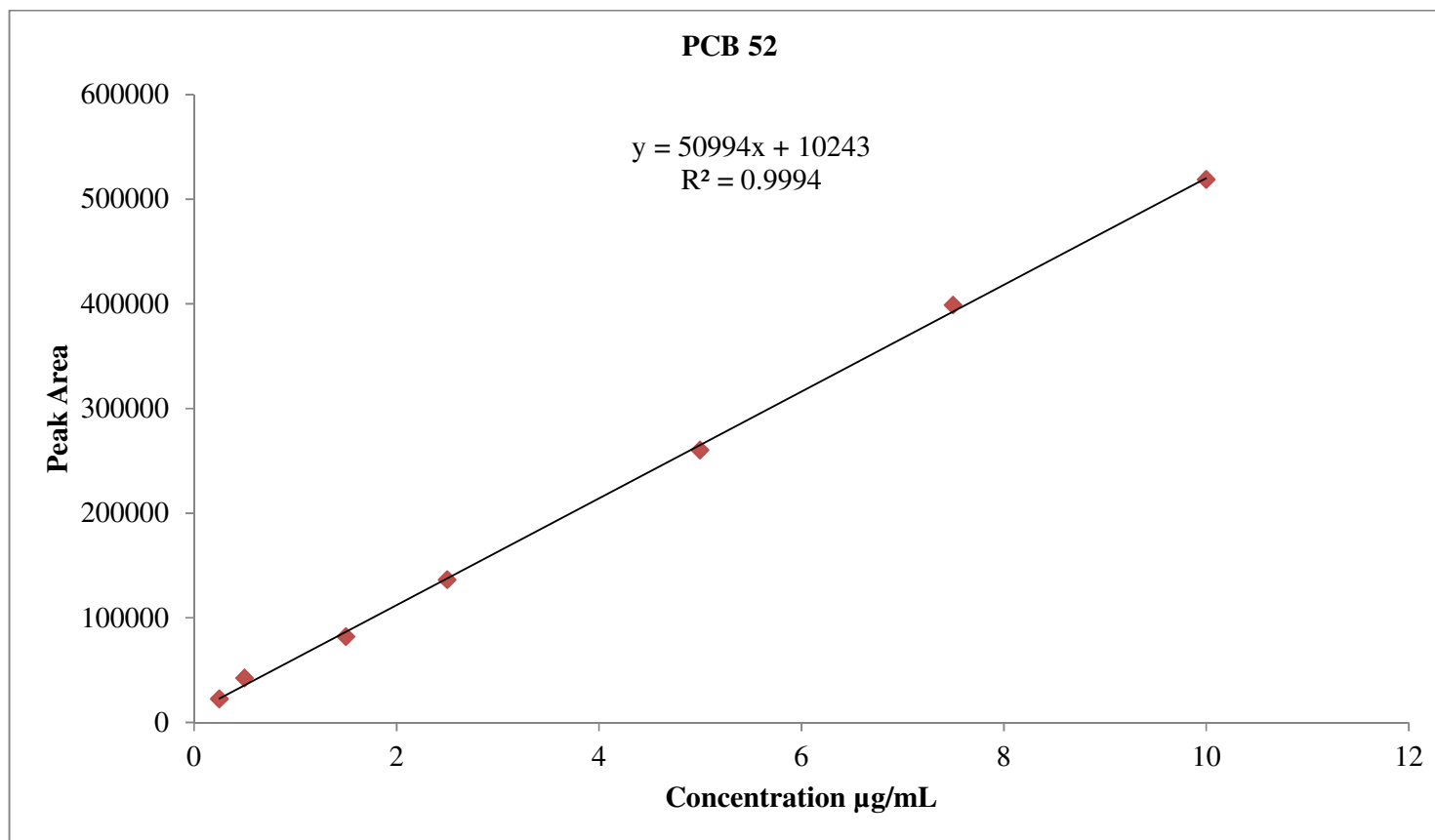
Appendix A 2.2 – GC-MS chromatogram of OCPs in cleaned water sample.

Appendix B:

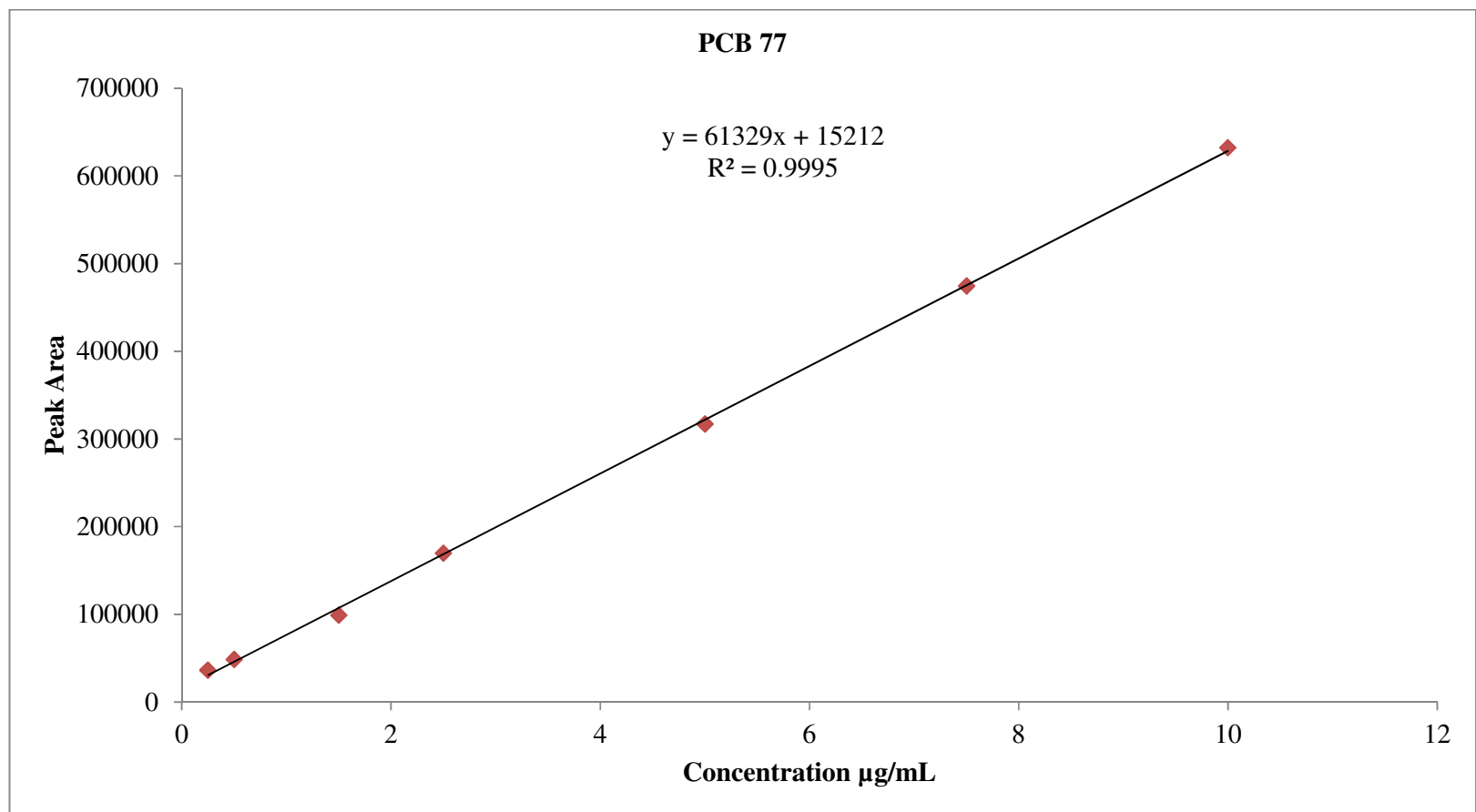
Representative calibration curves for PCBs and OCPs standards.



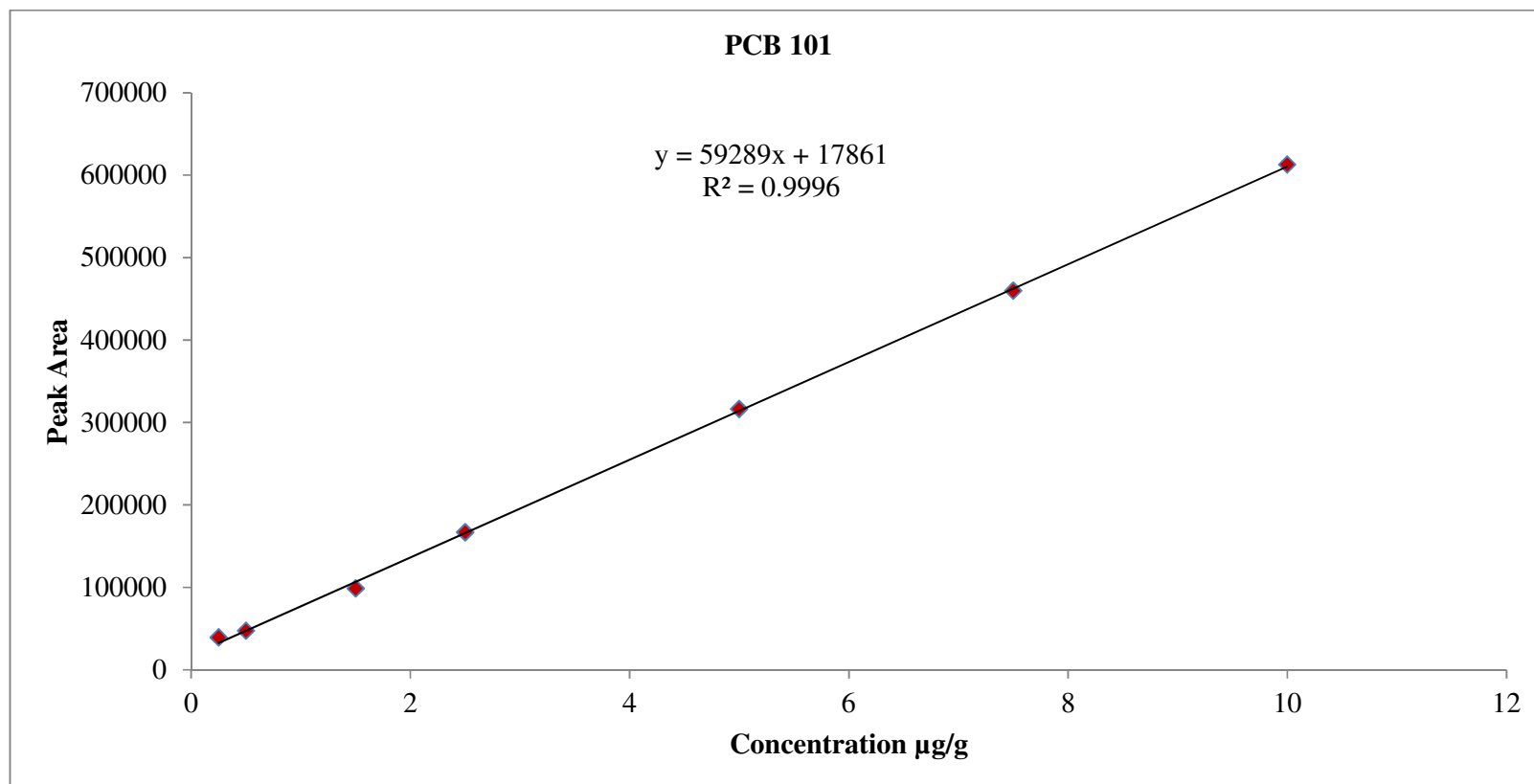
Appendix B 1.1 – Representative calibration curve for PCB 28.



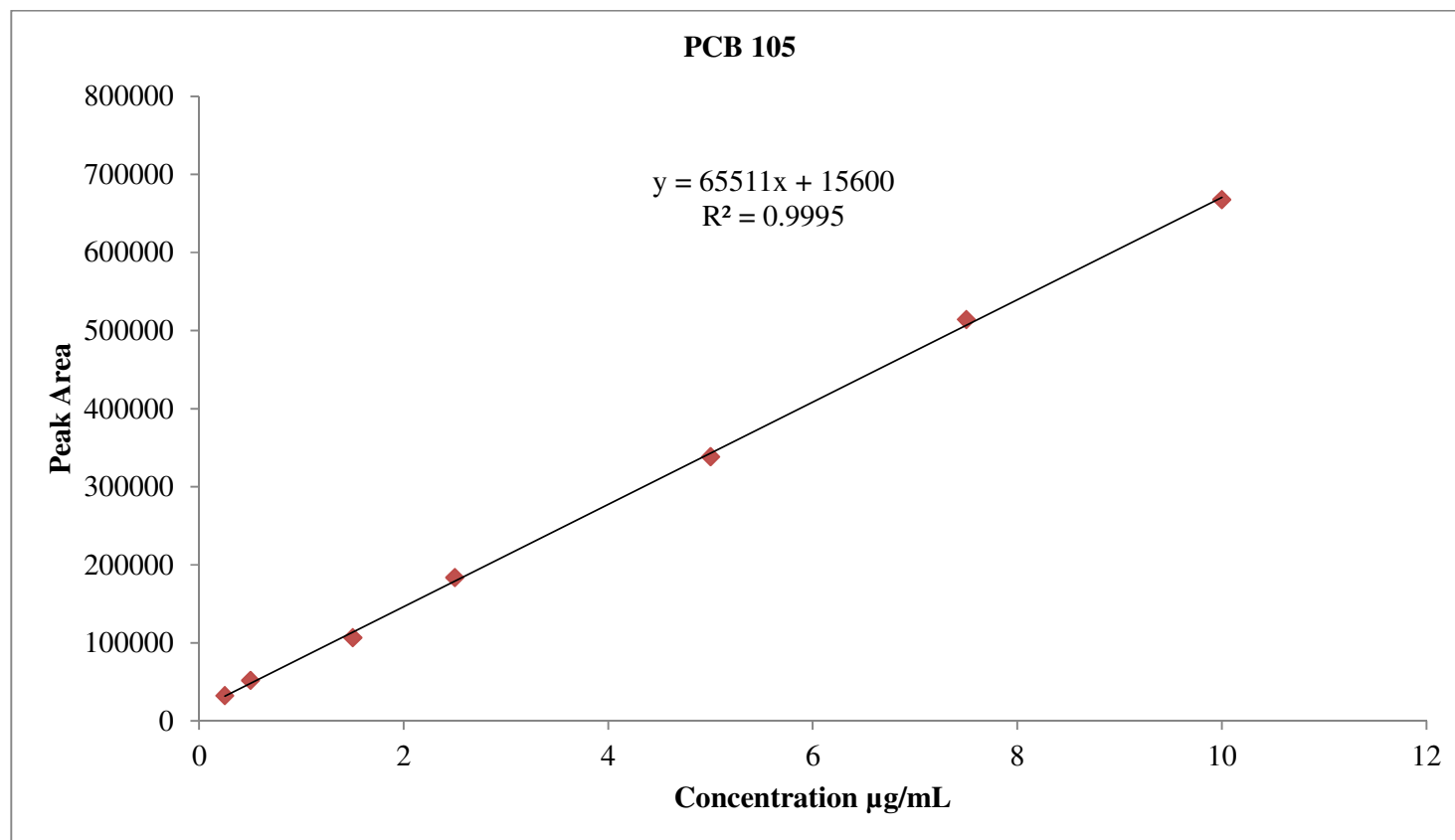
Appendix B 1.2 – Representative calibration curve for PCB 52.



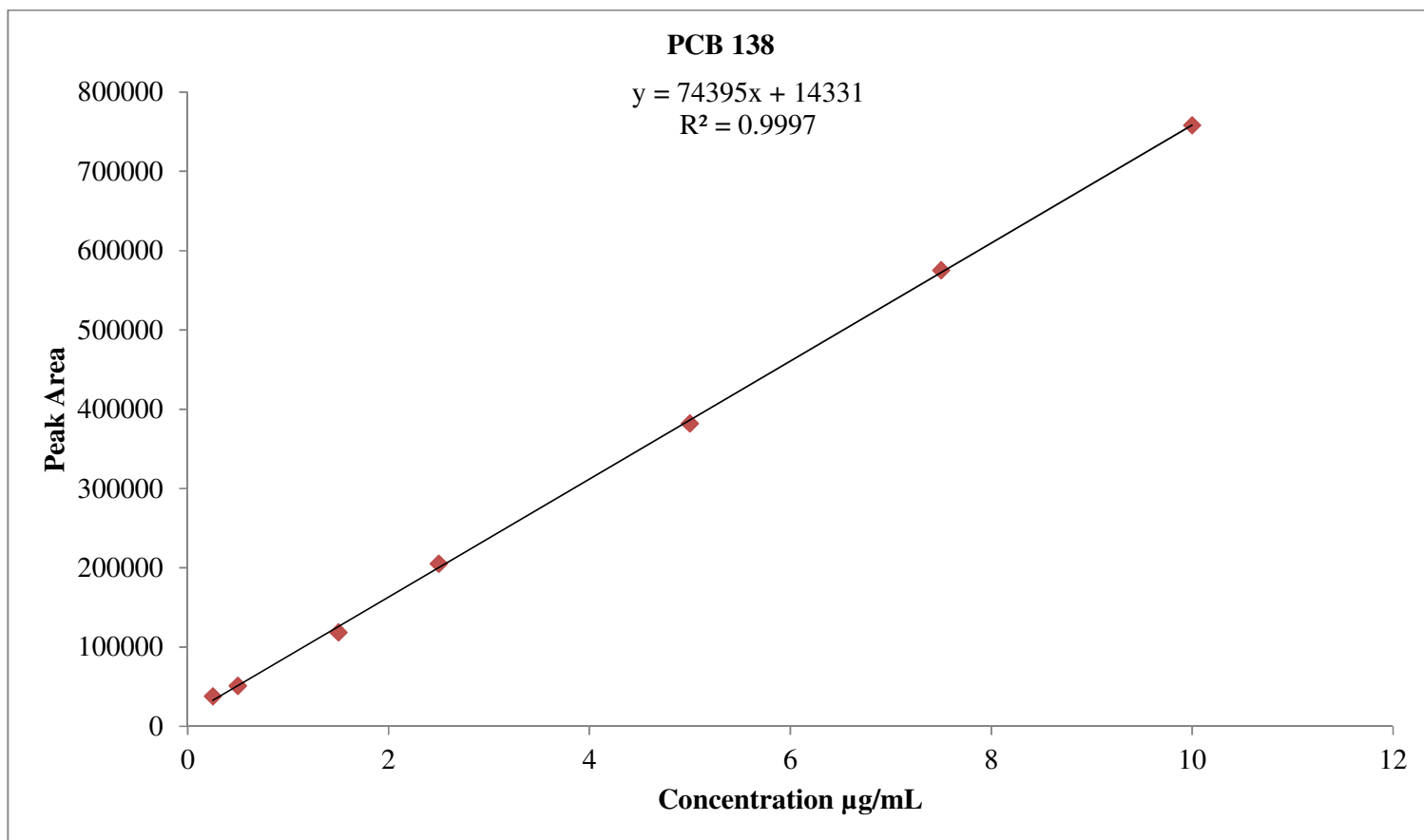
Appendix B 1.3 – Representative calibration curve for PCB 77.



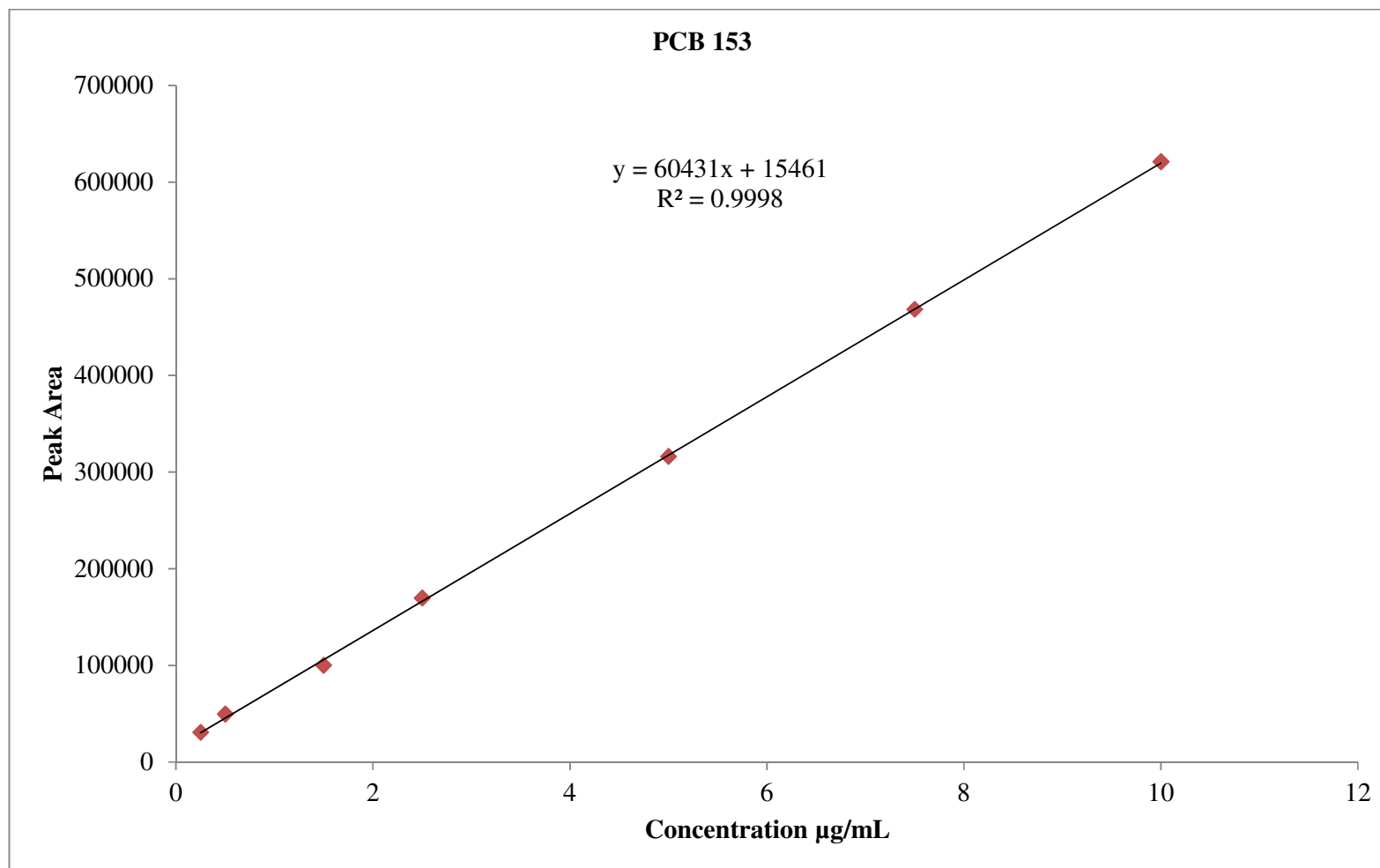
Appendix B 1.4 – Representative calibration curve for PCB 101.



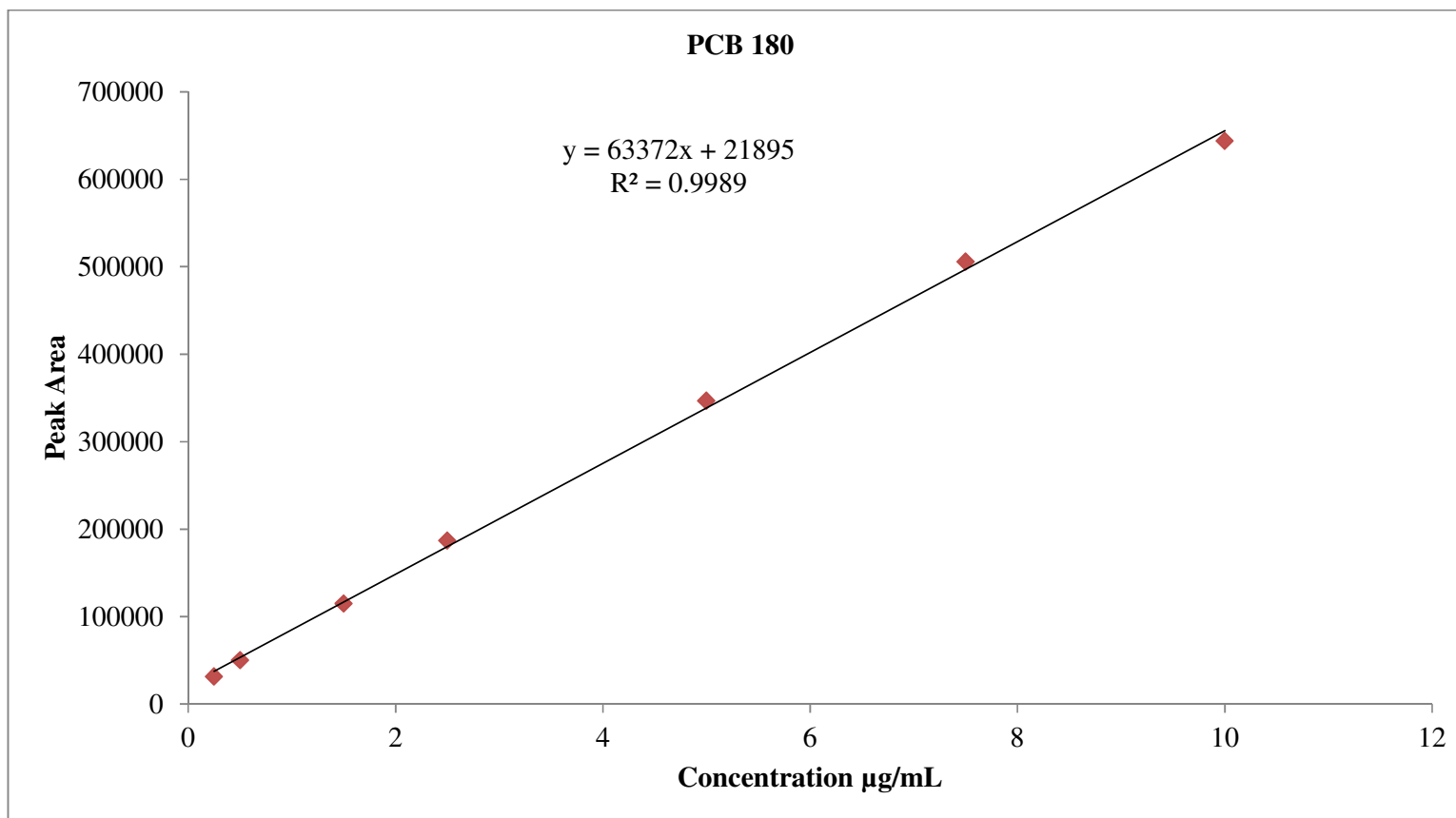
Appendix B 1.6 – Representative calibration curve for PCB 105.



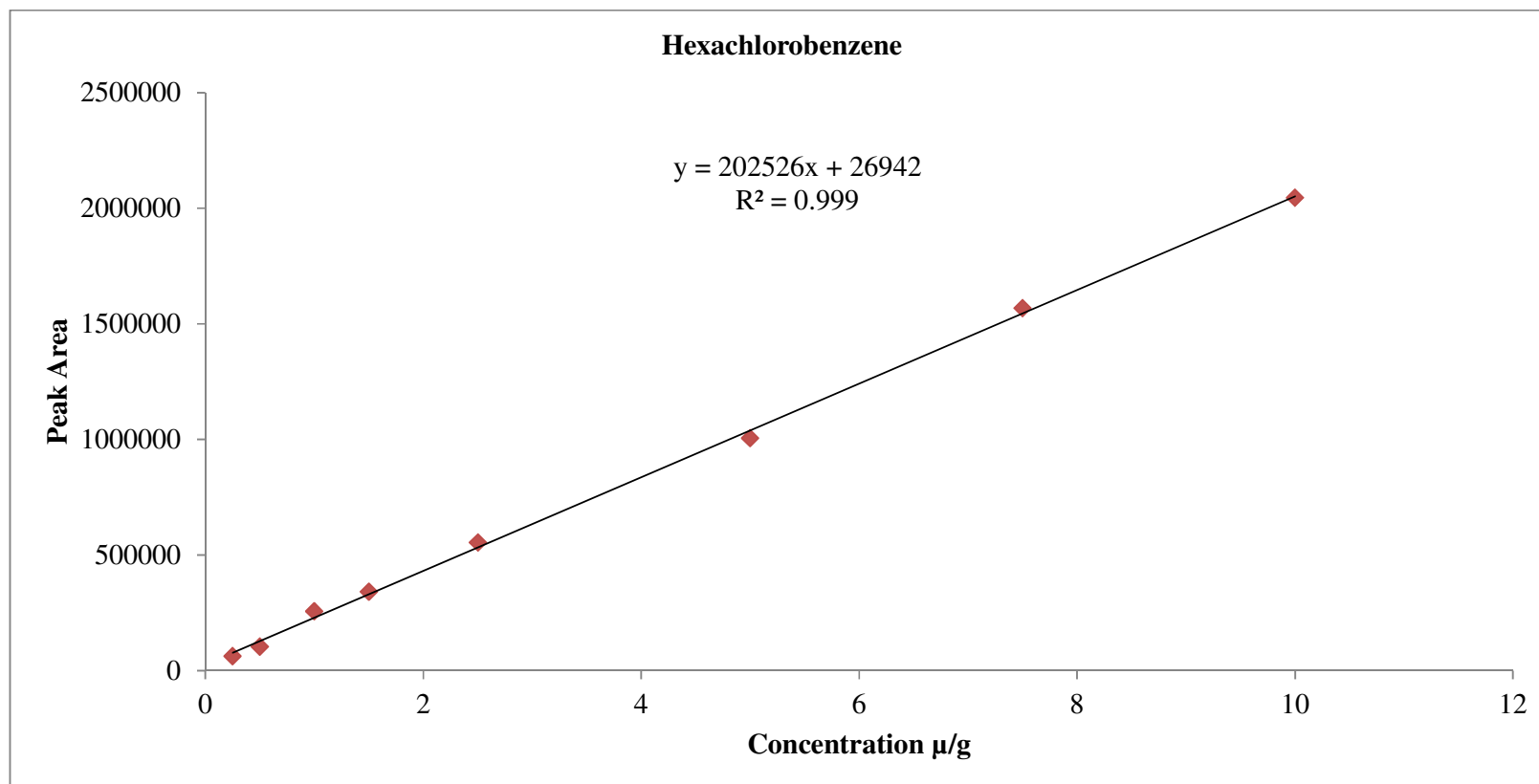
Appendix B 1.6 – Representative calibration curve for PCB 138



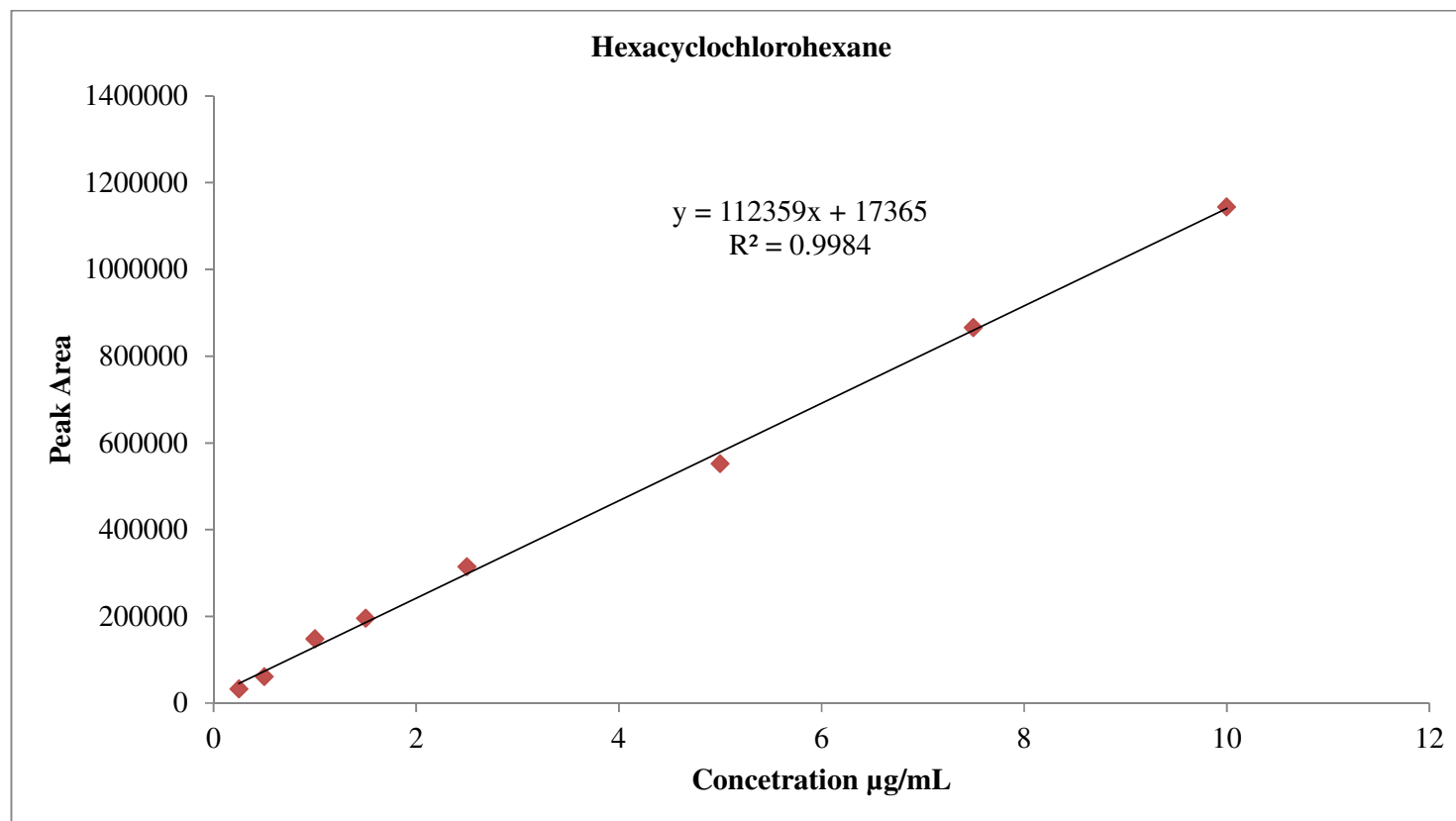
Appendix B 1.7 – Representative calibration curve for PCB 153.



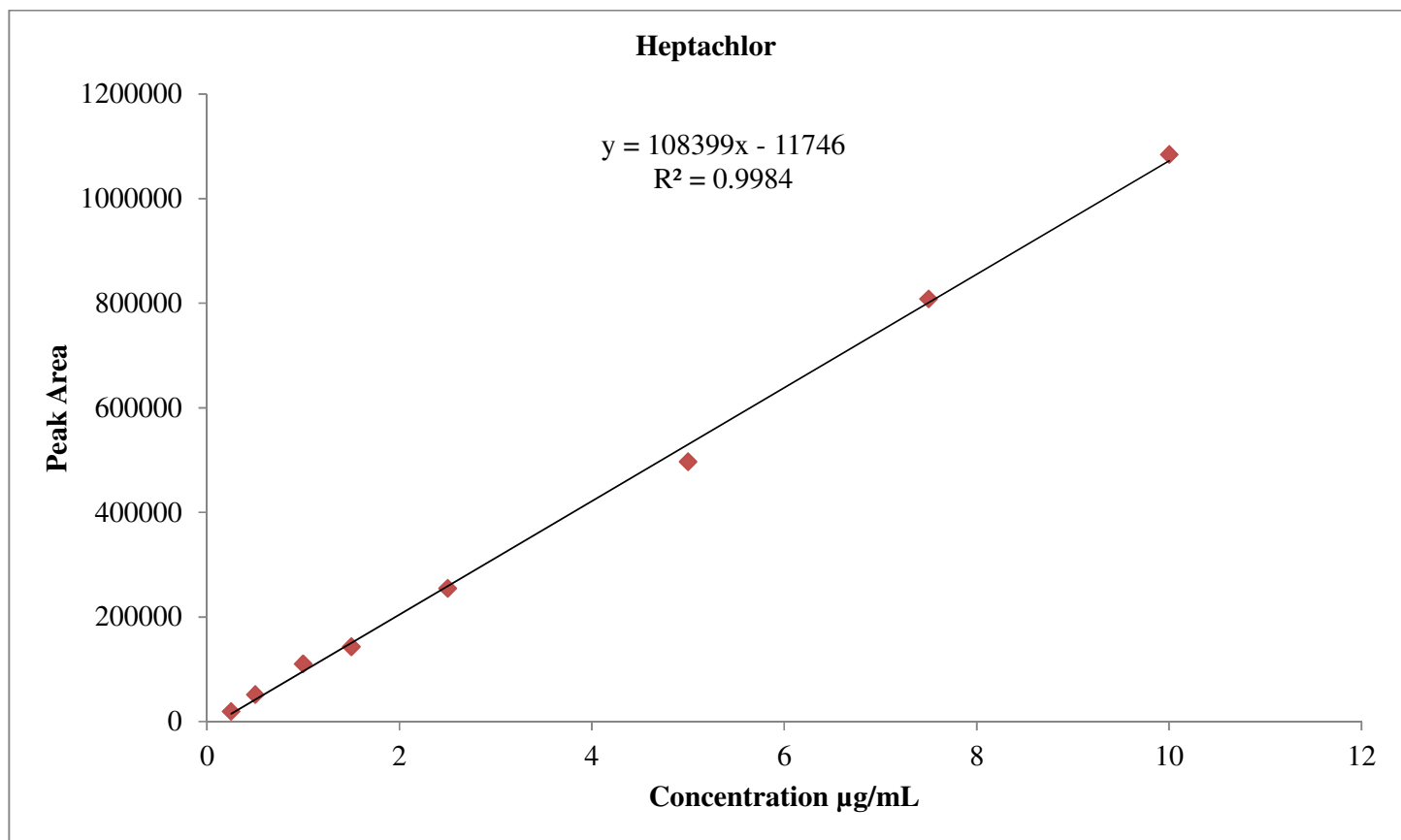
Appendix B 1.8 – Representative calibration curve for PCB 180.



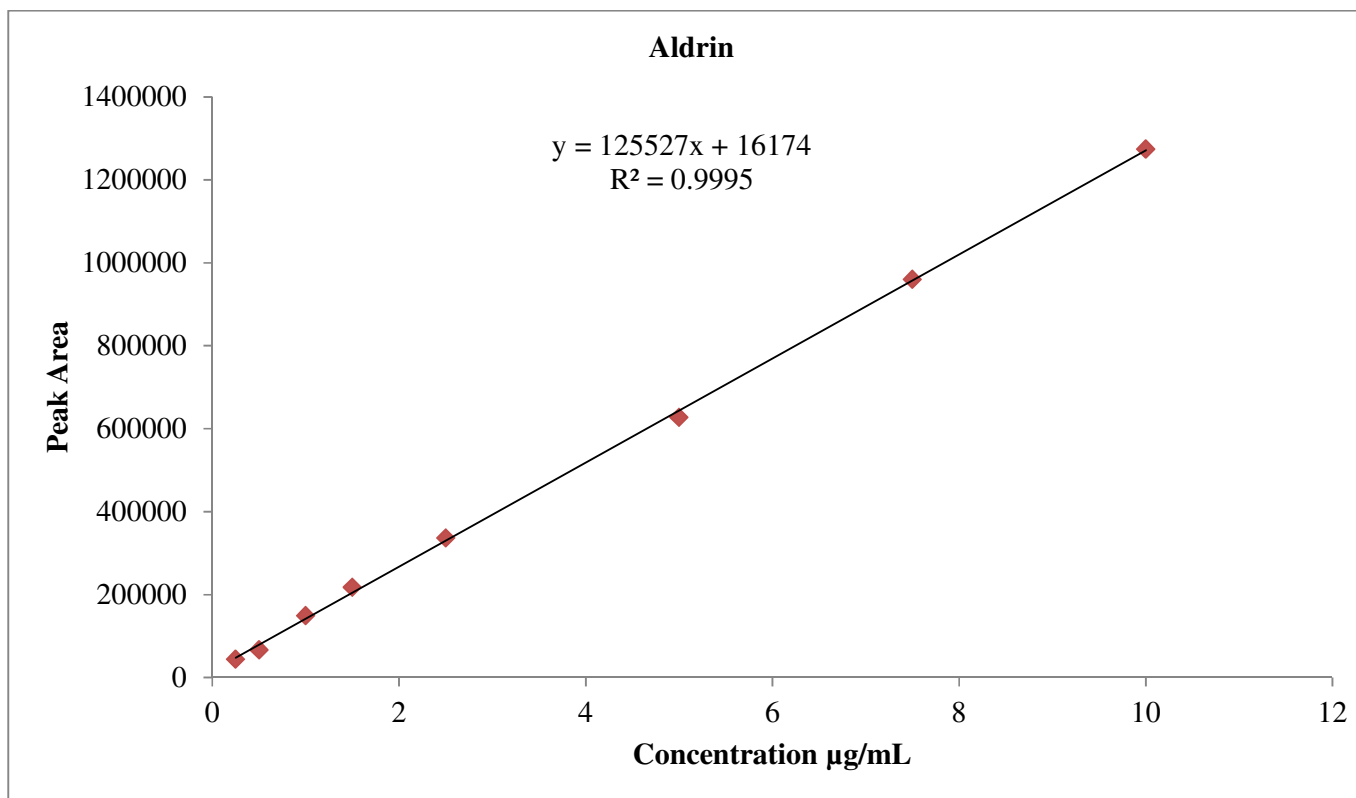
Appendix B 2.1 – Representative calibration curve for hexachlorobenzene.



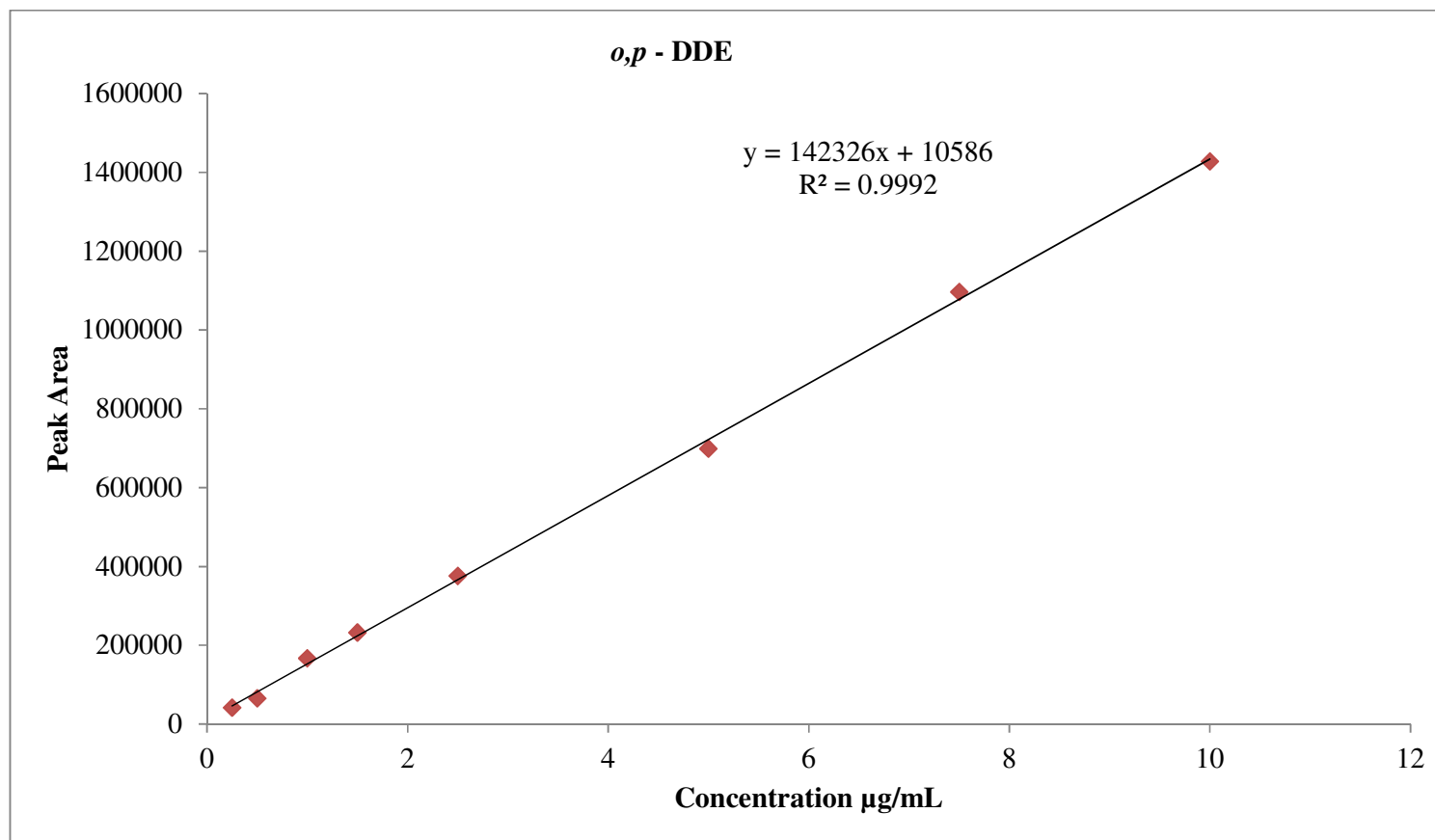
Appendix B 2.2 – Representative calibration curve for hexacyclochlorohexane.



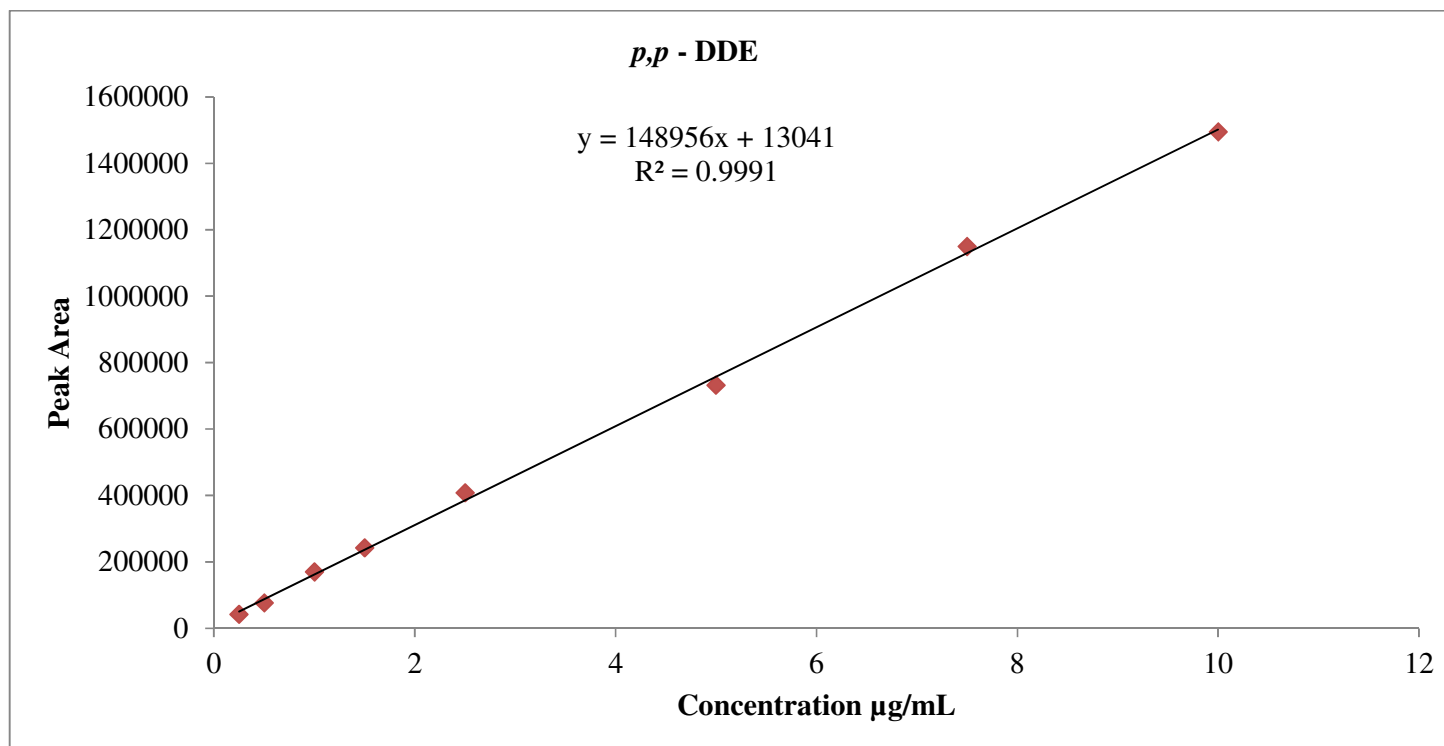
Appendix B 2.3 – Representative calibration curve for heptachlor.



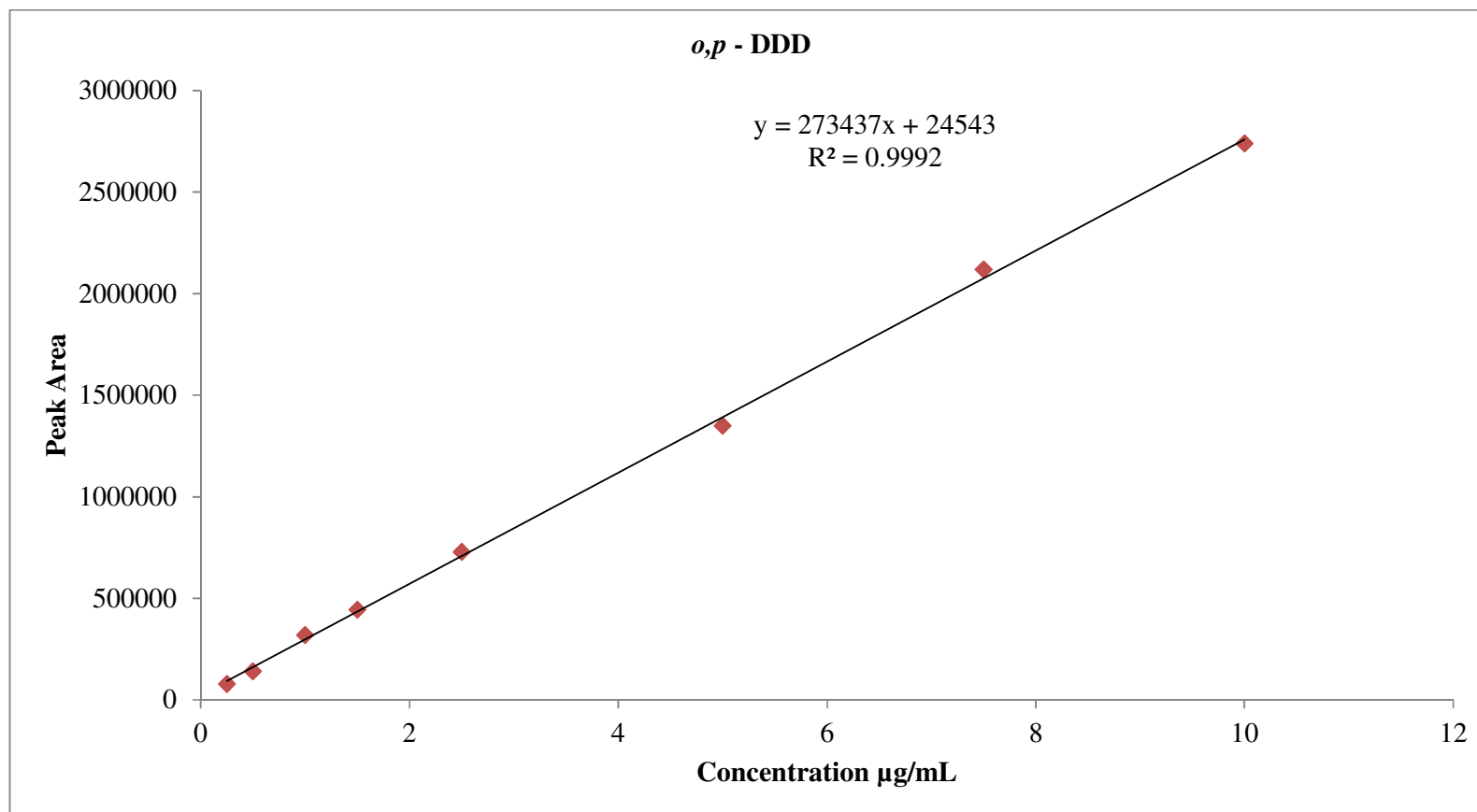
Appendix B 2.4 – Representative calibration curve for aldrin.



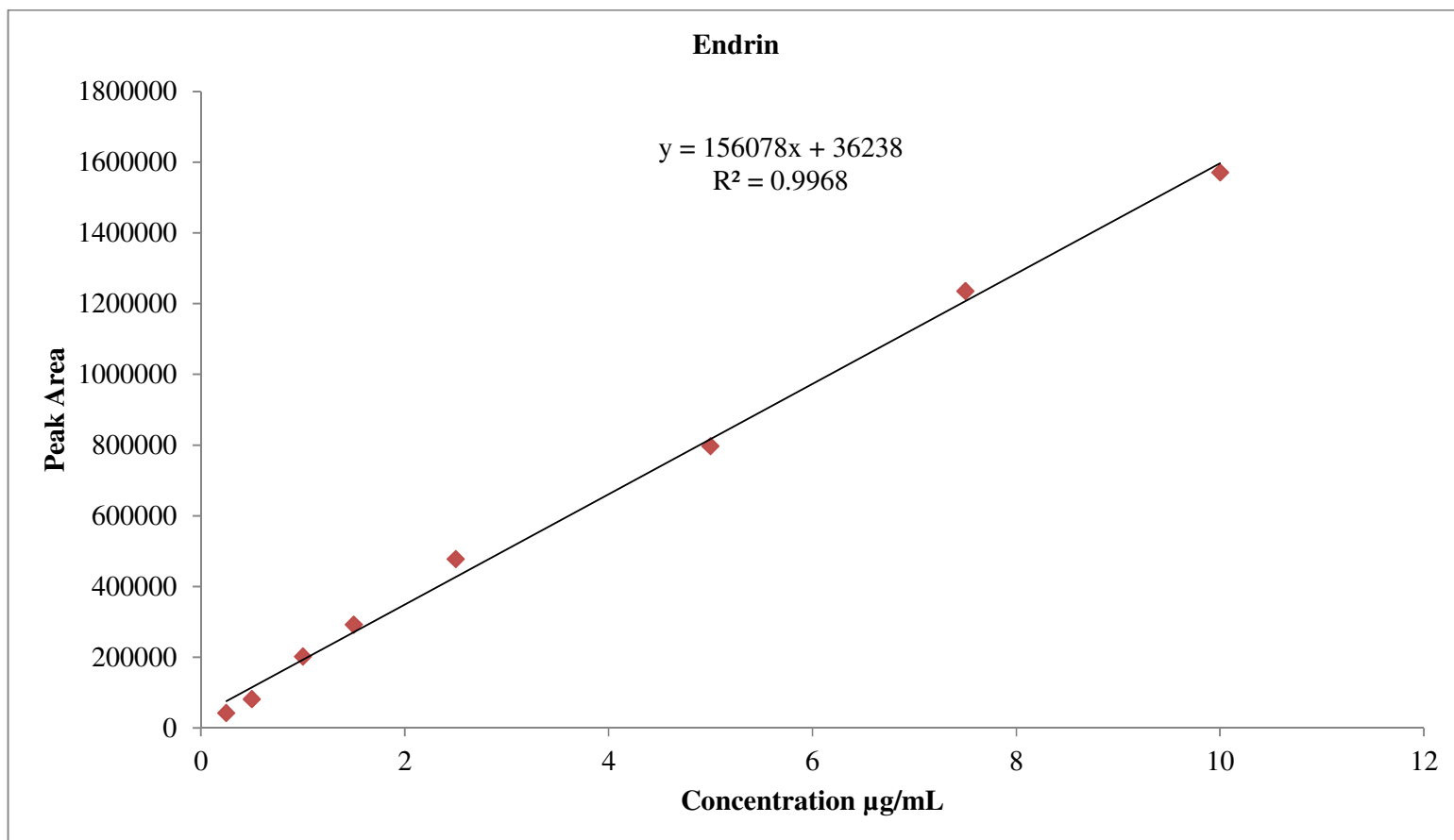
Appendix B 2.5 – Representative of calibration curve for *o,p* - DDE.



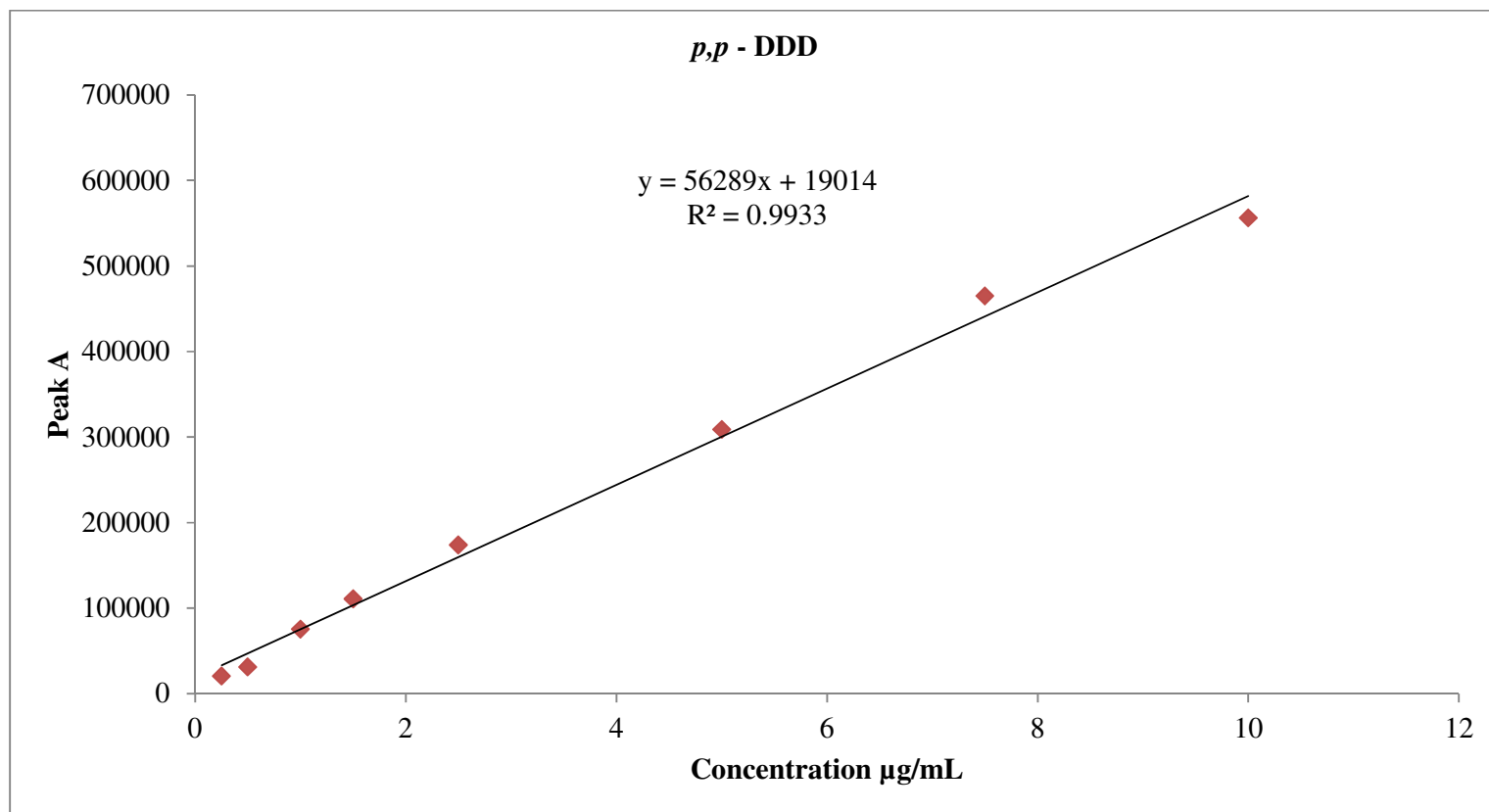
Appendix B 2.6 – Representative of calibration curve for *p,p* - DDE.



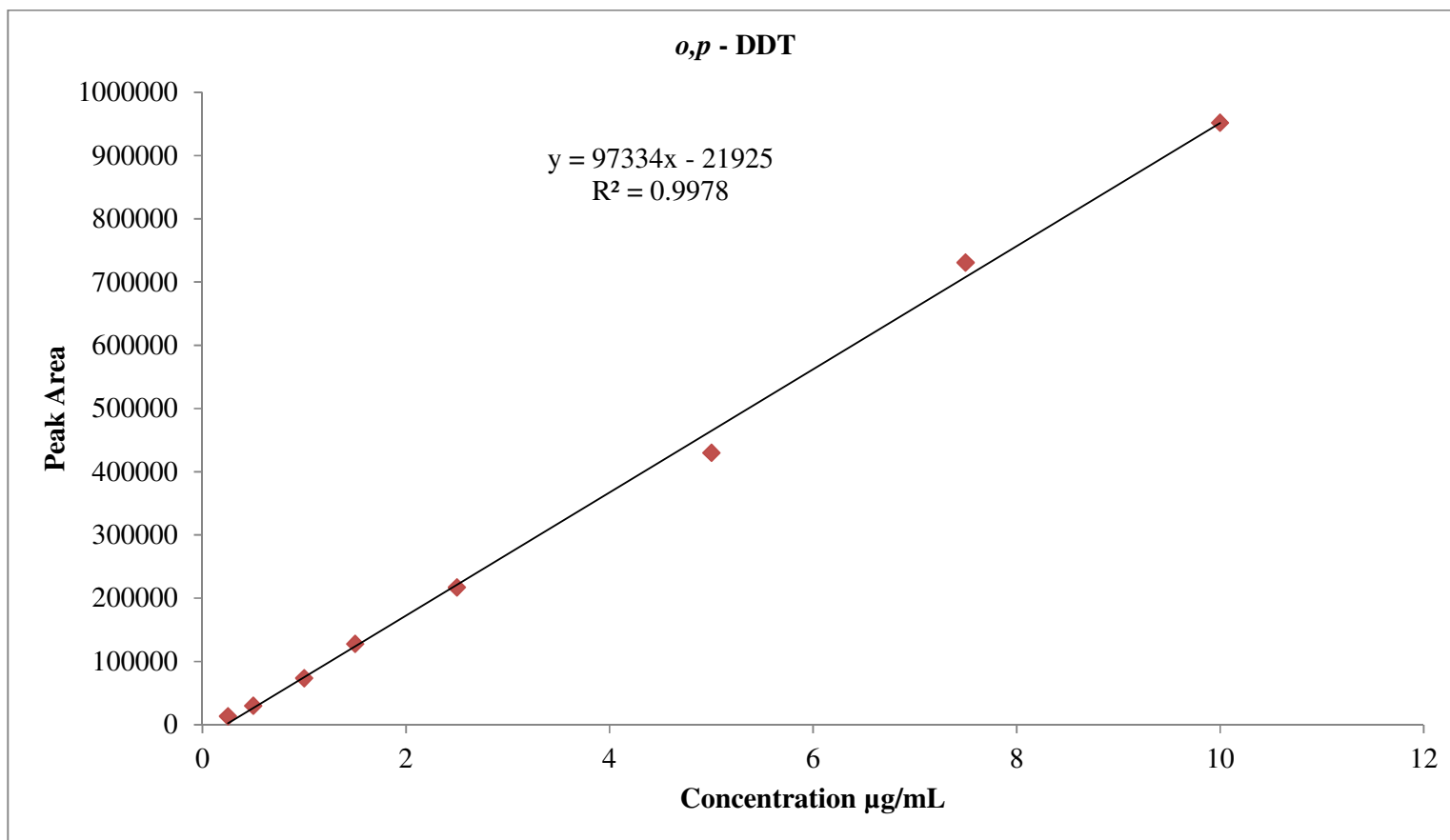
Appendix B 2.7 – Representative of calibration curve for *o,p* - DDD.



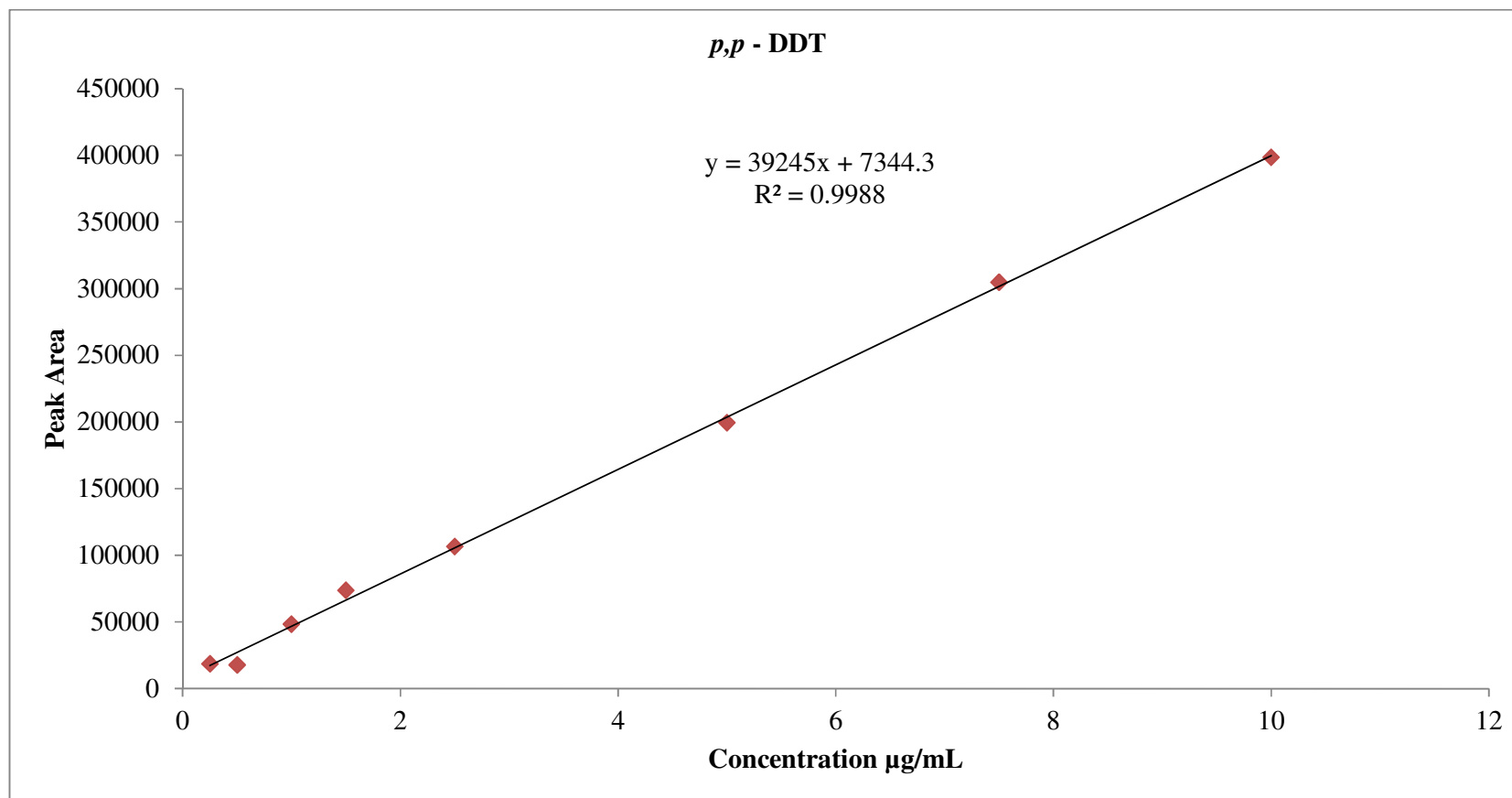
Appendix B 2.8 – Representative of calibration curve for endrin



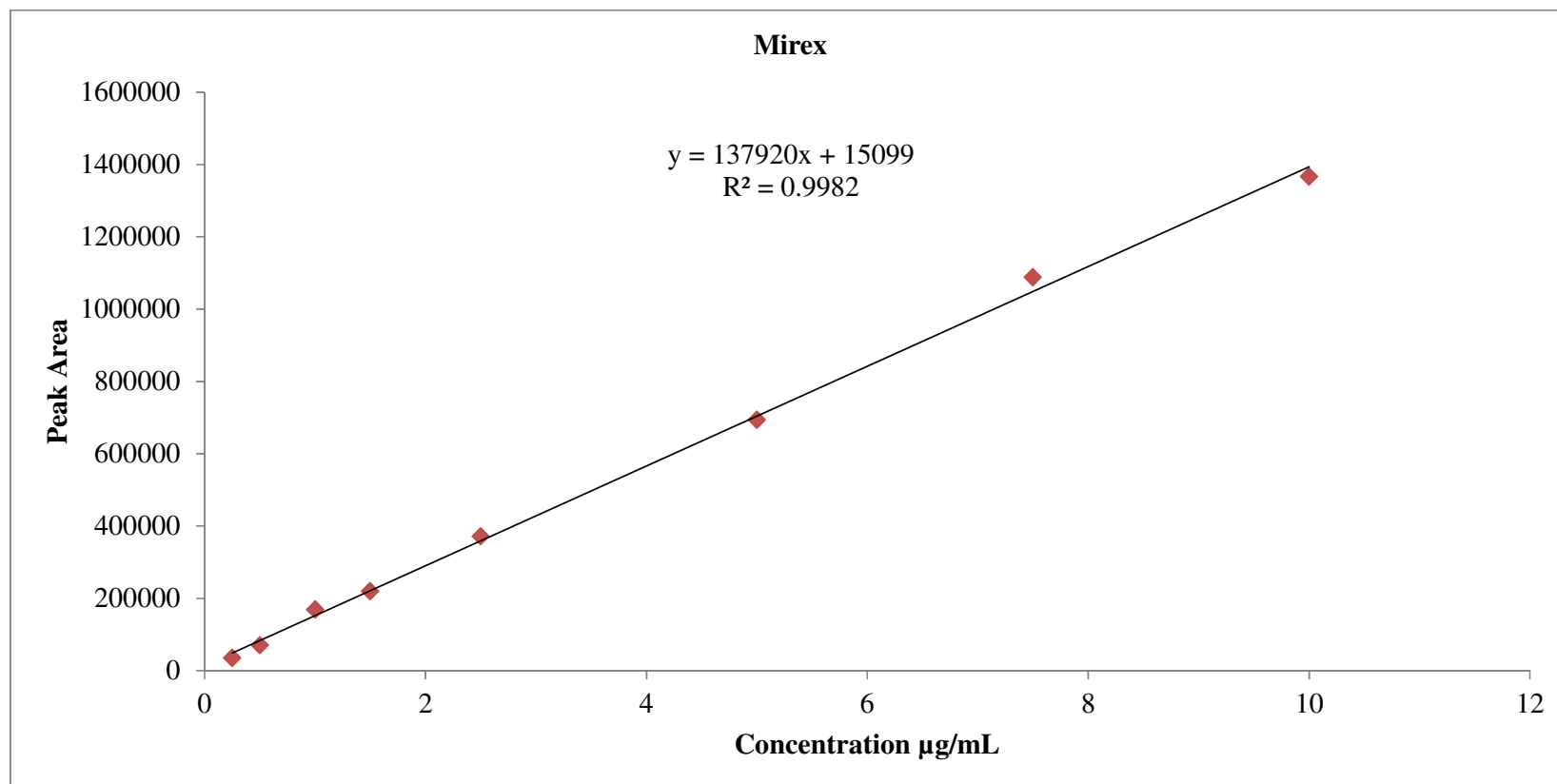
Appendix B 2.9 – Representative of calibration curve for *p,p* - DDD



Appendix B 2.10 – Representative of calibration curve for *o,p* - DDT



Appendix B 2.11 – Representative of calibration curve for *p,p* – DDT



Appendix B 2.12 – Representative of calibration curve for mirex

Appendix C:

Calculation of Toxicity Equivalence (TEQ) for dioxin-like PCBs (PCB 77 and PCB 105) in sediment and soil samples of Msunduzi River during summer season

Example: Toxicity Equivalence of PCB 77 with a concentration of 27.32 µg/kg can be calculated using toxic equivalent factor of 0.0001 WHO₂₀₀₅TEF as:

Using the formula $TEQ = C_i \times TEF$,

Where TEQ is toxicity equivalence, TEF is toxicity equivalence factor assigned for dioxin-like compound (DLC) and C_i is individual concentration of dioxin-like compound in environmental media.

$$27.32 \mu \frac{\text{g}}{\text{kg}} \times 0.0001 = 2.73 \times 10^{-3} \mu \frac{\text{g}}{\text{kg}}$$

$$= 2.73 \text{ ng/kg} = 2.73 \text{ ng/kg WHO}_{2005}\text{TEQ or } 2.73 \text{ ng WHO}_{2005}\text{TEQ kg}^{-1}.$$

Appendix C 1.1: Toxicity Equivalence (TEQ) of dioxin-like PCBs (PCB 77 and 105) in sediment samples of Msunduzi River during summer season

SITE CODE	C_i PCB 77 (µg/kg)	TEF PCB 77 WHO₂₀₀₅TEF	PCB 77 TEQ ng/kg WHO₂₀₀₅TEQ	C_i PCB 105 (µg/kg)	TEF PCB 105 WHO₂₀₀₅TEF	PCB 105 TEQ ng/kg WHO₂₀₀₅TEQ	ΣTEQ PCB (77+105) TEQ ng/kg WHO₂₀₀₅TEQ
HND	27.32	0.0001	2.73	16.31	0.00003	0.50	3.22
CMD	14.97	0.0001	1.50	15.57	0.00003	0.47	1.96
DUT	22.14	0.0001	2.21	45.84	0.00003	1.38	3.60
WWT 1	42.47	0.0001	4.25	108.09	0.00003	3.24	7.50
WWT 2	32.34	0.0001	3.23	20.28	0.00003	0.61	3.84
AGA	32.09	0.0001	3.21	27.76	0.00003	0.83	4.04
MST	30.81	0.0001	3.08	35.18	0.00003	1.06	4.14
NGD	1.42	0.0001	0.14	14.81	0.00003	0.44	0.60
UMJ	22.67	0.0001	2.27	20.58	0.00003	0.62	2.88

Appendix C 1.2: Toxicity Equivalence (TEQ) of dioxin-like PCBs (PCB 77 and 105) in soil samples of Msunduzi River during summer season

SITE CODE	C_i PCB 77 (µg/kg)	TEF PCB 77 WHO₂₀₀₅TEF	PCB 77 TEQ ng/kg WHO₂₀₀₅TEQ	C_i PCB 105 (µg/kg)	TEF PCB 105 WHO₂₀₀₅TEF	PCB 105 TEQ ng/kg WHO₂₀₀₅TEQ	ΣTEQ PCB (77+105) TEQ ng/kg WHO₂₀₀₅TEQ
HND	36.13	0.0001	3.61	14.18	0.00003	0.43	4.04
CMD	14.92	0.0001	1.49	6.53	0.00003	0.20	1.69
DUT	16.20	0.0001	1.62	8.12	0.00003	0.24	1.86
AGA	42.50	0.0001	4.25	25.48	0.00003	0.76	5.01
MST	52.55	0.0001	5.26	12.64	0.00003	0.38	5.63
NGD	36.17	0.0001	3.62	25.22	0.00003	0.76	4.37
UMJ	37.23	0.0001	3.723	47.24	0.00003	1.4172	5.14

APPENDIX D:

Appendix D 1.1: Indicative Indices of parent DDTs in sediment

Sampling code	Σ DDTs	Σ DDE	Σ DDD	DDD+DDE/DDTs	Σ DDD/ Σ DDE
M 1	84.02	159.3	99.1	2.49	0.62
M 2	67.94	125.08	103.02	2.60	0.82
M 3	87.98	228.56	110.4	3.23	0.48
W 1	96.93	86.81	39.56	1.10	0.46
W 2	85.14	146.21	40.12	1.95	0.27
M 4	58.94	139.07	102.54	3.23	0.74
M 5	90.09	115.84	109.86	1.90	0.95
M6	85.54	106.23	87.24	1.75	0.82
M 7	72.15	164.12	105.5	3.01	0.64

Appendix D 1.2: Indicative Indices of parent DDTs in soil samples

Sampling code	Σ DDTs	Σ DDE	Σ DDD	DDD+DDE/DDTs
M 1	78.49	124.95	119.44	3.11
M 2	121.73	210.57	115.62	2.68
M 3	99.31	177.77	121	3.01
M 4	89.24	131.39	102.42	2.62
M 5	60.95	128.69	110.1	3.92
M6	94.81	103.32	102.84	2.17
M 7	111.42	121.72	122.82	2.19

Appendix D 1.3: Ratio of DDD/DDT and DDE/DDT to evaluate DDT contamination along the sampling sites

Sampling code	Σ DDTs	Σ DDE	Σ DDD	Σ DDD/ Σ DDT	Σ DDE/ Σ DDT
M 1	84.01902	159.3	99.1	1.18	1.90
M 2	67.93896	125.08	103.02	1.52	1.84
M 3	87.98367	228.56	110.4	1.25	2.60
W 1	96.93069	86.81	39.56	0.41	0.90
W 2	85.14096	146.21	40.12	0.47	1.72
M 4	58.93826	139.07	102.54	1.74	2.36
M 5	90.09205	115.84	109.86	1.22	1.29
M6	85.54093	106.23	87.24	1.02	1.24
M 7	72.15258	164.12	105.5	1.46	2.27