ANALYSIS AND MONITORING OF PERSISTENT ORGANIC POLLUTANTS IN THE UMGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

By

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for the degree of

Doctor of Philosophy in Analytical Environmental Chemistry

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PREFACE

The research contained in this thesis was completed by the candidate while based in the Discipline of Chemistry, School of Chemistry and Physics of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Durban, South Africa; from February 2012 to July 2015. The research was financially supported by the University of KwaZulu-Natal, the Water Research Commission of South Africa and the Government of Rwanda.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

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Signed: Dr Brenda Moodley

    Supervisor

Date: 28th January 2016

DECLARATION 1-PLAGIARISM

I, Emmanuel GAKUBA, declare that:

     (i)   the research reported in this dissertation, except where otherwise indicated or acknowledged, is my original work;

     (ii)   this dissertation has not been submitted in full or in part for any degree or examination to any other university;

     (iii)   this dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons;

     (iv)   this dissertation does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

     a)   their words have been re-written but the general information attributed to them has been referenced;

     b)   where their exact words have been used, their writing has been placed inside quotation marks, and referenced;

     (v)   this dissertation is primarily a collection of material, prepared by myself, written as journal articles under review or ready to be submitted for publication or presented as a poster and oral presentations at conferences. In some cases, additional material has been included;

     (vii)   this dissertation does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the dissertation and in the References sections.

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Signed: Emmanuel Gakuba

Date: 28th January 2016

DECLARATION 2-PUBLICATIONS

1. Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. 2015. Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of Umgeni River, KwaZulu-Natal, South Africa. Environmental monitoring and assessment, 187:568, DOI 10.1007/s10661-015-4790-1(Published)

2. Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. 2015. Partition distribution of selected organochlorine pesticides in water, sediment pore water and surface sediments from Umgeni River, KwaZulu-Natal, South Africa. Environmental Science and Pollution Research (submitted).

3. Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. 2015. Evaluation of contamination of bank soils of Umgeni River in the province of KwaZulu-Natal, South Africa, with persistent organochlorine pesticides and polychlorinated biphenyls. (to be submitted soon).

4. Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. 2015. Seasonal variation of the distribution of polychlorinated biphenyls in the water, pore water and sediment systems in the Umgeni River, KwaZulu-Natal, South Africa. (to be submitted soon).

5. Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. 2015. Seasonal variations of chlorinated pesticides in surface water, sediment pore water and surface sediment of Umgeni River, KwaZulu-Natal, South Africa. (to be submitted soon).

6. Assessment and seasonal variation of polychlorinated biphenyls and organochlorine pesticide residues in the Umgeni River bank soil system, KwaZulu-Natal, South Africa (to be submitted soon).

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Signed: Emmanuel Gakuba

Date: 28th January 2016

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Poster presentation

● The UKZN College of Agriculture, Engineering and Science 2013 Postgraduate
   Research day: 01st November 2013 at UKZN, Howard College

Oral presentation

●WRC project: Detection and quantification of emerging organic pollutants in Durban waterways and remediation options integrating nanostructured materials and advanced oxidation processes. The annual progress reference group meeting. 12th Agust 2014 at UKZN, Westville

DEDICATION

This research is dedicated to my wife, Petronille Mukakarera and our daughters Bénigne Ishimwe Gakuba and Bella Iradukunda Gakuba, for unconditional and everlasting love they offered me.

"Access to Safe Water is a Fundamental Human Need, and therefore a Basic Human Right" … **Kofi Annan**

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ABSTRACT

abstract
Persistent organic pollutants (POPs) are identified by their persistence, toxicity, bio-amplification and long-range transport. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are among POPs that were classified by the Environmental Protection Agency (EPA) and the Stockholm Convention, as the "dirty dozen". They are a global health threat since they can be found in any environmental compartment even where they have never been produced or used before. This study is focussed on the analysis and monitoring of persistent organic pollutants, especially OCPs and PCBs in the samples seasonally collected from the Umgeni River, KwaZulu-Natal, South Africa. Different environmental matrices such as water, sediment pore water, surface sediment and bank soil, were investigated in order to fully understand the occurrence, significance, distribution and seasonal variation of the above-mentioned contaminants in the Umgeni River. Liquid-liquid extraction was used for water and pore water sample preparation and soxhlet extraction was preferred for sediment and soil samples. All extracted samples were analysed using gas chromatography–mass spectrometry (GC-MS). The results obtained showed that generally the highest PCB concentrations were found in winter where the mean values were 1.36 ± 0.39 ng/mL, 14.60 ± 7.30 ng/mL, 24.31 ± 8.92 ng/g and 25.47 ± 13.21 ng/g for water, sediment pore water, surface sediment and bank soil respectively. The lowest concentration was found in summer with the mean concentration being, 0.71 ± 0.15 ng/mL, 4.72 ± 1.80 ng/mL, 13.50 ± 8.07 ng/g and 11.79 ± 7.15 ng/g for water, sediment pore water, surface sediment and bank soil respectively. The OCP levels were also high in winter, with mean concentrations of 1.19 ± 0.25 ng/mL, 11.01 ± 5.04 ng/g, 30.87 ± 7.38 ng/g, for surface water, sediment pore water and surface sediment respectively compared to the lowest concentrations in summer with values of 0.90 ± 0.36 ng/mL, 5.16 ± 1.38 ng/mL, 18.41 ± 11.20 ng/g in surface water, sediment pore water and surface sediment respectively. Note that in case of soil the highest OCP levels were recorded in autumn (42.62 ± 10.41 ng/g) while the lowest was noted in summer (13.50 ± 5.33 ng/g). For all matrices, there was always a statistically significant difference between summer levels and other seasons ($p < 0.05$). The difference between autumn and spring levels was not generally significant ($p > 0.05$). Generally the levels of PCBs and OCPs in sediment were higher than in soil, sediment pore water and surface water. The most contaminated sites were those close to the Northern Waste Water Treatment Works. In general

the PCB180 was found to be the most abundant congener in the river and *p,p´*-DDE was the major OCP. Levels of PCBs and OCPs in the Umgeni River were generally higher than the USEPA, WHO and EU guideline values. However, when compared to Ontario Sediment Quality Guidelines, most of the pollutants investigated were found lower than their lowest effect level (LEL). All the investigated PCBs and OCPs concentrations, in the Umgeni River, were far below their severe effect level (SEL).

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LIST OF ABBREVIATIONS

APHA – American Public Health Association

ATSDR – Agency of Toxic Substances and Diseases Registry

AWWA – American Water Works Association

CCME– Canadian Council of Ministers of the Environment

CNS – Central nervous system

CWA– Clean water act

DANIDA – Danish International Development Agency

DCM – Dichloromethane

DOC – Dissolved organic carbon

EC – European Commission

EPA– Environmental Protection Agency

FAO – Food and Agriculture Organisation

GC-MS – Gas chromatography-mass spectrometry

GNIP – Ghana National Implementation Plan

GPA – Global Programme of Action

GTZ – Gesellschaft Technische Zusammenarbeit

HEPA– High Efficiency Particulate Air

HPLC – High performance liquid chromatography

HSDB – Hazardous substances data bank

IARC – International Agency for Research on Cancer

INCHEM – International programme on chemical safety

ISQG – Interim fresh water sediment quality guidelines

K_{ow} – Octanol-water partition coefficient

LEL – Lowest effect level

LOD – Limits of detection

LOQ – Limits of quantification

MECW – Monitoring and environmental chemistry working group

NAS – National Academy of Science

nd – Not detected

NDH – National Department of Health

NIP – National Implementation Plan

NIST – National Institute of Standards and Technology

OCP – Organochlorine pesticides

OECD – Organisation for Economic Co-operation and Development

PAH – Polycyclic aromatic hydrocarbon

PCBs – Polychlorinated biphenyls

PCDD – Polychlorinated dibenzodioxins

PCDF – Polychlorinated dibenzofurans

PEL – Probable effect level

PFOSF – Perfluorooctanesulfonyl fluoride

POP – Persistent organic pollutant

SCPOP – Stockholm Convention on Persistent Organic Pollutants

SEL – Severe effect level

SETAC – Society of environmental toxicology and chemistry

SIM – Selective ion monitoring

TDS – Total dissolved solids

TEQ – Toxic equivalent

TSS – Total suspended solids

UNEP – United nations for Environmental Programme

USA – United States of America

USAID – US Agency for International Development

USEPA–United States Environmental Protection Agency

WEF – Water Environment Federation

WHO – World Health Organization

CHAPTER ONE

GENERAL INTRODUCTION

1.1 WATER NECESSITY

Water is an important commodity that plays a vital role on earth without which life is impossible. Water consumption by humans increases by 64 billion cubic meters every year (Worldometers, 2013). The previous UN Secretary General Mr Kofi Annan, in his well-known declaration, when addressing the water issue on 22nd March 2001, mentioned that "Access to safe water is a fundamental human need, and therefore a basic human right"(Annan, 2001). Nevertheless an efficient clean water supply is still out of reach for many people in remote areas of the developing world. This problem is severe in Africa where more than 300 million people live in water-scarce environments (Bureau and Strobl, 2012) of which South Africa is one of the dry countries around the world. The global average rainfall is 860 mm per annum but the South African average is only 450 mm per year and the available water per capita is 1000 m^3 per person per year (CSIR, 2010).

In addition, one should not only focus on quantity alone but also on the quality of the water supply because although water maintains life on earth, it may also be harmful and even deadly when it is polluted. According to the United Nations for Education, Science and Culture Organization (UNESCO) and Food and Agriculture Organization (FAO), about 80% of diseases in developing countries are connected with contaminated water. Research has shown that children coming into contact with contaminated water often end-up with diarrhea which kills 5000 children every day (Worldometers, 2013).

In a country like South Africa, where 12 million people do not have access to clean water and where safe and accessible water supply is provided to less than half of the rural population (Thwala, 2010), the investigation of the quality of available water resources such as lakes, rivers and other water bodies is very important for protection of a scarce resource to avoid a serious water crisis in the country.

1.2 THE PURPOSE OF ANALYSIS OF WATER

Physical appearances of a body of water such as colour, odour, cloudiness, solid particles and floating foam can indicate if water is badly polluted. But several components, whether harmful or beneficial in water, are invisible and odourless. It is therefore imperative to further investigate other components in water than what is observable in order to determine the dissolved pollutants in water. Therefore chemical and microbiological analyses must also be conducted.

Analysis of a natural body of water such as the Umgeni River helps us understand the extent of pollution in the river as well as the risk the contaminated water poses to wildlife or human life in general. The results of such an investigation help in identifying the source of pollution which then allows the municipality set up policies and guidelines to control the dumping of unwanted waste into rivers as well as allowing for remediation of polluted waters. The quality of discharged wastewaters by treatment plants is just as important as the portability of the water. A wastewater treatment plant's discharge along a river often means that one locality's wastewater may be the next vicinity's water supply. Therefore proper and adequate treatment processes at the wastewater treatment plant is also important to ensure that it allows "clean" water to be discharged back into the river. The seasonal factors of a region dictate the environmental behaviour of pollutants in water. The study of seasonal variations affecting different pollutants also helps to understand their trends throughout the year and the effect of changes in climate conditions.

1.3 CHEMICAL POLLUTION IN AFRICA

Chemical pollution in Africa as well as in other parts of the world is a serious threat to the health of humans and animals. The threat of chemical pollution becomes even more of a global problem when it is due to persistent organic pollutants (POPs) because they not only affect the health of people living in areas where it is produced or used but spreads out to almost every corner of the earth due to several means of transport together with the POPs resistance to degradation (SETAC, 1998, Lohmann et al., 2007a). Africa produces very little to no POPs but it is polluted by them. It was found that some pollutants originate from the Organisation for

Economic Co-operation and Development (OECD) countries, imported as pesticides or hazardous waste to be dumped (Clapp, 2001).

The African continent fell victim to several toxic substances in the 1980s, when it was unfortunate enough in being the first choice for dumping European wastes (Bernstorff and Stairs, 2001). Some localities such Kassa Island in Guinea, Koko in Nigeria and even South Africa, were well-known for serving as places of trans-shipments of hazardous substances (Bernstorff and Stairs, 2001). These hazardous substances contained various kinds of compounds including POPs such as pesticides, polychlorinated biphenyls, etc. In Rwanda, there were 451 tonnes of pesticides from Japan, Germany, France, Italy and Switzerland which had to be disposed. In South Africa, there were 603 tonnes of pesticides which were disposed and among them were aldrin, DDT and dieldrin (Bernstorff and Stairs, 2001).
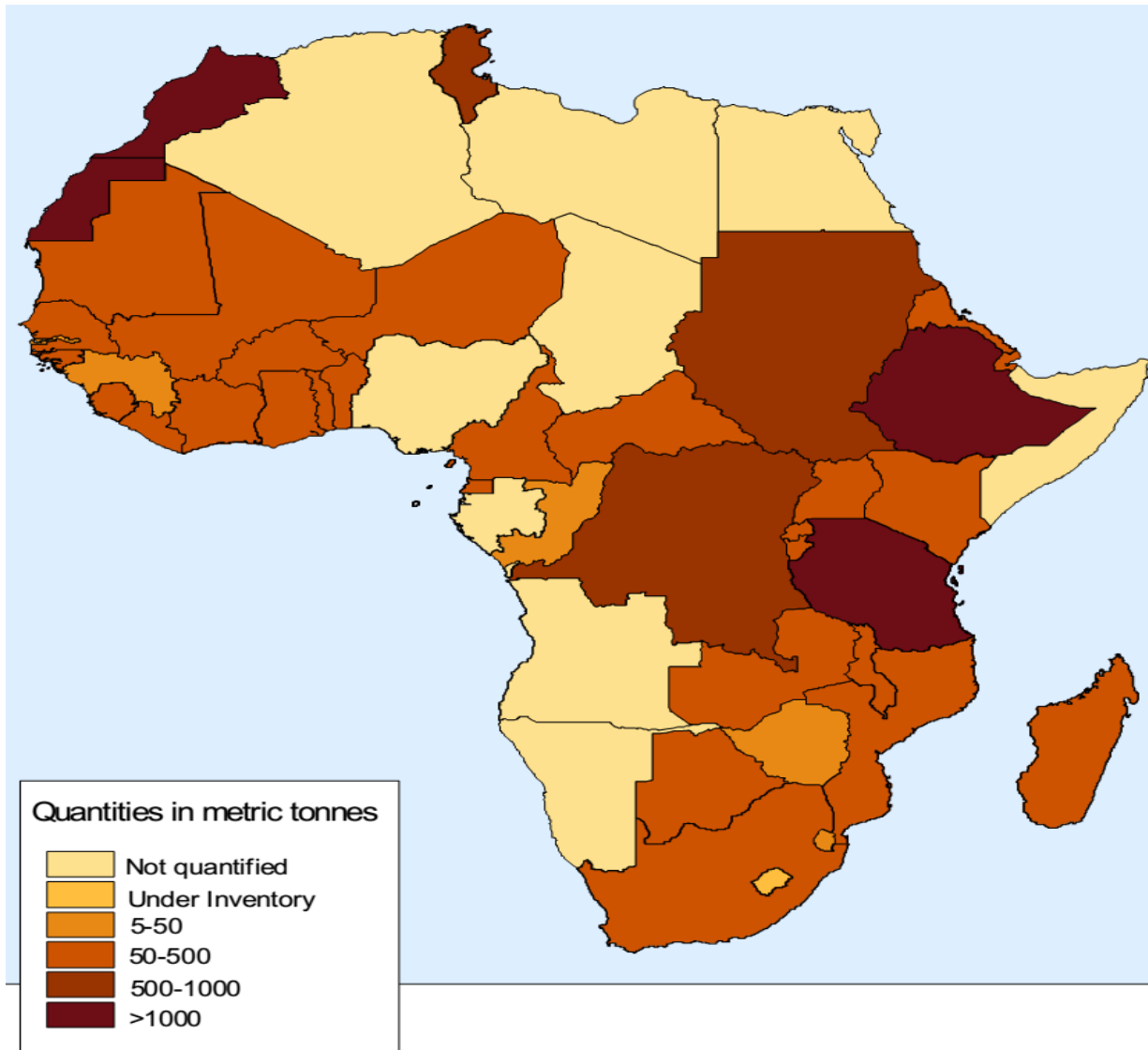
Figure 1.1 Inventory of absolute and unwanted pesticides stockpiles dumped in Africa (1980-2000)

(adapted from (Bernstorff and Stairs, 2001).

Many other African countries had several tonnes of such hazardous unwanted substances from the developed world disposed on their land (Bernstorff and Stairs, 2001). Figure 1.1 shows a map of absolute and unwanted pesticide stockpiles in Africa. In 1992, during the Rio conference, Africa's representatives suggested the ban of industrialised countries' exports of hazardous waste to less industrialized nations. The dumping of hazardous waste however continued and it was only in 2001 when the. United Nations Environmental Protection Programme (UNEP) approved

the banning of the "dirty dozen" worldwide which included organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), dioxins and furans (Athanasios and Konstantine, 2002, Bernstorff and Stairs, 2001) did the dumping of contaminated waste in African countries stop. With the support of organisations such as Gesellschaft Technische Zusammenarbeit (GTZ), Danish International Development Agency (DANIDA) and US Agency for International Development (USAID), the unwanted stocks of hazardous substances were entirely or partly removed from some African countries to European hazardous waste treatment facilities (Bernstorff and Stairs, 2001). Since these pollutants are transboundary facilitated by atmospheric transportation and are found in areas where they have not been produced or used, a global effort from both developed and less developed countries is needed in order to reduce their concentrations in the environment around the world (Stroebe et al., 2004, Stroebe et al., 2006).

Long range atmospheric transport has favoured the presence of these pollutants in all environmental compartments (Kongo et al., 2005, Castro-Jiménez et al., 2008, Zhang et al., 2008, Zhao et al., 2010a, Wang et al., 2012, Barakat et al., 2013) and hence they are a growing global concern (Zhou et al., 2001, Zhang et al., 2004, Feng et al., 2011). Many countries around the world proceeded by banning POP production, storage and usage, but due to POPs resistance to photochemical, chemical, and biochemical degradation (Bandala et al., 2002) and bioaccumulation through the food chain, they are still being detected in the environment today. In addition, some POPs such as OCPs are still being used today, for example, DDT is a powerful pesticide and is still used in some African countries to control vector diseases, such as malaria, which still kills more than one million people per year (Bouwman et al., 2006). This insecticide is also used in malaria endemic regions of South Africa such as Northern KwaZulu-Natal (Humphries, 2013, Channa et al., 2012, Bouwman et al., 2006) and Limpopo (Dalvie et al., 2004d).

1.4 SOURCE OF POLLUTION OF UMGENI RIVER CATCHMENT

South Africa is one of the countries that has signed and ratified the Stockholm convention of persistent organic pollutants which was adopted in 2001 and whose aim was to safeguard human health and the environment from highly harmful chemicals which affect the well-being of

humans as well as wildlife (EPA, 2009). It is therefore important that the presence of organic pollutants in South Africa in general and in the Umgeni River catchment in particular, be fully delineated. The Umgeni River is one of the major rivers found in the province of KwaZulu-Natal in South Africa. It has a surface area of 4416 km^2 and travels a distance of 225 km from source to mouth (Groundspeak, 2013). It is one of the main sources of water for many people in this province, especially in Durban, Pietermaritzburg and Howick, where almost the entire urban population depends on it for its water supply. However, pollution along the river makes it unsafe to both humans and animals. There are many sources of pollution along the Umgeni River. One such source is the informal human settlements along the banks of the river. Residents of these informal settlements use the river water for bathing, washing and irrigating due to unavailability of treated water. Their latrines are placed on the banks of the Umgeni River resulting in human faeces contaminating the water. This has caused water-borne diseases such as bacterial diarrhea, hepatitis A, and typhoid fever and water contact diseases such as schistosomiasis[1] and leptospirosis[2] (Indexmundi, 2013). Furthermore, the constant rise in the number of people who live in squatter camps around the Umgeni River has caused an increase in contamination of its surface water.

Other sources of contamination of the Umgeni River include industrial waste that makes its way into the water, engine oils, the overflow of sewage, leaking pipes due to poor maintenance, the use of pesticides, fungicides and herbicides by farmers, which are washed away by rainwater, rubbish like plastic bags, bottles, paper and tins which are carelessly thrown on the ground and blown by the wind or washed down storm-water drains into the river, etc. Industrial chemical waste is one of the main sources of organic pollutants in this river. The Umgeni River passes through urban areas such as Howick and Durban, where industrial activities predominate. The effluent overflow from these chemical industries also contribute to the pollution of the Umgeni River, resulting in pollutants accumulating in the river sediments, bank soil or dissolving in the river water (DEAT, 2006).

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[1] Schistosomiasis is a parasitic disease caused by blood flukes (trematodes) of the genus Schistosom.
[2] Leptospirosis is a bacterial disease that affects humans and animals. It is caused by bacteria of the genus Leptospira. In humans, it can cause a wide range of symptoms.

Pollutants such as heavy metals and bacteria in the Umgeni River basin were reported (Pegram and Bath, 1995). Previous studies found this river to be contaminated with mercury, its main source being Thor Chemicals (a metal producing plant) which discharged it into the Mngceweni River, a tributary of the Umgeni River (Barratt and Combrink, 2002). Many researchers have been interested in metal and bacterial contamination of the Umgeni River (Barratt and Combrink, 2002, Dikole, 2013, Olaniran et al., 2014) but up to now little is known about the organic pollutants that are present in the Umgeni River water and its basin. Organic chemical pollution causes much harm to the health of the KwaZulu-Natal population in general and particularly to people living in Durban, Howick and Pinetown and can at times be just as toxic as metal pollutants. In this project organic pollutants from the Umgeni River were investigated with special emphasis on persistent organic pollutants.

1.5 TOXIC AND PRIORITY POLLUTANTS

The Environmental Protection Agency (EPA), in its Clean Water Act (CWA) of 1977 established two lists of substances for water quality control. These are known as the list of toxic pollutants and the list of priority pollutants. The toxic pollutants list was discussed among parties and the agreement was referred to as the Toxics Consent Decree (Keith and Telliard, 1979a). This list comprised of 65 compounds such as 2,4-dichlorophenol and classes of compounds such as phthalate esters (EPA, 2012). The priority pollutants were chemical pollutants for which regulations and methods of analysis were published by EPA. Unlike the list of toxic pollutants which included open-ended groups of pollutants, the list of priority pollutants contained 126 pollutants described by their individual specific names. These substances were reported to occur in water bodies with a frequency of at least 2.5% (EPA, 2012). These included 2-chloronaphthalene, phenanthrene, chlorobenzene, 4-nitrophenol, etc.

1.6 ENVIRONMENTAL FATE OF ORGANIC POLLUTANTS

Organic pollutants such as POPs are characterized by their persistence, bioaccumulation, toxicity and their long-range transport (Pennington, 2001, Leip and Lammel,2004, Ilyina, 2007). Intentionally produced POPs such as PCBs and pesticides and accidentally formed by-products

including PCDDs and PCDFs are found in various environmental matrices such as soil, sediment, water, air and biota. Some places such coastal shelves are considered as reservoirs or permanent "sinks" of PCBs mainly due to accumulation of organic matter (Lohmann et al., 2007a).

POPs are partitioned in different environmental compartments (Figure 1.2) and undergo different environmental phenomena which transform them from one phase to another, depending on the environmental media in which they are transported. The environmental fate of organic pollutants is a result of many processes such us physical transport, multimedia partitioning and biogeochemical reactions (Lohmann et al., 2007a). Organic carbon plays a key role in the fate of POPs as well as their spatial, horizontal and vertical variability in soil (Cousins et al., 1999) while soot carbon is known as an important vector for POP transport and partitioning in marine environments (Lohmann et al., 2005, Persson et al., 2002). The reintroduction of sediment in the water column of a body of water was assigned to sediment resuspension (Jurado et al., 2007). The following figure shows an example of how pesticides are transported and distributed in the environment.
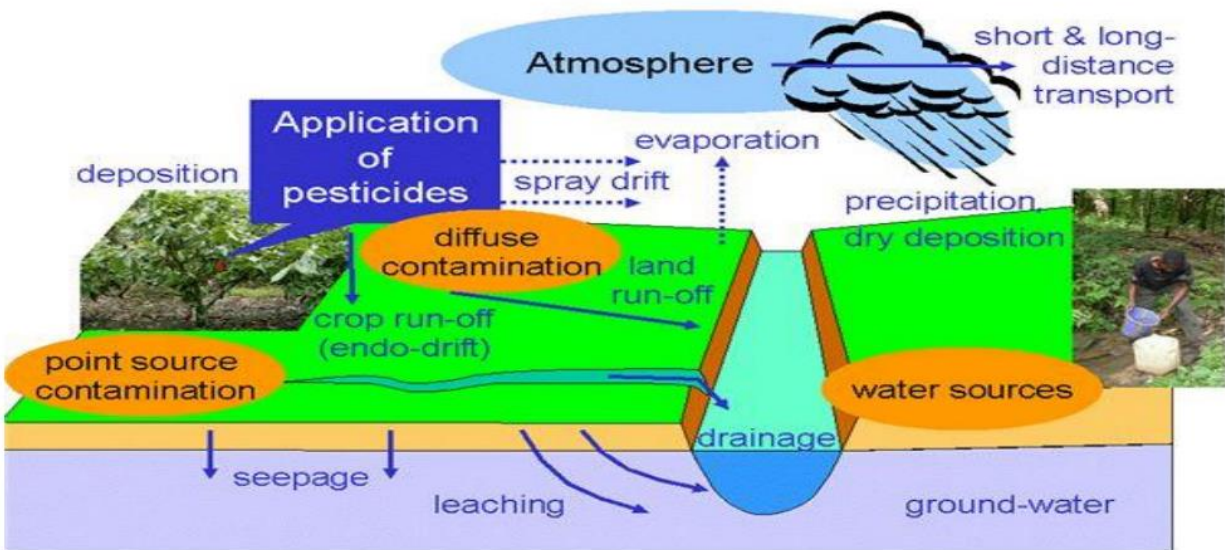
Figure 1.2 Environnemental fate of POPs

(adapted from (HUB, 2012))

1.7 HYPOTHESES OF THE STUDY

This study focuses on the pollution of the Umgeni River with regard to persistent chlorinated organic pollutants namely polychlorinated biphenyls and organochlorine pesticides.
The following hypotheses were set:

● The Umgeni River is polluted by polychlorinated biphenyls and organochlorine pesticides.
● The levels of polychlorinated biphenyls and organochlorine pesticides in the Umgeni
   River are affected by spatial and seasonal variations.
● The pollutants found in sediment are mainly in solution in its pore water

1.8 SCOPE OF THE STUDY

This study focused on determining the levels of persistent chlorinated organic pollutants in the Umgeni River and their spatial distribution and seasonality along this river in the province of KwaZulu-Natal, South Africa. Previous studies showed the presence of various organic pollutants including POPs in other South African rivers such as the Jukeskei River, Vaal River, Mooi River, Crocodile River and Olifants River (Sibali et al., 2008, Chokwe et al., 2015, Vosloo and Bouwman, 2005). The current study focused on the Umgeni River because it is one of the main rivers in KwaZulu-Natal which is the main source of water to the eThekweni district, however very little research has been conducted on it with regard to organic pollutants and any research that was conducted, is now outdated. Also research that has been done has focused on inorganic pollutants rather than organic pollutants. In addition, this is the first study involving pore water analysis in a South African river as well as seasonal and spatial distribution of these organic pollutants. The results provide new knowledge on the climatic effects on the distribution and concentration of organic pollutants in the environment.

Sampling sites were chosen along the river based on the various surrounding activities that may affect the concentrations of organic pollutants. The analysis was carried out on different matrices including surface water, sediment pore water, surface sediment and river bank soil. The bio-

solids from the wastewater treatment plant (Northern Wastewater Works) which discharges its treated water into the Umgeni River were also analysed. The detailed description of the sampling sites is mentioned in section 5.2.3. The PCBs monitored in this study included PCB28, PCB52, PCB77, PCB101, PCB105, PCB138, PCB153 and PCB180. Except PCB77 and PCB 105, the other PCBs were chosen for the study because they are indicator PCBs and are recommended by the European Union for assessing PCB pollution (EC, 1999, EFSA, 2010). PCB77 and PCB105 were included because they are among the most toxic dioxin-like PCBs and are recommended by World Health Organization (WHO) for monitoring (Moysich, 2015, WHO, 2003b). The OCPs investigated were hexachlorobenzene, hexachlorocyclohexane, heptachlor, aldrin, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, endrin, dieldrin and mirex. These OCPs were chosen because they are recommended by the EPA and the Stockholm Convention for analysis and monitoring of environmental pollution (UNEP, 2005a). Apart from HCH and HCB, all the other assessed OCPs are included in the dirty dozen (UNEP, 2001). The seasonal variations of all the analytes was studied in four South African seasons' namely winter, summer, autumn and spring.

1.9 THE AIM OF THE RESEARCH

Organic pollutants are of great concern because of their exponential increase in the manufacturing industry. They are potentially toxic as well as have carcinogenic, mutagenic and teratogenic effects (Radojevic and Bashkin, 2007). Some organic compounds are not biodegradable and yet their degradation and removal efficiency during water treatment is practically unknown (Mamabolo, 2006). People continue to use water from rivers and other sources without knowing its chemical composition and without any proper and suitable treatment, which eventually leads to poor health and sometimes even death. The main aim of this project was to investigate, analyze and monitor the Umgeni River surface water, sediment pore water, surface sediment and bank soil with regard to selected toxic and priority organic pollutants, especially persistent organic pollutants known as pesticides and polychlorinated biphenyls (PCBs).

1.10 OBJECTIVES OF THE PROJECT

South Africa is among many other countries that played a major role in the negotiation and implementation of the Stockholm Convention on POPs. In December 2000, the final text of the convention was successfully negotiated in Johannesburg (Vosloo and Bouwman, 2005). South Africa ratified it on 23rd May 2001. It also played a leading role in the development of a strategic approach to international chemical management (SAICM) (NIP, 2011). This research contribution towards these South African initiatives and engagements is therefore needed; and, it is in this framework, the project of "Analysis and quantification of persistent organic pollutants in the Umgeni River" fits. The specific objectives of this study were:

➢ To determine the existence of selected toxic and priority organic pollutants such as the dirty dozen in surface water, sediment pore water, surface sediment and bank soil samples collected from the Umgeni River.

➢ To determine the distribution and fate of 8 selected PCBs and 12 OCPs in the Umgeni River water, pore water, sediment and river bank soil.

➢ To quantify two categories of pollutants (selected pesticides and PCBs) found in the Umgeni River water, sediment pore water, surface sediment and river bank soil.

➢ To assess the Umgeni River water quality by comparing the concentrations determined experimentally with international standards and concentrations detected in other parts of the world.

➢ To monitor the seasonal variations of OCPs and PCBs in the Umgeni River for one year

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CHAPTER TWO
REVIEW OF PERSISTENT ORGANIC POLLUTANTS

2.1 INTRODUCTION AND BACKGROUND

The increasing health risk caused by persistent organic pollutants is a global problem. On the 7th of June 1978, a court settlement known as "EPA Consent Decree" involving EPA and several other environmental complainants was put in place and one of its components was a list of 65 classes of toxic chemicals known as "toxic pollutants list" (Keith and Telliard, 1979b). However, this toxic pollutants list had some shortcomings in that each of the 65 classes of compounds comprised of several individual compounds and this would make difficult the development of analytical methods for their analysis, since their physical and chemical properties were different. To avoid analytical challenges caused by the above toxic pollutants list, EPA established a more detailed and specific list comprised of 129 individual compounds as the "list of priority pollutants" (Callahan et al., 1979, Chapman et al., 1982).

Later in 1981, the EPA removed three compounds from the above list of pollutants because their properties did not satisfy their inclusion on the list. These pollutants were dichlorodifluoromethane, trichlorofluoromethane and bis(chloromethyl) ether, and hence reduced the current list of priority pollutants to 126 specific compounds (EPA, 2012, Chapman et al., 1982b). The high priority given to these specific pollutants is because these compounds were frequently found in wastewater and hence were used to develop water quality criteria and establish limits for effluent guidelines (Chapman et al., 1982b).

Among the compounds that made the priority pollutants list, were compounds that remained in the environment for long periods of time and resisted chemical, photolytic or biological degradation. They also bioamplifed through food chains and extended their effect to areas where they were not manufactured or utilized due to their long-range transport (Alegria et al., 2008, Park et al., 2011). These chemicals were characterized as persistent organic pollutants (POPs) (Buccini, 2003).

2.2 PERSISTENT ORGANIC POLLUTANTS

Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin that are toxic and bioaccumulative. They are resistant to photolytic, chemical and biological degradation and may remain in the environment for long periods and can be widely distributed geographically since they are capable of long-range transport (SETAC, 1998). They are therefore found in areas where they have never been used or produced. POPs are highly hydrophobic and consequently can easily bio-accumulate in the fatty tissues of living organisms and can be integrated into the food chain by bio-magnification. POPs also cause undesirable health effects in humans and animals including mainly chloracne, hyperpigmentation, endocrine disruption, immune-nervous and reproductive system defects and even cancer (WHO, 2003a). In 2005, Vosloo, R. and Bouwman, H. carried out a survey of certain POPs in 22 major South African waters and reported that all 22 main waters contained polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at different concentrations. According to the above-mentioned report, the PCB-toxic equivalent (PCB-TEQ) of Umgeni River mouth was 0.32 ng/kg and 1.19 ng/kg for PCB and PCDD/PCDF respectively (Vosloo and Bouwman, 2005). These pollutants cause health risks to dwellers along the Umgeni River, be it humans, animals, aquatic life and microorganisms. Studies have also been carried out on the toxicity of halogenated aromatics which has led to the development of structure-activity relationships for this class of compounds (Safe, 1990).

2.3 TRANSPORT OF PERSISTENT ORGANIC POLLUTANTS

Since the POPs that were investigated in the Umgeni River were not necessarily produced and/or used in KwaZulu-Natal or in South Africa, an understanding of the means of long-range transport of these POPs is in order. There are many ways by which these chemicals can reach areas long distances from where they are produced or used. The first means of movement is air transportation. When these compounds are in gaseous phase they are transported by air currents and travel long distances since they are resistant to degradation. Once they reach cold regions, they tend to condense and pollute that region along with its biota. Studies by Kallenborn and co-workers on atmospheric transport of POPs identified air transportation, as the main source of

contamination of Bear Island (Norway) (Kallenborn et al., 2007). Research has shown that dust clouds containing POPs and microorganisms can cross vast expanses such as the Atlantic and Pacific Oceans from Asia and North Africa and reach North America within only a few days (USEPA, 2002, Atlas and Giam, 1981, Oehme and Mane, 1984).

The second means of movement of POPs is water transport, whereby because of their low solubility in water, a significant amount of organic pollutants can be transported long distances *via* oceans and even other small water bodies like rivers. The total concentration (dissolved+particle-bound) of a pollutant in a body of water at a fixed point, results from a combination of sources, sinks and mechanical transport of a flow disribution. The flow disribution plays a key role in determining the pollutant's distribution in sea water systems (Ilyina et al., 2006).

The third means of movement is transportation by migratory species of animals and bird life. Pollutants are transported from one place to another by harvesting or migratory species such as birds and fish. Many animals change their habitat for various reasons. Birds migrate between hunting regions due to seasonal variation of their prey and some fish like salmon reproduce in fresh water but the adults spend their lives in the ocean. Research has found that before migration, these species accumulate lipids that will be used for energy and gonad development during the migration journey (Ewald et al., 1998). It is during this build-up of lipids that the amassing of concomitant lipophilic organic pollutants, especially POPs, also occurs (Vosloo and Bouwman, 2005, USEPA, 2002) which is then transferred to new migratory areas.

The fourth means is trading. This is an anthropogenic transport whereby pollutants are taken to different regions *via* trade of POP products such as pesticides or *via* POP contaminated products or wastes (Vosloo and Bouwman, 2005). Due to their major mode of chemical transport behavior on a global scale through air, transferring to higher latitudes and their movement through water currents, POPs were classified as flyers, multi-, single hoppers and swimmers respectively (Lohmann et al., 2007a, Wania, 2000).

2.4 THE DIRTY DOZEN

The health threats caused by POPs became of global concern to the extent that the governing council of the United Nations Environmental programme (UNEP) decided to start an investigation on POPs in May 1995, beginning with a short list of twelve pollutants known as the "dirty dozen". The dirty dozen is a group of twelve toxic persistent organic pollutants. These POPs are potentially lethal in high concentrations. It was approximated that out of 1215 cases registered in Ghana, 74 deaths resulted from organochlorine pesticide poisoning due to consumption of contaminated food and water and breathing contaminated air (GNIP, 2007). Investigations in the Sindhikela village of Orissa state of India in 2008, showed that out of 65 cases of pesticide poisoning, 3% resulted in death due to contaminated water (Panda et al., 2009). Exposure to pesticides can cause health problems including liver and kidney diseases, they are disruptors of immune, endocrine, reproductive and nervous systems and most of them are carcinogenic (Schecter et al., 2006). Most of the compounds on the "dirty dozen" list were used as pesticides for protecting crops while others were used for the control of diseases such as malaria, and are still used in certain countries for the same purpose even today. The table below (Table 2.1) shows their global historical use and their current status in the United States of America (EPA, 2009, SCPOPs, 2014).

The "dirty dozen" were among those compounds discussed during an international environmental treaty signed in Stockholm in Sweden, on 22nd May 2001 and operational since May 2004, known as the Stockholm Convention on Persistent Organic pollutants (SCPOP). The aim of this convention was to eliminate or severely restrict the production and use of POPs (Miniero and Lamiceli, 2012). The provision also allowed the identification of new POPs; hence during the 4th conference of SCPOP parties, held in Geneva from 4-8th May 2009, in addition to the dirty dozen, the following contaminants were included on the list of POPs: α-HCH, β-HCH, γ-HCH (lindane), chlordecone, hexabromobiphenyl, hexabromodiphenyl ether, heptabromodiphenyl ether, pentachlorobenzene, tetrabromodiphenyl ether, pentabromodiphenyl ether, perfluorooctanesulfonic acid (PFOS) and its salts and perfluorooctanesulfonyl fluoride (PFOSF). The 5th conference held in Geneva in April 2011 also included endosulfan and the 6th

Table 2.1 List of the "dirty dozen" pollutants, their use and current US status (EPA, 2009, SCPOPs, 2014)

POP	Global historical use/source	Overview of U.S. Status	Cas No.
Aldrin and Dieldrin	Insecticides used on crops such as corn and cotton; also used for termite control.	1. No U.S. registrations; most uses cancelled in 1969; all uses by 1987. 2. All tolerances on food crops revoked in 1986. No production, import, or export	309-00-2 60-57-1
Chlordane	Insecticide used on crops, such as vegetables, small grains, potatoes, sugarcane, sugar beets, fruits, nuts, citrus, and cotton. Used on home lawn and garden pests. Also used extensively to control termites	1. No U.S. registrations; most uses cancelled in 1978; all uses by 1988. 2. All tolerances on food crops revoked in 1986. No production (stopped in 1997), import, or export. Regulated as a hazardous air pollutant.	57-74-9
DDT	Insecticide used on agricultural crops, primarily cotton, and insects that carry diseases such as malaria and typhus.	1. No U.S. registrations; most uses cancelled in 1972; all uses by 1989. 2. Tolerances on food crops revoked in 1986. No U.S. production, import, or export. DDE (a metabolite of DDT) regulated as a hazardous air pollutant. Priority toxic pollutant in 1986	50-29-3
Endrin	Insecticide used on crops such as cotton and grains; also used to control rodents.	No U.S. registrations; most uses cancelled in 1979; all uses by 1984. No production, import, or export. Priority toxic pollutant.	72-20-8
Mirex	Insecticide used to combat fire ants, termites, and mealy bugs. Also used as a fire retardant in plastics, rubber, and electrical products.	No U.S. registrations; all uses cancelled in 1977. No production, import, or export	2385-85-5
Heptachlor	Insecticide used primarily against soil insects and termites. Also used against some crop pests and to combat malaria.	1. Most uses cancelled by 1978; registrant voluntarily cancelled use to control fire ants in underground cable boxes in early 2000. 2. All pesticide tolerances on food crops revoked in 1989. No production, import, or export.	76-44-8
Dioxins and Furans	Unintentionally produced during most forms of combustion and, and industrial processes. Wood preservatives, and in PCB mixtures.	Regulated as hazardous air pollutants. Dioxin in the form of 2, 3, 7, 8-TCDD is a priority toxic pollutant.	various
Toxaphene	Insecticide used primarily on cotton.	Most uses in the U.S. were banned in 1982, and all uses in 1990.	8001-35-2
HCB	Pesticide and fungicide used on seeds, also an industrial by-product	Not widely used in the United States since 1965.	118-74-1
PCBs	Polychlorinated biphenyls, widely used in electrical equipment and other uses.	Manufacture of PCBs banned in the United States in 1977.	various

conference in April-May 2013, added hexabromocyclododecane to the list of POPs. All these modifications came into force on 26 November 2014.

This project particularly focused on the following organochlorine pesticides HCH, HCB, heptachlor, aldrin, DDT and its metabolites (*o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE and *p,p'*-DDE), dieldrin, endrin, mirex and PCBs. All the above pesticides and PCBs are recommended by the Stockholm Convention for environmental monitoring.

2.5 ORGANOCHLORINE PESTICIDES

Organochlorine pesticides (OCPs) are hydrocarbons that contain chlorine atoms in their structures. These compounds were mainly used in agriculture to protect crops from pests and also in disease control especially for malaria (Hogarh et al., 2014). Today they are globally banned or their use and production is restricted by SCPOPs due to their multiple health effects. For example, it was estimated that every year three million people are poisoned with pesticides worldwide and among them about 200,000 die, with most cases reported in developing countries (FAO/WHO, 2000, Sarkar et al., 2008a).

2.5.1. Hexachlorocyclohexane (HCH)

2.5.1.1. Chemical and physical properties
HCH ($C_6H_6Cl_6$) has a molar mass of 290.8 g/mol and comprises of five isomers including α, β, γ, δ and ε-HCH (Figure 2.1). This pesticide was not considered as a POP initially, but due to its characteristics such us persistence, bioaccumulation, bio-amplification, toxicity and long-range transport, it was, later, in May 2009, included and considered by SCPOPs and consequently was banned. It was an effective insecticide for the protection of crops such as cotton, cereals, sugar beet and oilseed from insects such as leaf hoppers, stem borers and wireworms (INCHEM, 2001). The technical product which appears as solid flakes or a yellow or white powder, is normally a mixture of the above-mentioned isomers but γ-HCH or lindane, which is the principal component (40-45%) is more toxic than the other isomers (Willet et al., 1998). The comparison of γ-HCH with other OCPs showed that it is more soluble (7.3 mg/L) in water and more volatile.
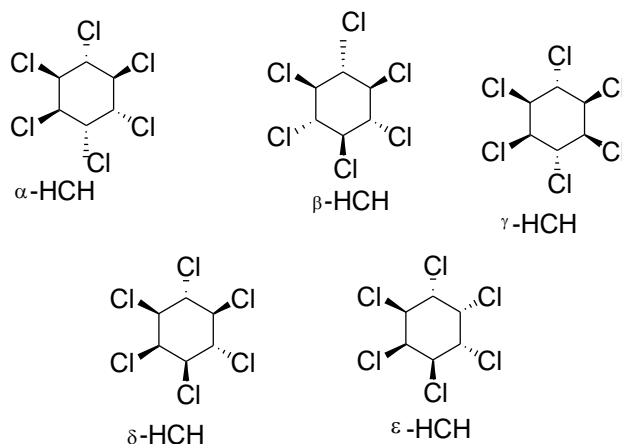
Figure 2.1 Chemical structures of HCH-isomers

2.5.1.2. Sources of HCH

Although its use and production were severely limited, its residues are still detected in the environment. It is believed that it enters the environment due to leaching from waste disposal sites and also from its use in controlling lice and mites in different countries (ATSDR, 2007a, Bhatt et al., 2009). Its use for agricultural purposes to increase crop yields is a non-point source through run-off, as well as atmospheric deposition and industrial wastewater also contribute to its presence in the environment (Mishra et al., 2013, Iwata et al., 1994). Note that technical HCH was globally banned before the year 2000 and China and India were its world first producers and users and hence the two main sources of this pesticide (Li and Macdonald, 2005).

2.5.1.3. Environmental fate

HCH persists in various matrices of the environment. In the atmosphere, HCH can exist in the form of vapour or bound to solid particulates such as dust. The particulate bound form is more persistent than the gaseous form (ATSDR, 2007a). For example, concentrations of 1000 pg/m^3 were detected in air samples over the Bay of Bengal and the Arabian Sea, while in surface water its concentrations were higher than 1000 pg/L due to climatic factors (Iwata et al., 1993). Due to its low polarity, once released or atmospherically deposited, it tends to associate with soil and sediments where its half-life was approximated to 15 months (Andreu and Pico, 2004, Sarkar et al., 1997). HCH can also be absorbed by plants from soil or immediately absorbed though leaves. This pesticide has been detected in various plant materials such as tree bark, pine needles,

lichens, moss, and mango leaves (Willet et al., 1998) as well as animals and birds (Dhananjayan, 2012, Charruau et al., 2013). Studies revealed that HCH was one of the most abundant organochlorine residues in tree bark samples collected from around the world (Simonich and Hites, 1995). However, algae, fungi and bacteria are able to break down HCH to less toxic components (Manonmani et al., 2000, Lal et al., 2010).

2.5.1.4. Health effects

Considering insecticidal activity, γ-HCH (CAS No. 58-89-9) is the most active of all HCH isomers which targets primarily the central nervous system and causes long-term psychological and neurological complications (Willet et al., 1998). The brutal convulsions resulting from stimulation of the CNS normally causes death, if not recovered within 24 hours (Smith, 1991). Other HCH affected organs include renal and liver function, haematology, and biochemical homeostasis. A study by Xu and co-workers showed that the population living in areas where there is high γ-HCH contaminated soil in China, were exposed to high cancer-risks (Xu et al., 2013).

2.5.2. Hexachlorobenzene (HCB)

HCB (C_6Cl_6) (Figure 2.2) was detected in all matrices of water, air and biota worldwide (Muir et al., 1992, Smonich and Hites, 1995, Fellin et al., 1996, Guzzella et al., 2005). Its historical use includes use as a fungicide for crops such as onion, sorghum and wheat, and in the manufacture of synthetic rubber. Nowadays, it is banned in most countries and is mentioned on the list of SCPOPs (UNEP, 2005a).
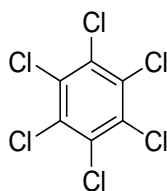
Figure 2.2 Chemical structure of hexachlorobenzene

2.5.2.1. Chemical and physical properties

HCB is a polychlorinated aromatic hydrocarbon. At ambient temperature, it appears as a white crystalline solid insoluble in water (solubility: 0.0062 mg/L at 25 °C) but soluble in organic solvents such as ether, benzene, chloroform etc. The boiling point and melting point are 323-326 and 231 °C respectively. Its moderately high lipophilicity (log K_{ow} = 5.50) induces its bioaccumulation (MECW, 2005). The technical HCB for agricultural use is a mixture of 98% HCB, 1.8% pentachlorobenzene and 0.2% tetrachlorobenzene (ATSDR, 2002a).

2.5.2.2. Sources

HCB was first introduced as a fungicide in 1945, but was banned in most countries in 1960. Its presence in environmental compartments originated from different sources such as industrial and agricultural application, a by-product produced unintentionally during industrial chemical processes and incomplete combustion processes (Bailey, 2001). Its residue may also result from its historic use as a fungicide. It was reported that lindane can be biologically transformed into HCB in mammals and in plants during its metabolism (Gopalaswamy and Aiyar, 1984, Kohli et al.,1976, Steinwandter and Schulter, 1978).

2.5.2.3. Environmental fate

HCB is persistent in the environment. Its half-life was approximated to 1.9 years in air and 6.3 years in water and sediment (MacKay et al., 1992). Its hydrophobicity results in its preferential partitioning from any fluid matrices, be it water or air, into sediments, soils or plants. It is also known for its bioconcentration in the lipid tissues of organisms, due to its lipophilicity (Gabrielsen et al., 1995). Finally HCB was also reported in foodstuffs such as vegetables, fruits, milk, eggs, meat, oils, fish and seafood which is another means of exposure for humans (Falcó et al., 2003, Kannan et al., 1992a, Kannan et al., 1994a, Kannan et al., 1994b, Nakata et al., 2002b).

2.5.2.4. Health effects

Animals and humans are intoxicated by HCB mostly by ingestion of contaminated food. Experiments carried out on animals showed that HCB caused acute toxicity, chronic toxicity, porphyria, genetic toxicity and carcinogenicity. The most marked effect of HCB in humans was shown in Turkey between 1954 and 1959, where patients ingested HCB-treated seeds. Among

the symptoms shown by the patients, included photosensitive skin lesions, hyperpigmentation, hirsutism[3], colic, severe weakness, porphyrinuria[4], and debilitation with a mortality rate of 14%. (IARC, 1979, Peters et al., 1966, Ecobichon, 1996, Glynn et al., 2003). Research showed that if pregnant women and those with suckling infants swallowed the seeds, they transferred the HCB to their children through placental transfer and maternal milk (Ando et al., 1985, Eggesbø et al., 2009).

2.5.3. Heptachlor (Hpchlor)

Hpchlor (Figure 2.3) was, in the past, manufactured essentially as an insecticide used in homes and buildings and on food crops. Since 1988, it was no longer permitted for such uses in the US. It was used in controlling fire ants in transformers (ATSDR, 2002b).
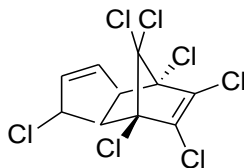
Figure 2.3 Chemical structure of heptachlor

2.5.3.1. Chemical and physical properties

Heptachlor ($C_{10}H_5C_{l7}$) also known as 3-chlorochlordene, is a white crystalline solid with a molecular weight of 373.32 g/mol. Its melting and boiling points are 95-96 and 145 ^{o}C respectively. Its solubility in water is 0.05 mg/L at 25 ^{o}C and log K_{ow} = 5.34 (Noegrohati and Hammers, 1992). Heptachlor can quickly oxidise into 2,3-heptachlor epoxide and is a reaction that occurs photochemically and biologically in the natural environment (Davidow and Radomski, 1953). The heptachlor epoxide then formed is the major contaminant, is very stable and more persistent in the environment than heptachlor (NAS, 1977).

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[3] Excessive hair growth in certain areas of woman's face and body, such as moustache and beard that creates a "male appearance".

[4] The excretion of abnormal concentrations of porphyrins and related compounds in the urine. It is also called purpurinuria.

2.5.3.2. Sources

Hpchlor and hpchlor epoxide originates from different hazardous waste sites. Humans are exposed by consuming contaminated drinking water and contaminated food. In the US, it is still used to control fire ants in buried or underground electric and electronic equipment such as power transformers, television and telephone cable packets (USEPA, 1992).

2.5.3.3. Environmental fate

Hpchlor and its epoxide-like chlorinated pesticides are persistent and hydrophobic, and in the aquatic environment tend to stick to soil, sediment and plants. They also undergo bio-amplification through the food chain. Heptachlor can be metabolised by microorganisms such as rot fungi belonging to genus *phlebia* into its corresponding isomers such as heptachlor epoxide (Xiao et al., 2011) or undergo photolysis and be converted into its photoisomers such as photoheptachlor by exposure to long wave ultra-violet light (Hühnerfuss et al., 2005) (Figure 2.4). This reaction may also be catalysed by sunlight and occurs on the surface of plant leaves (Podowski et al., 1979). Note that the heptachlor photolysis products are more toxic than heptachlor; for instance photoheptachlor is 20, 47 and 264 times more toxic to rats, bluegill, and goldfish respectively (Podowski et al., 1979).
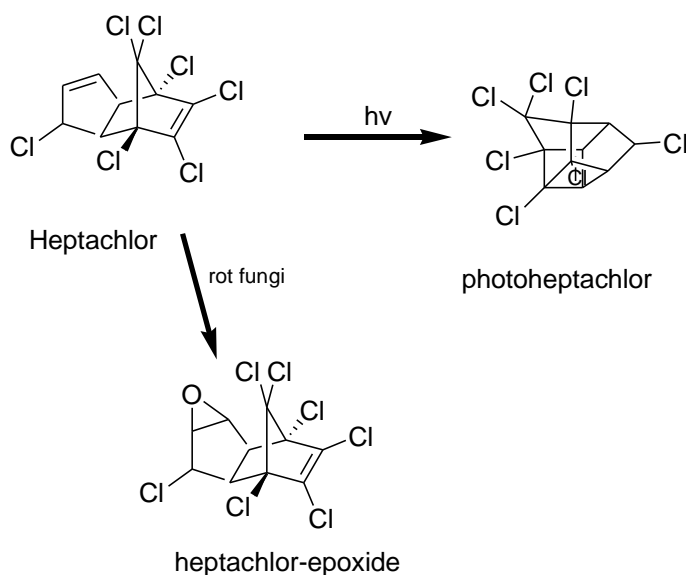
Figure 2.4 Transformation of heptachlor into heptachlor-epoxide and photoheptachlor

2.5.3.4. Health effects

The toxicity of both hpchlor and its epoxide in animals and humans has been reported. The various effects may be due to dermal exposure, oral exposure or inhalation. Experiments done on laboratory animals showed that oral administration of hpchlor caused different diverse effects in various organs such as the liver and reproductive system. It also caused neurological and developmental effects (USEPA, 1992). The very likely target of hpchlor in organisms is lipid-containing cell-membranes which favour its binding due to high hpchlor lipophilicity (Suwalsky et al., 1997).

2.5.4. Aldrin and Dieldrin

Aldrin is very closely related to dieldrin in structure (Figures 2.5 and 2.6). Aldrin biologically breaks down to form dieldrin. It was widely used before 1970 in controlling pests like termites that can damage crops such as corn and potato, as well as for the use of timber preservation, termite-proofing of plastic and rubber coverings of communication cables, and electric and electronic equipment (ATSDR, 2002a). Dieldrin is also an effective insecticide used on fruits and seeds. In addition, it was also used to eradicate disease vectors such as tsetse flies in countries like Botswana, Cameroun, Cote d'Ivoire, Kenya, Niger and Tanzania (GPA, 2000, Kurugundla et al., 2009). Their uses were banned in most developed countries but aldrin is still used as a termicide in some African countries.
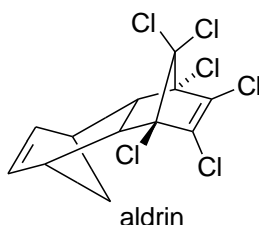
Figure 2.5 Chemical structure of aldrin

2.5.4.1. Chemical and physical properties

Aldrin and dieldrin ($C_{12}H_8Cl_6$ and $C_{12}H_8Cl_6O$) are polychlorinated aromatic hydrocarbons. Their molar masses are 364.91 g/mol and 380.91 g/mol respectively. Both pollutants appear as white crystals. Aldrin and dieldrin have melting points of 104-105.5 and 175-177 ^{o}C, boiling points of

145 and 330 ^{o}C and their solubility in water is 0.20 mg/L and 0.1-0.195 mg/L at 25 ^{o}C respectively (EPA, 2003).

2.5.4.2. Sources

These compounds do not occur naturally in the environment but reach different environmental compartments through anthropogenic activities. Due to its low cost and its effectiveness in killing insects that damage crops, aldrin is still being used either legally or illegally in some developing countries (Zhang et al., 2011a). Aldrin in soil is converted to dieldrin by soil microorganisms such as trichoderma, fusarium and penicilium (Tu et al., 1968, Kumar et al., 2013b). Aldrin and dieldrin may accumulate in soils due to long-term irrigation of soil with industrial effluent and municipal wastewater (Ansari and Malik, 2007, Graaff et al., 2002, Aleem et al., 2003, Aleem and Malik, 2003). Landfills and dumping sites are also among other sources.

2.5.4.3. Environmental fate

Aldrin and dieldrin were detected in different matrices including air, water, soil and biota. Sunlight and microorganisms transform aldrin to dieldrin. This conversion can also occur in the presence of peracetic acid (Nestorovska-Krsteska and Zdravkovski, 2006), therefore dieldrin may be found in matrices which were rich in aldrin in the past. The insolubility of the two substances results in them binding to solid particles in the environment and is the reason for their residue being more concentrated in soil and sediment than in water and air (ATSDR, 2002c). Dieldrin also binds to solid particles in air and as a result may be transported for long distances. It can be absorbed by plants from soil. These chemicals are also known to bioaccumulate and bioamplify through the food chain (ATSDR, 2002c).
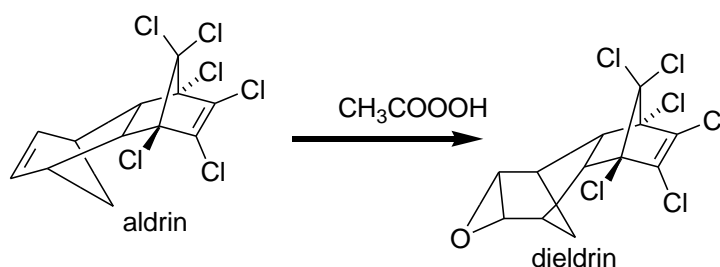
Figure 2.6 Conversion of aldrin into dieldrin in the presence of peracetic acid

2.5.4.4. Health effects

Results of animal experiments suggest that aldrin and dieldrin are possible carcinogens (Walborg et al., 1999). People who were poisoned with aldrin or dieldrin, showed symptoms such as convulsions, kidney damage, dizziness, irritability and vomiting (ATSDR, 2002c). In rats, these contaminants caused hemorrhagic urinary bladders, enlargement of the liver, and an increased incidence of nephritis[5] while in dogs they caused loss of weight and convulsions, kidney and bone marrow changes and even death when the dose was increased (Fitzhugh et al., 1964). Cases of death in humans resulting from aldrin poisoning were reported at Madhya Pradesh in India (Gupta, 2004).

2.5.5. Endrin

Endrin is an insecticide that was used on cotton, sugarcane, rice, cereals, and grains. It can also be used to control mice, rodents and prevent grasshoppers in recreational fields (EPA, 2014). In addition to its ability to accumulate in adipose tissue, it is tremendously persistent with a half-life of about 12 years (UNEP/GPA, 2000).

2.5.5.1. Chemical and physical properties

Endrin, a white and odourless substance with molecular formula $C_{12}H_8Cl_6O$ (Figure 2.7) and molar mass 380.91 g/mol, has melting and boiling points of 235 °C and 245 °C respectively. It is practically insoluble in water (0.200 mg/L at 25 °C) and its Log K_{ow} = 4.56 (Noegrohati and Hammers, 1992); however it is soluble in organic solvents, such as hexane, benzene, dichloromethane, toluene, xylene and acetone (Fan and Alexeeff 1999).
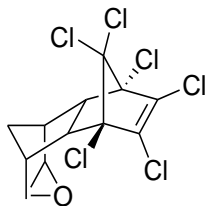
Figure 2.7 Chemical structure of endrin

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[5] Inflammation of the kidneys which may involve the glomeruli.

2.5.5.2. Sources of endrin

Endrin and endrin aldehyde, an impurity and break down product of endrin or endrin ketone which is a product resulting from the reaction of endrin and light, has various sources such as incineration of waste containing endrin, hazardous waste disposal sites, residue on imported food items and unused stock (ATSDR, 1996).

2.5.5.3. Environmental fate

Endrin and its metabolites, endrin aldehyde and endrin ketone, are very persistent, especially in soil onto which they adsorb strongly and tend to become immobile (Kenaga, 1980, Sharom et al., 1980a). Endrin may also make its way into the atmosphere by binding onto air dust particles. Significant levels of endrin transformation products such as endrin ketone, endrin aldehyde and endrin alcohol, have been detected in plants grown in soil treated by endrin as long as 16 years prior to planting (Beal et al., 1972, Nash and Harris, 1973). When endrin reaches water systems, it adsorbs onto sediments and bioaccumulates in aquatic organisms (Swann et al., 1983).

2.5.5.4. Health effects

Endrin is very toxic to aquatic animals such as fish and invertebrates. Studies showed that it causes both acute and chronic toxicity to various avian species as well (Blus et al., 1989). An overdose of endrin was reported to cause death in humans (Baron et al., 1992) and in dogs (Quick et al., 1989). Studies by Reuber confirmed that endrin is carcinogenic for rats (Reuber, 1979). In humans, the target organ is the nervous system where toxic doses of endrin may lead to excitability, convulsions, twitching muscles, mental confusion and seizures which may be followed by death within 2 to 12 hours if no appropriate treatment is administered (UNEP/GPA, 2000).

2.5.6. Dichloro-diphenyl-trichloro-ethane (DDTs)

DDTs include 1,1-dichloro-2,2-bis(*o*-chlorophenyl)ethylene (*o,p'*-DDE), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p'*-DDE), 1,1-dichloro-2,2-bis(*o*-chlorophenyl)ethane (*o,p'*-DDD), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane   (*p,p'*-DDD),   1,1,1-trichloro-2,2-bis(*o*-chlorophenyl)ethane (*o,p'*-DDT) and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT) (Figure 2.8). DDT was first synthesized in 1874 and was widely used in the US as a pesticide.

The production of large amounts of DDT by the US started after the 2nd World War for control of vector-borne diseases including typhus and malaria, and later after 1945 DDT became a popular pesticide due to its low cost and effectiveness as an insecticide (USEPA, 2000). Technical DDT is a mixture of four isomers including 75% *p,p'*-DDT, 15% *o,p'*-DDT, 5% *p,p'*-DDE and trace amounts of *o,p'*-DDD (Metcalf, 1973, Bopp et al., 1982). In 1983 all uses of DDT in agriculture, were banned but DDT is still used today by many countries (including South Africa) as an essential pesticide to fight malaria (NIP, 2011) because it is widely known to reduce malaria effectively (WHO, 2011). In South Africa, four provinces, namely KwaZulu-Natal, Mpumalanga, Limpopo and the North-West are affected by malaria (NDH, 2010) and in 2004, the SCPOPs secretariat allowed an exemption for the use of DDT, for malaria eradication in South Africa (NIP, 2011).
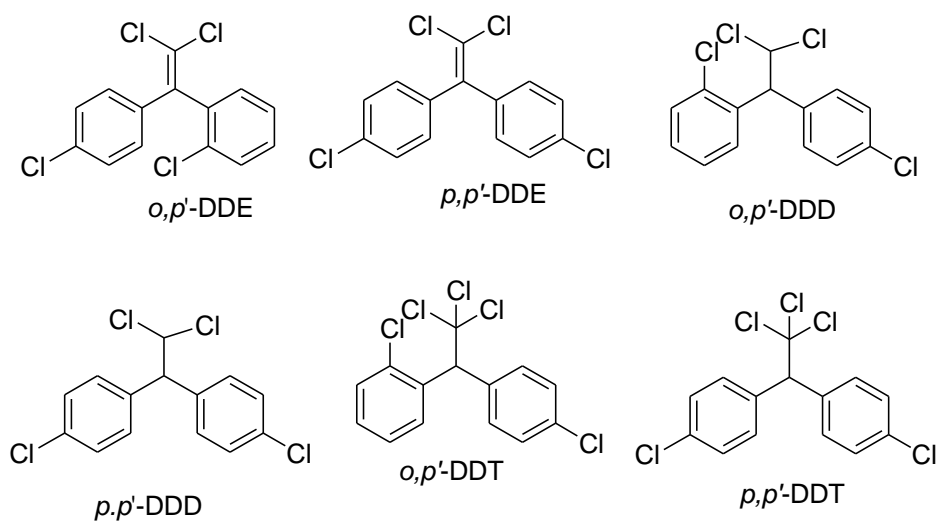
Figure 2.8 Structures of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT

2.5.6.1. Chemical and physical properties

DDT is present as colourless to off-white needles or a powder with a slight aromatic odour at room temperature. The physical and chemical properties of DDT and its metabolites are mentioned in the table below (Table 2.2)

Table 2.2 Physical properties of DDT and its metabolites (HSDB, 2010, Ritter et al., 2005)

Properties	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT
Molecular formula	$C_{14}H_8Cl_4$	$C_{14}H_8Cl_4$	$C_{14}H_{10}Cl_4$	$C_{14}H_{10}Cl_4$	$C_{14}H_9Cl_5$	$C_{14}H_9Cl_5$
Molecular weight	318.03	318.03	320.05	320.05	354.49	354.49
Boiling point (°C), 20 mmHg	†	336	†	350	†	260
Melting point (°C)	†	89	76-78	109-110	74.2	109
Solubility in water (µg/mL) at 25 °C	0.14	0.12	0.1	0.09	0.085	0.025
Partition coefficient (log K_{ow})	6	6.51	5.87	6.02	6.79	6.91
Vapour pressure (mmHg) at 20 °C	6.00×10^{-5}	6.00×10^{-6}	1.94×10^{-6}	1.35×10^{-6}	1.10×10^{-7}	1.60×10^{-7}
Henry constant (atm-m^3/mol) at 25°C	1.80×10^{-5}	2.10×10^{-5}	8.17×10^{-7}	4.00×10^{-6}	5.90×10^{-7}	8.30×10^{-6}

† : data not available

2.5.6.2. Source of DDT

DDT was first synthesised in 1874 by a chemist called Zeidler and in 1945, it was industrially produced in the United States where it was used to control malaria, typhus and body lice (ATSDR, 1994, HSDB, 2009, WHO, 1979). It was also used as a powerful insecticide to control pests against many crops such as beans, cotton, soybeans, sweet potatoes, tomatoes, corn, cabbage, peanuts and other crops (Casida and Quistad, 1998). Following its carcinogenicity, bioaccumulation and several health effects on wildlife, DDT was banned in many countries. In South Africa, its general use was prohibited in the 1980's (DEAT, 2005) but it is still legally used in malaria endemic areas of South Africa (Kumar et al., 2008, Lee et al., 2001) including the northern and eastern parts of Limpopo, the north-eastern parts of Mpumalanga and northern KwaZulu-Natal (Bouwman et al., 1992).

2.5.6.3. Environmental fate

DDT was known as a persistent organic pollutant since 1979 and is almost immobile in soil due to its tendency to associate with it. It therefore tends to be more retained in soil containing much organic matter. DDT can be degraded by environmental phenomena such volatilisation, photolysis, and biodegradation (Beard et al., 2000). DDT has similar properties as its main breakdown products, DDE and DDD in the environment (ATSDR, 2002b). DDT and its metabolites adsorb onto particulate matter once introduced into the environment where sediment is known to be its main "sink". It is also known to bio-magnify through the food chain (Ford and Hill, 1991, Zeng et al., 1999). It also makes its way into the atmosphere due to volatilisation where 50% of it is adsorbed onto solid particles and 50% occurs in the vapour form. However it can be removed from the atmosphere by precipitation or wet and dry deposition back to soil and water bodies (Bidleman, 1988).

2.5.6.4. Health effects

DDT and its metabolites have been detected in water, soil, air, animal and plant tissues and in human blood and milk. Being omnipresent, DDT causes various health effects in animals and humans. The reported health effects in animals are eggshell thinning, alteration of gonad development in birds, it affects organs such as the liver and the nervous system and can also affect reproduction due to endocrine disruption in animals exposed to it (FAO/WHO, 2001, Zeng

et al., 1999). In humans, DDT is metabolised into DDE and DDD and excreted rapidly; however it can be stored in fatty tissue and can potentially cause health effects (ATSDR, 2002b). A study by Bouwman and his team reported that in the Limpopo province, women living in DDT sprayed areas gave birth to 33% more boys with urogenital birth defects than women in unsprayed areas. Cases of leukemia in agricultural workers exposed to DDT, were reported in Lowa and Minnesota (Morris-Brown et al., 1990).

2.5.7. Mirex

Mirex ($C_{10}H_{12}$) (Figure 2.9) is a polychlorinated hydrocarbon that was mainly used to control fire ants. Its use was extended to mitigation of leaf cutter ants especially in South America, mealybugs in Hawaii and harvester termites in South Africa (ATSDR, 1995). It is odourless, inflammable and appears as solid white crystals at room temperature and does not burn easily (HSDB, 2009). The use of mirex was prohibited in 1976.
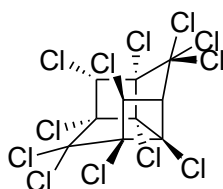
Figure 2.9 Structure of mirex

2.5.7.1. Physical and chemical properties

Mirex is almost insoluble in water (0.6 mg/L at 25 °C) (Kenaga, 1980) but highly soluble in organic solvents such as chloroform, dioxane, benzene, methyl ethyl ketone, and xylene (ATSDR, 1995). It is stable in the environment with a half-life of 10 years. Like other organochlorine pesticides, mirex is persistent, bioaccumulative, toxic and has long-range transport (ATSDR, 1995). Its low water solubility, high lipophilicity and stability allow it to bind to sediments. Its vapour pressure is 3 x 10^{-7} mmHg at 25 °C and its Log K_{ow} is 5.28 (Verschueren, 1983).

2.5.7.2. Sources of mirex

The first synthesis of mirex occurred in the 1940s. It was produced by dimerization of hexachlorocyclopentadiene in the presence of an aluminium chloride catalyst (Sittig, 1980). Its technical mixture contains 95.12% mirex and 2.58% chlordecone. In addition to its insecticidal properties, mirex was used as a fire retardant in plastics, rubber, paint, paper and electrical goods (ATSDR, 1995). Nowadays, the presence of mirex in the environment is due to its historical use, disposal, and accidental spillages and volatilisation, or leaching from old stockpiles.

2.5.7.3. Environmental fate of mirex

The fate of mirex in the environment is mainly governed by processes such as adsorption and volatilisation (ATSDR, 1995). Its presence in soil, sediment and water is due to its capacity to bind to organic particulates and its lipophilicity allows it to biomagnify through the food chain. It can be degraded by photolysis to photomirex (Carlson et al., 1976).

2.5.7.4. Health effects

Mirex has various health effects on both plants and animals. Some plants were reported to have the capacity to uptake and accumulate mirex in their tissues (Mehendale et al., 1972, Rajanna and de la Cruz, 1975). Mirex can also reach plant tissues from the atmosphere by aerial deposition and from volatilisation from soil (Fries, 1995). Animal studies showed that the health effects caused by mirex included loss of body weight, change in liver cell shape and cataract formation. Malignant liver tumours were reported in rats and mice exposed to mirex (Akron, 2009, Bloom et al., 2005). Mirex is also considered a potential human carcinogen (IARC, 1987).

2.6 POLYCHLORINATED BIPHENYLS

2.6.1. Uses and Properties

Polychlorinated biphenyls (PCBs) are a group of 209 chlorinated organic compounds that were artificially synthesised and have been used either as colorants or lubricants in transformers, capacitors and other electric devices (ATSDR, 2014). They were also used in applications such

as plasticizers, surface coatings, adhesives, pesticides, carbonless copy paper, inks, dyes, and waxes. PCBs are persistent with long half-lives (8-15 years) (ATSDR, 2000). PCBs have no known natural sources and can exist as oily liquids or colourless to yellowish solids (ATSDR, 2014). Their solubility in water is very low and their relative octanol-water partition coefficients (K_{ow}) allow them to adsorb to organic matter rather than dissolve in water (Table 2.3). They are resistant to burning and are good insulators, which is the reason for their use in many countries but as a result they build up in the environment causing serious health problems.
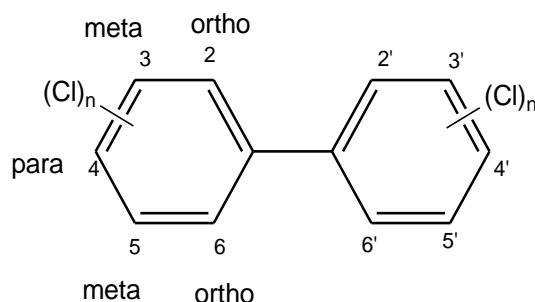
Figure 2.10 General structure of PCBs

They consist of two benzene rings joined by a single carbon-carbon bond that allows the benzene ring to rotate (Figure 2.10). When the benzene rings rotate, the PCB can have a coplanar conformation like that of PCDDs (Schecter et al., 2006) or non-coplanar conformation. Those with coplanar conformation are called 'dioxin-like PCBs' and those with non-coplanar conformation are referred to as 'non-dioxin like PCBs' (Figure 2.11).

Coplanar/non-ortho substituted/ dioxin-like PCBs   Non-coplanar/ortho-substituted/non-dioxin-like PCBs
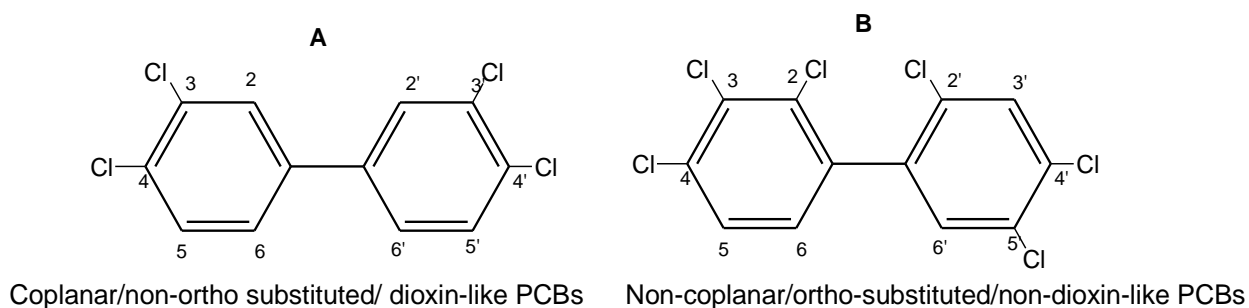
Figure 2.11 Chemical structure of dioxin-like and non-dioxin-like PCBs, with 3,3',4,4'-tetrachlorobiphenyl (PCB77) being representative of dioxin-like PCBs (A) and 2,2',3,4,4',5'-hexachlorobiphenyl (PCB138) being representative of non-dioxin-like PCB (B)

Table 2.3 Chemical and physical properties of PCB congeners investigated

PCB congeners	Formula	Molecular weight	Mp (°C)	Bp (°C)	Water solubility (mg/L)	Log K_{ow}	Vapour pressure (mm Hg at 25 °C)
PCB28	$C_{12}H_7Cl_3$	257.54	57-58	206-207	0.0085	5.69-5.71	2.8×10^{-2}
PCB52	$C_{12}H_6Cl_4$	291.98	87-89	268	0.046	6.09	7.3×10^{-3}
PCB77	$C_{12}H_6Cl_4$	291.98	173	360	0.175	6.53	4.4×10^{-7}
PCB101	$C_{12}H_5Cl_5$	326.43	77	-	0.00012	6.31	2.9×10^{-3}
PCB105	$C_{12}H_5Cl_5$	326.43	-	-	0.0034	6.64	6.5×10^{-6}
PCB138	$C_{12}H_4Cl_6$	360.88	78.5-80	400	0.016	7.44	4.0×10^{-6}
PCB153	$C_{12}H_4Cl_6$	360.88	103-104	no data	0.00091	7.75	3.8×10^{-7}
PCB180	$C_{12}H_3Cl_7$	395.32	109-110	240-280	0.31×10^{-2}-0.66×10^{-1}	6.82-7.37	-

(HSDB, 2010, Ritter et al., 2005, Shiu and Mackay, 1986)

2.6.2. Sources of PCBs in the Environment

PCBs originate mostly from industries where they are formed as by-products. However, they can also be generated by combustion processes of PCB-containing waste such as incineration of municipal hazardous and medical waste as well as the release of fumes from vehicle exhausts (Safe, 1994, Ritter et al., 2005) (Figure 2.12). The occurrence of PCBs in the environment was first observed by Jensen in 1966 by investigating wildlife and human samples (Jensen, 1989).

PCBs can also be distributed into the environment by PCB-containing equipment such as railroad transformers, heat transfer systems, hydraulic systems, mining equipment, natural gas pipelines, scientific instruments such as oscillatory flow birefringence[6] and viscoelasticity[7], electromagnets, switches, voltage regulators, circuit, breakers, recloses and cables (USEPA, 2002).
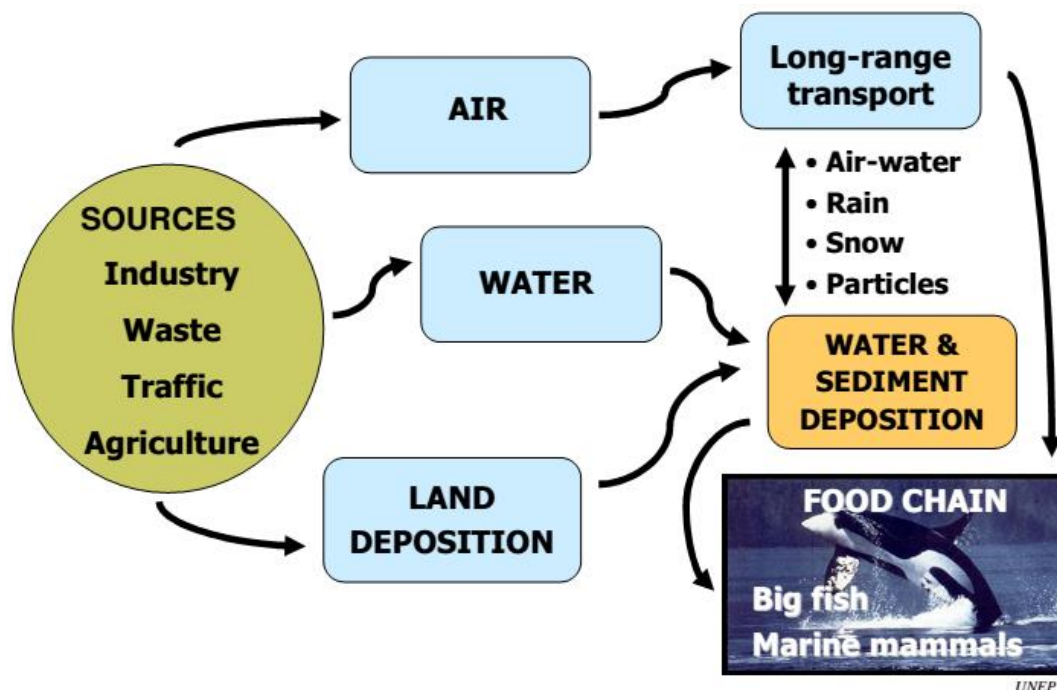
Figure 2.12 Sources and dissemination of OCPs and PCBs in the environment

(adapted from (WHO, 2008))

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[6] Optical property of a material having a refractive index that depends on polarization and propagation direction of light.
[7] Property of materials that exhibit both viscous and elastic characteristics when undergoing deformation.

2.6.3. Environmental Fate of PCBs

While in the environment, PCBs can be degraded in different ways such as biological and chemical transformations. In the case of such transformations, the negative environmental effects are minimised (Abramowicz, 1995). PCBs are decomposed into simpler compounds by enzymes produced by microorganisms. This biological degradation can occur either in the form of mineralisation, whereby the organism uses the pollutant as its source of carbon and energy and reduces it into its simple elements, or in the form of co-metabolism in which the source of carbon and energy for the microorganism is another substance, it is reduced together with the concerned pollutant (Dobins, 1995). PCB biodegradation may take place in the absence of oxygen where it is termed 'anaerobic' degradation or in the presence of oxygen where it is called 'aerobic' degradation.

2.6.3.1. Anaerobic transformation of PCBs

The anaerobic dehalogenation phenomena was observed for the first time on substances detected in Silver Lakes and the Hudson River anaerobic sediments in Massachussetts (Brown et al., 1987a). In anaerobic transformation, the chlorinated organic compounds are dehalogenated where they become electron acceptors and consequently are reduced by substitution of chlorine by hydrogen (Morris et al., 1992, Quensen et al., 1990).

$$R\!-\!Cl + 2e^- + H^- \longrightarrow R\!-\!H + Cl^-$$
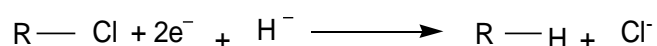
Some examples of dechlorinating bacteria which can degrade PCBs in soils and sediments include *desulfitobacterium, dehalobacter restrictus, dehalospirillum multivorans, desulforomonas chloroethenica* and *dehalococcoides ethenogenes* (Mohn and Tiedje, 1992). It was reported that temperature has a significant effect on dechlorination because there is an optimum temperature at which the growth of dechlorinating bacteria and enzyme catalytic activity are at maximum (Wiegel and Wu, 2000). In the process of dechlorination, the PCB loses its chlorine one by one resulting in its degradation (Figure 2.13).
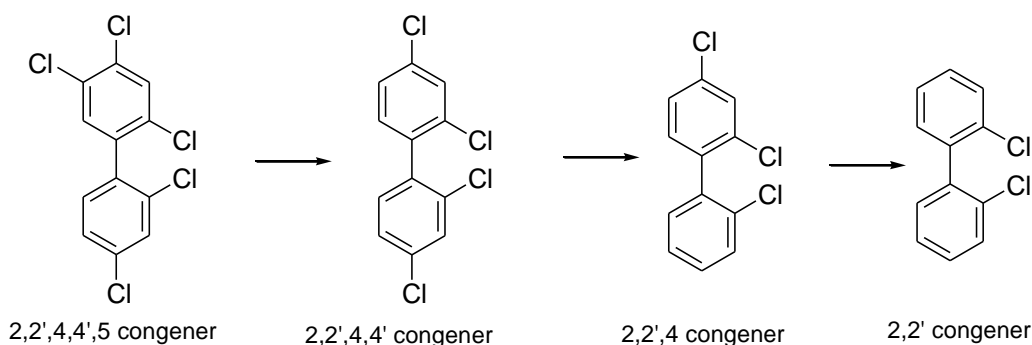
Figure 2.13 Potential pathway for anaerobic dechlorination of a highly chlorinated congener

(Fish and Principe, 1994)

2.6.3.2. Aerobic transformation of PCBs

The persistence of PCBs increases with their increasing degree of chlorination. The aerobic biodegradation occurs only for the low molecular weight PCBs and implicates the cleavage of the biphenyl ring (Fish and Principe, 1994). The responsible bacteria for PCB aerobic biodegradation includes *achromobactor, nocardia sp, micrococcus sp* and *pseudomonas sp* (Ahmed and Focht, 1972, Baxter et al., 1975). In aerobic oxidative degradation, the first step involves conversion of PCBs to chlorobenzoic acid (Figure 2.14) and the second step is the degradation of chlorobenzoic acid.
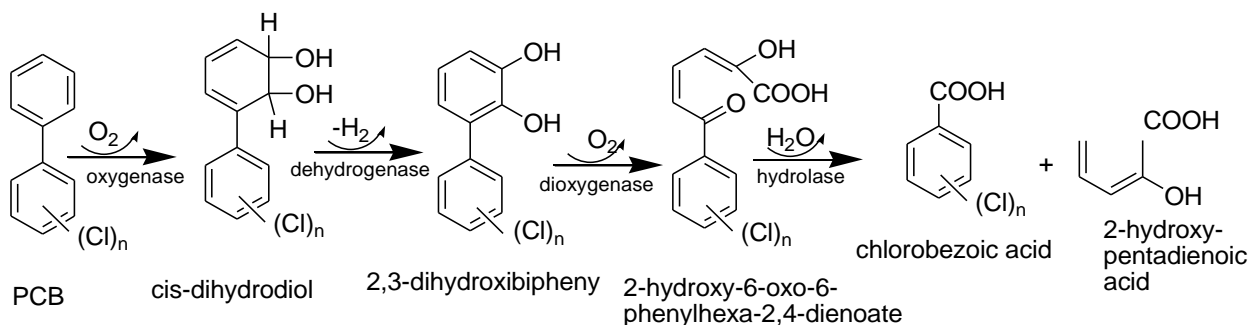
Figure 2.14 Major steps in the degradation of PCB into chlorobenzoic acid

(Sylvestre and Sandossi, 1994).

2.6.4. Health Effects of PCBs

PCBs cause a wide range of health effects in animals and humans and this largely depends on their level and position of chlorination on the biphenyl ring (Brouwer et al., 1999). Endocrine systems are among those which are affected by PCBs which include oestrogen and androgen

systems, the thyroid hormone, and retinoid and corticosteroid systems (Brouwer et al., 1999). Skin and hepatic problems such as skin rashes, chloracne, pigmentation of nails and skin and alterations in liver enzymes have been associated with PCB exposure and accidental ingestion of contaminated foods (Aoki, 2001). Also, some reproductive and developmental effects were recorded and these include menstrual disturbances in women and effects on sperm morphology in men which can result in difficulty in conceiving (ATSDR, 2000). Studies reported reproduction and fertility problems in animals such as rats, mice and monkeys (Sager et al., 1991, Sager and Girard, 1991). Immunological and neurological health effects were identified in humans. Problems of numbness, weakness and neuralgia of limbs, hypaesthesia, and headaches were recorded in patients exposed to the outbreak of PCBs that occurred in Yusho and Yu-Cheng in Japan and Taiwan (Chia and Chu, 1985). PCBs also showed inhibitory effects on the immune system of rhesus monkeys due to alteration of T-cells (ATSDR, 2000, Ritter et al., 2005). Cancer problems have been linked to PCB exposure. This was seen in the form of liver cancer in victims of the Yusho PCB outbreak in Japan. Workers involved in electrical capacitor manufacturing plants in New York and Massachusetts also exhibited cancer-related problems where a number of deaths were observed which was attributed to PCB exposure (Brown and Jones, 1981, Brown, 1987b).

2.7 MONITORING OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS

2.7.1. Introduction

The monitoring and investigation of POPs in general and of OCPs and PCBs in particular, were attempted in South Africa as well as in many countries around the world. The status of OCPs and PCBs in different environmental compartments cannot however, be fully known since the environment is dynamic and its composition changes with time. It is for this reason that regular monitoring is required.

2.7.2. Commonly Used Analytical Methods for Monitoring of OCPs and PCBs

From sampling to the final analysis of the analyte, a certain number of steps must be strictly followed. The isolation and/or enrichment of the analyte is a critical step and maximum care must be taken in order to minimize or avoid errors that may occur such as sample

contamination, analyte loss, diminution of analyte concentration, etc. In the case of organic contaminants such as pesticides and polychlorinated biphenyls in solid phase samples, it is imperative to replace the solid phase matrix in which the analyte sits with a liquid one. The analyte is transferred from the primary matrix such as soil into the secondary one which is normally a solvent. The analyte concentration is then increased to a level above the detection limit of the analytical technique, such as GC-MS and HPLC, to be used. At the end, the method used needs to be validated. The following figure describes the steps involved from sampling to final determination of analyte.
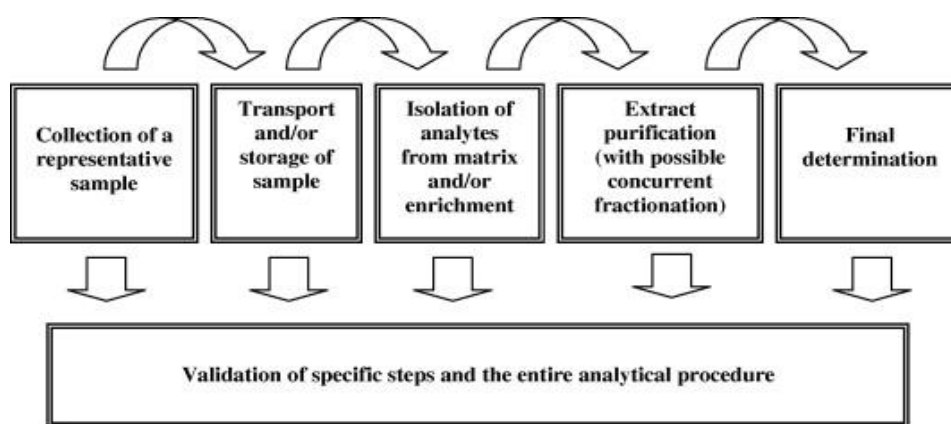
Figure 2.15. Main steps of analytical procedures used for determining organic pollutants (adapted from: Beyer, A and Biziuk, M., 2008).

2.7.2.1. Collection of a representative sample

The collection of a suitably representative sample is fundamental to any environmental analysis or monitoring. In case of samples for PCB analysis, contamination can take place on the field by electrical equipment and building products such as marine paints and joint sealants (Mohler, 2005) or by routine use of OCPs. Precautions must be taken, such as, the use of special clothing and disposable gloves, sealed chipping containers and field blanks (NOAA, 1998). PCB contamination can occur particularly in water samples due to ubiquitous contamination

2.7.2.2. Sample storage

An analytical laboratory involved in analysis of OCPs and PCBs must be equipped with a refrigerator and a freezer for sample storage and archiving. The basic approach is to assure

that the sample is kept in a room free of significant contamination as well as prevent any possible forms of degradation of the sample. A well-ventilated lab and air prefiltered through High Efficiency Particulate Air (HEPA) and carbon filters is ideal but any clean chemical laboratory may be acceptable for most work on OCPs and PCBs (Muir and Sverko, 2006).

2.7.2.3. Extraction and isolation

The extraction and isolation steps are very important in OCP and PCB analysis. Table 2.4 provides general guidance for extraction and isolation steps.

2.7.2.4. Final determination

Gas chromatography-mass spectrometry or high resolution GC-high resolution MS (HRGC/HRMS) are nowadays the most applied methods for analysis of PCBs and OCPs. The main advantage of the above-mentioned techniques is a reasonable precision in determining the identity and concentration of pollutants such as PCBs and OCPs (Safe, 1995). Other methods include biological methods such as bio-markers, cell or organ based bio-assays and protein-binding assays (Behnisch et al., 2001). The weakness of the bioassays is their inability to distinguish between several individual analytes with precision. Table 2.5 provides a general guidance on GC analysis for PCBs and OCPs.

Table 2.4 Extraction techniques used for environmental samples

Technique	Overview	Method reference
Conventional Soxhlet	Sample + desiccant mixture in glass or paper thimble is leached with warm (condensed) solvent for 4–24 hrs. Examples of solvents used are diethyl ether, DCM, hexane, toluene	EPA, 2000
Automated Soxhlet (e.g., "Soxtec")	Extraction thimble is immersed in boiling solvent (30–60 min) then raised for soxhlet extraction. Solvent can also be evaporated	EPA, 200
Supercritical fluid extraction (SFE	Sample (usually +desiccant) placed in high-pressure cartridge, and carbon dioxide at 150–450 atm and temp of 40–150 °C passed through. After depressurization, analytes are collected in solvent trap	EPA, 1996
High-speed blending	Useful for high water content samples such as plant material. Homogenizes sample with acetone and NaCl.	USFDA, 1999 Specht, 1995
Column extraction	Sample (+desiccant) placed in large column with filter and stopcock. Eluted with large volume of extraction solvent, e.g., hexane:DCM; hexane	Ribick, 1982
Sonication-assisted extraction	Sample in open or closed vessel immersed in solvent and vibrated with ultrasonic radiation using ultrasonic bath or probe	EPA, 2007
Microwave-assisted extraction (MAE)	Sample in open or closed vessel immersed in solvent and heated with microwave energy.	EPA, 2007
Pressurized liquid extraction (PLE)	Sample (usually +desiccant) placed in extraction cartridge and solvent (heated, pressurized) passed through then dispensed in extraction vial.	EPA, 1995 EPA, 2000
Liquid-liquid extraction	Sample + large volume of suitable solvent placed in separatory funnel and extracted 3 or more times with fresh solvent; eg DCM, hexane, etc	EPA,1996

Table 2.5 General guidance on GC analysis for PCBs and OCPs (Muir and Sverko, 2006)

GC detector	Analyte	Configuration	Advantages/disadvantages
Capillary GC - with electron capture detection	All ortho-subsituted PCBs & all OCPs on the POPs list except toxaphen	30 or 60 m×0.25 mm id. Column with H_2 carrier gas. Dual column nonpolar (DB-1) and intermediate polarity columns (DB-5)	Relatively inexpensive and easy to operate. Similar response factors for most OCs. Good sensitivity for all POPs. Adequate for routine tasks. High potential for misidentification of some POPs due to coeluting peaks
Quadrupole mass spectrometry in electron ionization (EI) mode	All PCBs & all OCPs on the POPs list except toxaphene	30 m×0.25 mm i.d. low-bleed columns with He carrier gas. Selected ion mode for target POPs	Moderately expensive and more complex to operate and maintain. Newer instruments (post 1997) have adequate sensitivity for routine POPs monitoring at low pg/μL concentrations. Much less potential for misidentification than with ECD.
Quadrupole mass spectrometry in electron capture negative ionization (ECNIMS) mode	Toxaphene and other highly chlorinated OCPs and PCB with >4 chlorines	30 m×0.25 mm i.d. low-bleed columns with He carrier gas. Selected ion mode for target POPs	Comparable sensitivity in ECNIMS mode to ECD in SIM mode for some POPs. Much less potential for misidentification than with ECD.
Ion trap mass spectrometry using MS/MS mode	All PCBs, All OCPs on the POPs list	30 m×0.25 mm i.d. low-bleed columns with He carrier gas. Same columns as quadrupole MS	Comparable sensitivity to ECD in MS/MS mode for some POPs. Much less potential for misidentification than with ECD.
High-resolution magnetic sector mass spectrometry in electron ionization (EI)	All PCBs, all OCPs on the POPs list except toxaphen	30 m×0.25 mm i.d. low-bleed columns with He carrier gas. Selected ion mode for target POPs at 10,000× resolution	Comparable sensitivity to ECD in SIM mode. Highly reliable identification at low pg/μL level

2.7.3. Global Monitoring of OCPs and PCBs

POPs are ubiquitous in the environment and may have anthropogenic origin such as industrial processes, waste, agriculture and traffic; but may also come from natural sources such as volcanic eruptions (WHO, 2008). They can even be present in areas where they have never been produced or used due to their worldwide distribution through air and ocean currents (WHO, 2008). Their presence in the environment has become a global problem in the last decade. While polycyclic aromatic hydrocarbon (PAH) transport and deposition are mainly associated with solid atmospheric particles, the movement of organochlorine pollutants such as OCPs and PCBs, which are the major constituents of POPs, from the atmosphere to terrestrial and aquatic systems is governed by gas exchange (Fernández and Grimalt, 2003). The worldwide distribution of POPs is facilitated by certain mechanisms including "global distillation effect and cold condensation" whereby the pollutants in the form of a gas are transported from warm to cooler regions of the globe and the "grasshopper effect" in which there is exchange of contaminants between air and terrestrial surfaces (Wania and Mackay, 1996) (Figure 2.15). This last mechanism is dependent on seasonal temperature variation and this is the reason why POPs are trapped in Polar Regions where the temperature is very low. This phenomenon is called "cold finger or cold trap" (Fernández and Grimalt, 2003).
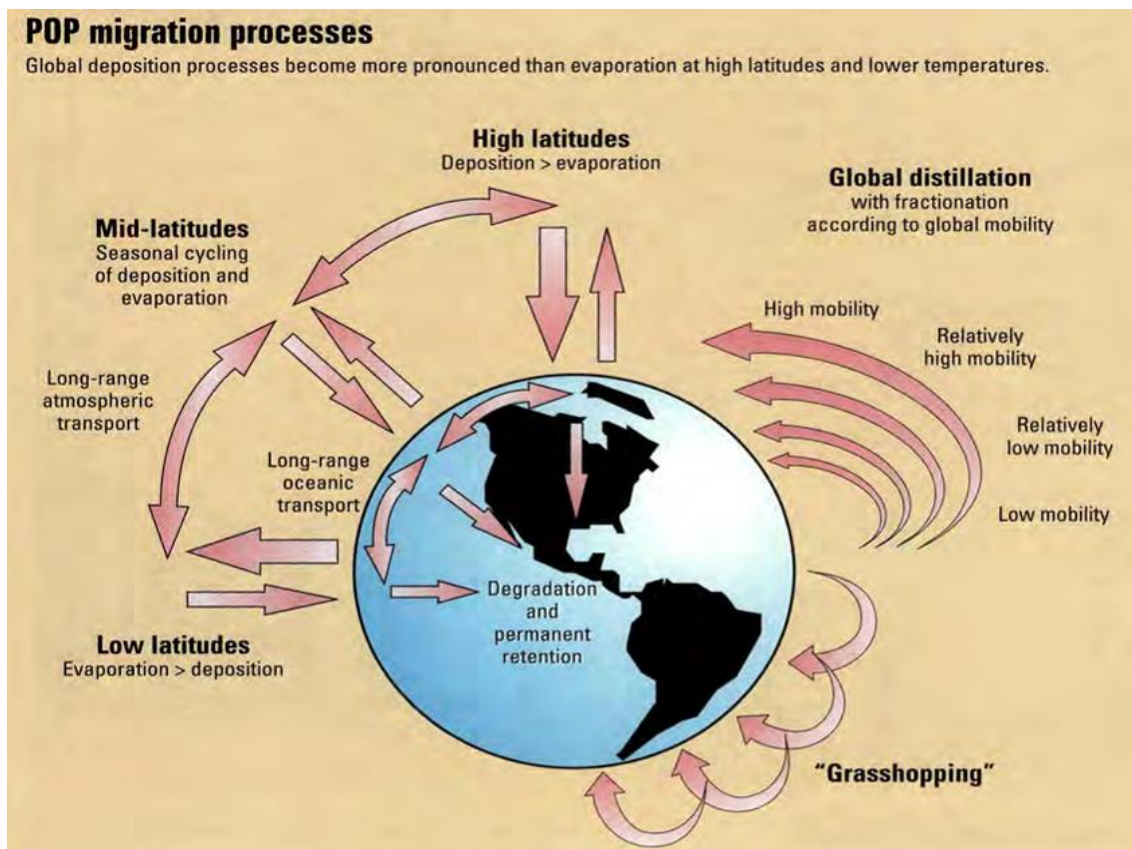
Figure 2.16 POP migration processes

(adapted from: (Wania and Mackay, 1996))

This is also the reason for their presence in arctic regions which are thousands of miles away from any known source (EPA, 2009). Since pollution by POPs such as OCPs and PCBs is a global issue, a global solution must be found in order to reduce or eradicate it. It is for this reason the international environmental treaty known as the Stockholm Convention was put in place in 2001 and was effective from 2004 in order to take global action aiming to eliminate or restrict the production or use of POPs worldwide (UNEP, 2008). Although restrictions have been put in place, these OCPs and PCBs are still being used in developing countries in Africa and in Asian Pacific regions (Ueno et al., 2003). Using skipjack tuna as a bio-indicator to monitor the organochlorine pesticides global pollution, Ueno and his co-workers found high concentrations (22 to 1300 ng/g lipid weight) of some OCPs such as DDT and HCH in the South China Sea, East China Sea, Japan Sea and Bay of Bengal, and concluded that these pesticides were being used in Russia, China, India and other developing countries on the Asian continent, mostly for

agricultural and public health purposes (Ueno et al., 2003). A study on the global distribution of OCPs and PCBs in 24 countries worldwide, by analysis of butter, revealed that the total concentration of PCBs varied by a factor of 60. Levels of these contaminants in butter were the highest in European and North American countries and lower in the southern hemisphere. The levels of DDT were higher in India, South and Central America and those of HCH were high in India, China and Spain (Kalantzi et al., 2000).

Africa has been a victim of POPs although it hardly produces any. This is because in the 1980s the African continent was chosen as a dumping site for European waste (Bernstorff and Stairs, 2001). Africa is still vulnerable to hazardous waste trade from industrialized countries such as the UK, Germany, France and USA in exchange for foreign currency which is much needed in most developing African countries (Koné, 2010). This was clearly illustrated by the toxic waste disposed in Abidjan, Cote d'Ivoire in August 2006 which was termed as the largest toxic dumping scandal of the 21st century (Koné, 2010). In 2001, the absolute pesticide stockpiles in Africa were established and several tonnes of hazardous wastes were noted in 45 African countries. For example, Algeria (207 tonnes), Benin (421 tonnes), Botswana (18247 tonnes), Rwanda (451 tonnes), South Africa (603 tonnes), Sudan (666 tonnes) and Swaziland (9 tonnes) were identified (Bernstorff and Stairs, 2001).

In recent years an effort to assess the occurrence and distribution of PCBs and OCPs in different locations in Africa has continued to be the focus of many research institutions and many research investigations where the monitoring of contaminants were carried out using various matrices such as water, sediment, soil, bio-solids, aquatic animals, human milk, cow milk, human blood, etc. A study by Benbakhta and his team, found the concentrations of OCPs along the Atlantic coast of Morocco in North Africa, varying between 2.40-25.40 ng/g of dry sediment (Benbakhta et al., 2014). The levels of PCBs in sediment collected from the port of Tamentfoust in Algeria, in the North of Africa, varied from 15 to 70 ng/g d.w. (Fouial-Djebbar et al., 2010). An investigation of OCPs and PCBs in fish from Lake Tanganyika, the main water body in Burundi, a central African country, showed the total concentration of 12 PCBs having 166.7±37.4 ng/g fat of *Oreochromis niloticus,* a species of Nile tilapia. The OCPs analysed were all detected in low concentrations, except for HCH (288.2±15.5 ng/g fat) and DDTs (909.1±42.5 ng/g fat)

(Manirakiza et al., 2002). In the southern part of the African continent, environmental monitoring research were also interested in organic pollution. For example the analysis of mothers' milk in Zimbabwe revealed that the mean total PCB levels in Kadoma mothers were 60 ng/g fat milk while the mean level of DDTs was 25.26 ng/g milk fat (Chikuni et al., 1997). West African researchers also made an effort to monitor the environmental contaminants in different environmental matrices. A monitoring study at the cocoa producing area of Ondo state, Southwest of Nigeria found the following OCP concentrations: cis-chlordane 30-6990; *α*-endosulfan 30-6990; *p,p'*-DDE 80-19040; and dieldrin 10-7620 ng/g in sediment and concluded that the main source of these pesticides was agricultural activities in the area (Adetutu et al., 2013). Analysis of OCPs and PCBs in the western part of Africa showed fish collected from Awassa Lake in the Ethiopian rift valley may cause a special health risk in children if that fish were consumed. In that study the sum ΣDDT varied from 19 to 56 ng/g wet weight, while the concentration of PCBs found in some fish species exceeded the reference dose (0.075 ng/g) indicated for 0 to 2 year old children (Ermias et al., 2014). Tables 2.4 and 2.5 show some worldwide monitoring studies carried out in recent years (2010-2015) for PCBs and OCPs respectively.

Table 2.6 Global monitoring studies of PCBs in recent years (2010-2015)

Location/country	Matrix	N° of PCBs	N° of samples	∑PCB (ng/mL or ng/g)	References
Delhi, India	River water	28	-	0.014-1.768	(Kumar et al., 2012)
Liaohe, China	Sediment	18	14	1853-75606	(Zhang et al., 2010)
Daliao River estuary, China	Sediment	41	39	0.83 -7.29	(Men et al., 2014)
Lake Qarun, Egypt	Sediment	29	34	1.48 -137.2	(Barakat et al., 2013)
Haihe River basin, China	Sediment	12	17	0.018.7 -0.0500	(Li et al., 2013)
Beijing/China	Soil	25	-	47.04 -3883.77	(Yuan et al., 2014)
United Kingdom	Soil	7	-	1.00-750	(Vane et al., 2014)
China	Soil	32	26	317.85 - 927.30	(Gao et al., 2015)
Russia	Soil		-	300.00-24250.0	(Agapkina et al., 2012)
Bulgaria	Soil	6	8	7.20-17.20	(Dimitrova et al., 2013)
Houston, US	Wastewater	209	16	0.001.01-0.008.12	(Balasubramani et al., 2014)
Ismir, Turkey	Soil	41	-	174-161000	(Elife et al., 2012)
Mediteranean Seas, Algeria	Sediment	27	30	15.00-70.00	(Fouial-Djebbar et al., 2010)
Tanzania	Fish (tilapia)	7	201	17	(Polder et al., 2014)
Zheng	Soil	29	-	0.036–0.679	(Zheng et al., 2014)
Ontario, Canada	Eels	44	44	384	(Byer et al., 2013)
Western Africa (median range)					
Cote d'Ivoire	Human serum	18	21	3–85	(Luzardo et al., 2014)
Gambia	Human serum	18	22	11–309	(Luzardo et al., 2014)
Ghana	Human serum	18	106	568–2943	(Luzardo et al., 2014)
Guinea	Human serum	18	41	48–390	(Luzardo et al., 2014)
Guinea Bissau	Human serum	18	15	54–256	(Luzardo et al., 2014)
Mali	Human serum	18	34	66–229	(Luzardo et al., 2014)
Nigeria	Human serum	18	109	85–439	(Luzardo et al., 2014)
Senegal	Human serum	18	26	25–182	(Luzardo et al., 2014)
Sierra Leone	Human serum	18	79	99–374	(Luzardo et al., 2014)
Central Africa					
Cameroon	Human serum	18	41	59–164	(Luzardo et al., 2014)
Congo Republic	Human serum	18	41	92–356	(Luzardo et al., 2014)
Equatorial Guinea	Human serum	18	385	621–1230	(Luzardo et al., 2014)

Table 2.7 Global monitoring studies of OCPs in recent years (2010-2015)

Location/country	Matrix	N° of OCPs	N° of samples	∑OCPs (ng/mL or ng/g)	References
North-Ouest Mediterranean sea	River water	10	6	0.002 -0.016	(Sánchez-Avila et al., 2012)
Mediterranean coastal Waters, Spain	Water	12	41	0.0019–0.0083	(Martí et al., 2011)
Lake Qarun, Egypt	Sediment	25	34	1.01 -164.8	(Barakat et al., 2013)
Lake Parishan, Iran	Water	6	4	0.055	(Kafilzadeh et al., 2012)
Lake Parishan, Iran	Sediment	6	4	9.84	(Kafilzadeh et al., 2012)
Lake Parishan, Iran	Fish	6	4	4.86	(Kafilzadeh et al., 2012)
Haihe River basin, China	Sediment	10	17	1.7–35.280	(Li et al., 2013)
India	Soil	22	-	129-1001	(Manohar et al., 2014)
Beijing,China	Soil	23	-	2.38-933.12	(Yuan et al., 2014)
Pakistan	Soil	15	11	216.00-541.00	(Sultana et al., 2014a)
Chao River,China	Soil	24	-	0.8145-16.8524	(Yu et al., 2014)
South-East Romania	Soil	15	10	58.00-1662.00	(Ene et al., 2012)
Western China	Soil	10	-	0.51-181.63	(Liu et al., 2013)
North-East Romania	Soil	11	-	4.40 -95.00	(Doina et al., 2013)
Tajikistan	Soil	25	-	52.83-247.98	(Zhonghua et al., 2013)
Poland	Soil	8	15	0.35-453.20	(Maliszewsk-Kordybach et al., 2014)
Argentina	Soil	15	15	38100 - 46500	(Gonzaleza et al., 2010)
Atlantic coast, Morocco	Sediment	14	40	13.17-27.53	(Benbakhta et al., 2014)
North-East Romania	Moss	14	-	5.80-95.00	(Doina et al., 2013)
North-East Romania	Tree-bark	14	-	11.00-440.00	(Doina et al., 2013)
Nile Delta, Egypt	Water	25	-	0.07-2.1567	(El Bouraie et al., 2011)
Nile Delta, Egypt	Sediment	25	-	1.73-2.11	(El Bouraie et al., 2011)

Table 2.7 continued

Location/country	Matrix	Nº of OCPs	Nº of samples	∑OCPs (ng/mL or ng/g)	References
Lake Awassa, Ethiopia	Fish	7	-	19.00-56.00	(Ermias et al., 2014)
Lake Koka, Ethiopia	Fish	7	-	0.05-72.53	(Deribe et al., 2011)
Densu bassin,Ghana	Fish	14	-	0.30 -71.3	(Afful et al., 2010)
Assam state, India	Human milk	9	205	2720-3210	(Mishra and Sharma, 2011)
Assendabo, Serbo and Jimma, Ethiopia	Human milk	9	-	2.66-12200	(Gebremichael et al., 2013)
Western Africa (median range)					
Cote d'Ivoire	Human serum	18	21	194–841	(Luzardo et al., 2014)
Gambia	Human serum	18	22	118–743	(Luzardo et al., 2014)
Ghana	Human serum	18	106	119–555	(Luzardo et al., 2014)
Guinea	Human serum	18	41	148–1016	(Luzardo et al., 2014)
Guinea Bissau	Human serum	18	15	56–407	(Luzardo et al., 2014)
Mali	Human serum	18	34	117–1558	(Luzardo et al., 2014)
Nigeria	Human serum	18	109	198–719	(Luzardo et al., 2014)
Senegal	Human serum	18	26	49–359	(Luzardo et al., 2014)
Sierra Leone	Human serum	18	79	247–968	(Luzardo et al., 2014)
Central Africa					
Cameroon	Human serum	18	41	254–916	(Luzardo et al., 2014)
Congo Republic	Human serum	18	41	372–1585	(Luzardo et al., 2014)
Equatorial Guinea	Human serum	18	385	126–1351	(Luzardo et al., 2014)

2.7.4. Monitoring of OCPs and PCBs in South Africa

Researchers have also investigated the occurrence and significance of OCPs and PCBs in the South African environment in various matrices such as water, sediment, aquatic life, birds and humans. In their study, London and his team reported varying levels of OCPs in the surface water of Piketburg and Grabouw Rivers of the Western Cape from 0.050 to 1.00 ng/mL (London et al., 2000a). Awofolu and Fatoki investigated OCPs in water and sediment systems in the Eastern Cape and their results showed the OCP levels in water varied from trace amount to 0.45 ng/mL in the Buffalo River, from trace to 0.18 ng/mL in Keiskamma River and from trace to 0.13 ng/mL in the Tyume River (Awofolu and Fatoki, 2003). The above mentioned levels of OCPs were not high but were, in all cases higher than the EPA guidelines (0.014 ng/mL). However, Sibali and co-workers found very high levels of OCPs in water (0.895 ± 0.01-9089 ± 0.08 ng/mL) and sediment (0.266 ± 0.01-22914 ± 2.85 ng/g) of the Jukskei River catchment area in Gauteng (Sibali et al., 2008). The above concentration in water (0.01-9089 ng/mL) is significantly higher than water criteria values recommended by the USEPA (0.014 ng/mL) and the South African Department of Water Affairs (DWAF) for the protection of the aquatic environment.

Table 2.8 PCB-TEQ in ng/kg in fish of major South African water bodies

(Vosloo and Bouwman, 2005)

Water body	PCB-TEQ (ng/kg)	Water body	PCB-TEQ (ng/kg)
Gariep River (mouth)	0.01	Richard's Bay (harbour)	0.01
Saldanha Bay harbour	0.01	Thulazihleka Pan	0.04
Berg River	0.02	Vaal Dam	0.01
Theewaterskloof Dam	0.02	Riet Spruit	0.31
Groot River (mouth)	0.02	Loskop Dam	0.01
Zwartkops Estuary	0.61	Hartbeespoort Dam	0.47
Vaal River (Douglas)	0.03	Modderfontein Spruit	1.58
Buffalo River	0.01	Riet Spruit (diverted brook)	10.01
Mooi River	0.02	Loch Vaal	0.65
Umlazi River (mouth)	0.3	Crocodile River	1.74
Umgeni River (mouth)	0.32	Olifants River	0.02

The report by Vosloo and Bouwman revealed that the total concentrations of PCBs ($\sum$12PCB) in sediment and different species of fish collected from 22 South African major water bodies, were 132000±22000 ng/g, 17000±2200 ng/g, 160000±31 ng/g, 41000±6700 ng/g in marsh sediment, grass shrimp, striped mullet and seatrout muscle, respectively. The same study showed that the PCB toxic equivalent factors (PCB-TEQ) were between 0.001 and 10.01 ng/kg. The PCB-TEQ values for different water bodies are tabulated in the Table 2.6 (Vosloo and Bouwman, 2005). The interim toxic equivalency factors for human intake of dioxin-like PCBs are, 0.0005, 0.0001 and 0.00001 for PCB77, PCB105 and PCB180 respectively (WHO, 2000).

The aquatic life in fresh waters was also investigated in some areas. The mean OCP concentrations in muscle samples of *Clarias gariepinus* collected from the Roodeplaat Dam, Rietvlei Dam and Hartbeespoort Dam, were found to vary from 86.45 to 288.75 ng/g, 55 to 336 ng/g and 71 to 131 ng/g respectively (Barnhoorn et al., 2015b).

A study conducted by Pieters and Focant on human serum, revealed that the mean of the total toxic equivalencies (ΣTEQ) of dioxin-like PCBs was 6.9±3.3 ng/kg lipid in the South African Tswana population, while the mean concentration in the same population with regard to dioxin-like PCBs was 70.1±42.8 ng/g lipid (Pieters and Focant, 2014). Birds are known as good transport agents of POPs and particularly OCPs and PCBs. A study on blood tissue from vultures collected in different locations in South Africa showed the total levels of DDT to be 9.63, 3.42, 7.17, and 16.18 ng/mL for vultures collected at Dronfield, Sandveld, Moholoholo and De Wildt respectively (van Wyk et al., 2001). Bird eggs also are known to accumulate POPs. Studies showed that the highest levels of OCPs were found in South African darter eggs, where the average concentrations were 370 ng/g and 300 ng/g for $\sum$OCPs and $\sum$PCBs (Bouwman et al., 2008). The past monitoring and analysis studies of PCBs and OCPs in South Africa are compiled in Tables 2.7 and 2.8 below.

Table 2.9 PCB analysis and monitoring studies in South Africa

Location	Matrix	N° of PCBs	N° of samples	∑PCB (ng/mL or ng/g)	References
Port Elizabeth Habour	Fish	8	9	14.48–21.37	(Kampire et al., 2015)
Cape Town and Port Elizabeth	Fish	22	100	9000	(Degger et al., 2011)
KwaZulu-Natal	Surface soil	82	6	109.64	(Batterman et al., 2009)
KwaZulu-Natal	Shallow soil	82	6	19.22	(Batterman et al., 2009)
KwaZulu-Natal	Cow milk	36	-	0.022	(Batterman et al., 2009)
Coastal endemic malaria	Human blood	7	37	2.85-79.5	(Röllin et al., 2009)
Vaal River	Soil	12	-	120-2700	(Nieuwoudt et al., 2009b)
Barberspan, Parys, Velddrif, Koppies	Eggs	34	43	1.9-720	(Bouwman et al., 2008)
North West province,	Serum	12	693	0.0191-60.604.2	(Pieters and Focant, 2014)
Major South African waters	Sediment	12	22	132000	(Vosloo and Bouwman, 2005)
Major South African waters	Fish (Grass shrimp)	12	22	17000	(Vosloo and Bouwman, 2005)
Major South African waters	Fish (Striped mullet)	12	22	160000	(Vosloo and Bouwman, 2005)
Major South African waters	Fish (Seatrout muscle)	12	22	41000	(Vosloo and Bouwman, 2005)
Kruger National Park (Crocodile farm)	Nile crocodile eggs	18	10	97-8800	(Bouwman et al., 2014)
Kruger National Park (Letaba)	Nile crocodile eggs	18	6	6.5-7.7	(Bouwman et al., 2014)
Kruger National Park (Olifants River)	Nile crocodile eggs	18	9	15-20.9	(Bouwman et al., 2014)
Hartbeespoort Dam (Crocodile River)	Dam water	7	-	0.038- 150	(Bouwman et al., 2014)
Vaal triangle and central South Africa	Soil	7	13	1.48-38.32	(Quinn et al., 2009)
Vaal triangle and central South Africa	Sediment	7	13	0.46-8.55	(Quinn et al., 2009)

Table 2.10 OCP analysis and monitoring studies in South Africa

Location	Matrix	N° of OCPs	N° of samples	∑OCP (ng/mL or ng/g)	References
Coastal endemic malaria	Human blood	17	11	2222.2-21188	(Rollin et al., 2009)
Limpopo province	Human milk	5	30	nd-1 930	(Okonkwo et al., 2008)
Jukskei River (Gauteng)	Water	13	7	0.895-9089	(Sibali et al., 2008)
Jukskei River (Gauteng)	Sediment	13	7	0.266-22 914	(Sibali et al., 2008)
Roodeplaat Dam	Fish	15	-	86.45-288.75	(Barnhoorn et al., 2015b)
Rietvlei Dam	Fish	15	-	55-336	(Barnhoorn et al., 2015a)
Hartbeespoort Dam	Fish	15	-	71-131	(Barnhoorn et al., 2015b)
Buffalo River	Fresh water	15	-	nd-0.450	(Awofolu and Fatoki, 2003)
Keiskamma River	Fresh water	15	-	nd-0.180	(Awofolu and Fatoki, 2003)
Tyume River	Fresh water	15	-	nd-0.130	(Awofolu and Fatoki, 2003)
Swartkops River	Fresh water	15	-	0.100	(Awofolu and Fatoki, 2003)
Piketburg and Grabouw rivers (Western Cape)	Fresh water	4	-	0.050-1.00	(Awofolu and Fatoki, 2003)
Buffalo River	Sediment	15	-	nd-184.00	(Awofolu and Fatoki, 2003)
Keiskamma River	Sediment	15	-	nd-16.00	(Awofolu and Fatoki, 2003)
Tyume River	Sediment	15	-	19.00	(Awofolu and Fatoki, 2003)
Swartkops River	Sediment	15	-	30.00	(Awofolu and Fatoki, 2003)
Hartbeespoort Dam (Crocodile River)	Water	11	-	9.477-10.793	(Amdany et al., 2014)
KwaZulu-Natal	Breast milk	3	-	1000-59300	(Bouwman et al., 1990)
KwaZulu-Natal	Human blood	3	23	29.4-316.5	(Bouwman et al., 1992)
Mlambongwenya (KwaZulu-Natal)	Human serum	3	63	131.4-175.3	(Bouwman et al., 1994)
Vaal triangle and central South Africa	Soil	5	13	1.62-30.21	(Quinn et al., 2009)
Vaal triangle and central South Africa	Sediment	5	13	0.77-11.18	(Quinn et al., 2009)

Considering POP studies in past years in the South African environment, there is very limited or no information on the occurrence and concentrations of PCBs and OCPs in the Umgeni River and its catchment. Therefore this study focused on the quantification of the selected persistent organic pollutants in the water, sediment pore water, surface sediment and bank soil of the Umgeni River. In addition, the seasonal trends of the selected pollutants in the four above matrices were studied. To the best of our knowledge this is the first study on seasonality of POPs in a river system in South Africa. It adds new knowledge to the existing information on POPs in South Africa.

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CHAPTER THREE
GENERAL MATERIALS AND METHODS

This chapter outlines the experimental characteristics and various techniques and methods used to analyse OCPs and PCBs in different matrices. The significance of each technique for every step was highlighted.

3.1 DATA QUALITY CONTROL AND QUALITY ASSURANCE

The appropriate methods used in different steps of analysis and monitoring and first applied to piloting phase were underlined. The major feautures of analytes were given.

3.1.1. Analyte Recovery and Limit of Detection and Quantification

3.1.1.1. Analyte recovery
The recovery of analytes from any matrix indicates how good the extraction procedure is. The recovery percentages for various OCPs and PCBs in water and pore water samples analysed in this project were obtained using tap water (Hellar-Kihampa, 2011, Meharg et al., 2003) which should not contain significant amounts of these analytes. One litre of tap water was spiked with 1 mL of a 4 μg/mL multi-element standard solution of OCPs or PCBs and made up to mark resulting in a concentration of 0.004 μg/mL. The spiked tap water solution was then taken through the exact same procedure that samples were subjected to. The water was liquid-liquid extracted six times for a single sample using DCM (EPA, 1996a). Extracts were combined, concentrated, cleaned and analysed with GC-MS. The recovery percentage was obtained using Equation 3.1 (APHA et al., 1999). This procedure was repeated at least 3 times and the average concentration extracted was calculated as the percentage of analyte recovered. Apart from HCB and heptachlor, the percent recoveries of all analytes varied from 61.08 to 103.43%. All the values obtained for all the analytes were mentioned in chapters 4, 5, 7 and 8.

$$\text{Recovery (\%)} = \frac{\text{Concentration found (ng/mL)}}{\text{Concentration spiked (ng/mL)}} * 100 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.1)$$

The recovery of analytes from a solid matrix is a much debated procedure because it is difficult to obtain a clean matrix that does not contain the analytes of interest, yet still has the same components that affect analyte extraction. Thus the actual real soil matrix was used but was divided into two subsamples where one was spiked with a known concentration of the analytes and the other left unspiked. The concentration of analyte is determined for both spiked (X_S) and un-spiked (X_u) and the analyte percent recovery $(\%R)$ is calculated as follows: (Doolittle, 2014, Harry et al., 2008).

$$\%R = \frac{X_S - X_u}{k} * 100 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (3.2)$$

Where k is the known concentration of analyte added to the spiked subsample.

For sediment and soils samples analysed in this work, a sample was divided into two subsamples of 60 g (dry weight (dw)) each. One subsample was spiked with 1 mL of a 4 µg/mL multi-element standard of OCPs or PCBs and made up to mark to obtain a concentration of 0.067 µg/g. The samples were taken through the same procedure that the samples were subjected to. They were air dried, soxhlet extracted using DCM (EPA, 1996b) and concentrated to 2 mL and analysed with GC-MS. The recovery experiments were carried out in triplicate and mean percent recoveries were calculated using Equation 3.2 and were between 51.67 to 109.28%. The percent recovery values obtained for all analytes investigated were mentioned in chapters 4 - 9.

3.1.1.2. Limits of detection and quantification

IUPAC defines the limit of detection as "The smallest measure that can be detected with reasonable certainty for a given analytical procedure" and the ACS defines it as "The lowest concentration of an analyte that an analytical procedure can reliably detect" (Long and Winefordner, 1983). The limit of quantification was defined as the smallest concentration of an analyte in a sample which can be measured and reliable results obtained using a given analytical method (Shabir et al., 2007, Jibbons and Coleman, 2001).

For a linear calibration curve, the response "y" recorded by the instrument is linearly related to the standard concentration "x". This can be expressed by the following equation (Shrivastava and Gupta, 2011):

$$y = mx + b \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3.3)$$

Three calibration curves were drawn from triplicate analysis of calibration standards and the standard deviation and the average slope were determined. This was then used in equations 3.4 and 3.5 to determine the LODs and LOQs for each analyte.

$$LOD = \frac{3S}{m} .... (3.4)$$

$$LOQ = \frac{10S}{m} .... (3.5)$$

Where:

S = standard deviation of the response

m = the slope of the calibration curve

The standard deviation can be estimated from y-intercepts of the three regression lines (Shrivastava and Gupta, 2011). Note that in this project, the responses were peak areas obtained from the GC-MS. The LODs and LOQs obtained using the above equations were tabulated in Chapters 4 -9.

3.1.2. Determination of Analyte Sampling Variability

3.1.2.1. Pilot samples

Before the real sampling activity, pre-sample collection took place in order to determine the variability of the concentrations of analytes of interest (OCPs and PCBs) within the same site so that a suitable sampling method could be selected. This was done using sediment which was the less mobile matrix.

Five different subsamples of sediment were collected using an auger at Albert Falls outlet: (GPS coordinates: 29° 26' 31.94''S, 30° 19' 47.10''E) which is one of the designated sampling sites that is surrounded by mainly agricultural and recreational activity. The distance from one subsample to another was 1 meter (Figure 3.1). Sixty grams of each sediment sample were individually treated as described in section 3.1.1.1 above and the results compared. A composite sample was also prepared by combining 12 g of each sample collected above and its result compared to the individual sediment subsample results. The 5 subsamples of sediment are tabulated in Table 3.1.

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Table 3.1 Pilot subsamples analysed.

Code of the site	Full name of site
AFOSED1	Albert Falls outlet sediment one
AFOSED2	Albert Falls outlet sediment two
AFOSED3	Albert Falls outlet sediment three
AFOSED4	Albert Falls outlet sediment four
AFOSED5	Albert Falls outlet sediment five
AFOSED comp	Albert Falls outlet sediment composite
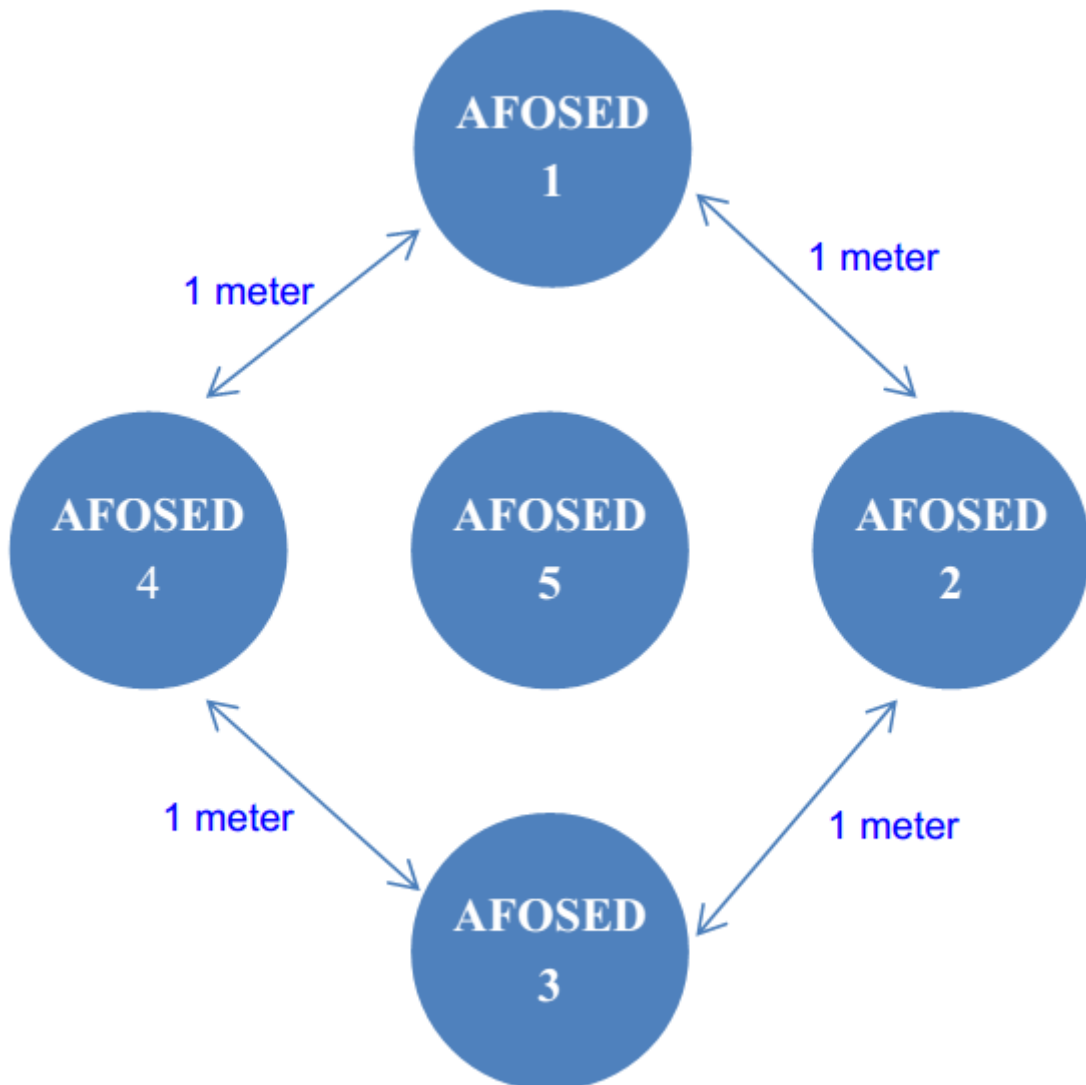
Figure 3.1 Distance between subsamples during collection at the sampling site.

Table 3.2 Parameters used for pilot samples analysis.

Parameter	Measure	Parameter	Measure	
# of rinses with Presolvent:	2	Linear Velocity:	36.7 cm/sec	
# of rinses with Solvent(post):	2	Purge Flow:	3.0 mL/min	
# of rinses with Sample:	2	Split Ratio:	1	
Plunger Speed(Suction):	High	High Pressure Injection:	OFF	
Viscosity Comp. Time:	0.2 sec	Carrier Gas Saver:	OFF	
Plunger Speed(Injection):	High	**Oven Temp. Program**		
Syringe Insertion Speed :	High	Rate	Temperature (°C)	Hold time (min)
Injection Mode:	Normal	-	120	0
Pumping Times:	5	14	290	2
Inj. Port Dwell Time:	0.3 sec			
Terminal Air Gap:	No	**GC Program**		
Plunger Washing Speed:	High	Ion Source Temp	200.00 °C	
Washing Volume:	8 uL	Interface Temp.	280.00 °C	
Syringe Suction Position:	0.0 mm	Solvent Cut Time	4.50 min	
Syringe Injection Position:	0.0 mm	Detector Gain Mode	Relative	
Solvent Selection:	All A,B,C			
Column Oven Temp.:	120.0 °C	**MS Table**		
Injection Temp.:	250.00 °C	Start Time	5.00 min	
Injection Mode:	Splitless	End Time	14.14 min	
Sampling Time:	1.00 min	ACQ Mode	SIM	
Flow Control Mode:	Linear Velocity	Event Time	0.30 sec	
Pressure :	76.8 kPa	Sample Inlet Unit	GC	
Total Flow:	4.9 mL/min	Use MS Program	ON	
Column Flow :	0.96 mL/min			

3.1.2.2. Method of analysis of pilot samples

The analysis of samples was carried out in triplicate using a Shimadzu GC-MS-QP2010 SE gas chromatograph-mass spectrometer. The GC system was fitted with a GL sciences capillary column, 0.25 mm i.d, 0.25 μm film thickness and 30 m length. Ultra-pure helium was used as the carrier gas. Samples were analysed using selected ion monitoring (SIM) mode. The method parameters are listed in Table 3.2.

3.1.2.3. Results and conclusion

The results obtained for the five subsamples and the composite subsample are shown in Table 3.3 and Figure 3.4.

Table 3.3 Variability of concentrations of OCPs in surface sediment (ng/g) within the Albert Falls outlet sampling site.

Subsample	Concentration of OCPs in sediment (in ng/g, dw)									
	HCB	HCH	heptachlor	aldrin	*o,p'-* DDE	*p,p'-* DDE	*o,p'-* DDD+dieldrin	endrin	*p,p'-* DDD+*o,p'-* DDT	mirex
AFOSED1	6.97	31.99	30.54	nd	25.75	31.04	29.03	63.17	21.66	17.72
AFOSED2	5.21	30.59	33.38	nd	24.91	27.18	30.27	56.61	20.76	20.02
AFOSED3	5.16	33.73	27.02	nd	25.14	24.20	22.21	58.68	24.28	16.78
AFOSED4	3.40	30.06	29.25	nd	20.36	25.49	26.44	51.83	22.37	17.33
AFOSED5	6.53	28.85	33.57	nd	17.20	25.79	26.85	59.46	24.53	16.72
AFOSED comp	7.59	28.26	27.24	nd	21.10	25.46	28.57	50.03	23.97	15.98
SD	1.53	2.03	2.88	nd	3.40	2.41	2.84	4.93	1.55	1.40
Mean AFOSED (1-5)	5.45	31.04	30.75	nd	22.67	26.74	26.96	57.95	22.72	17.71
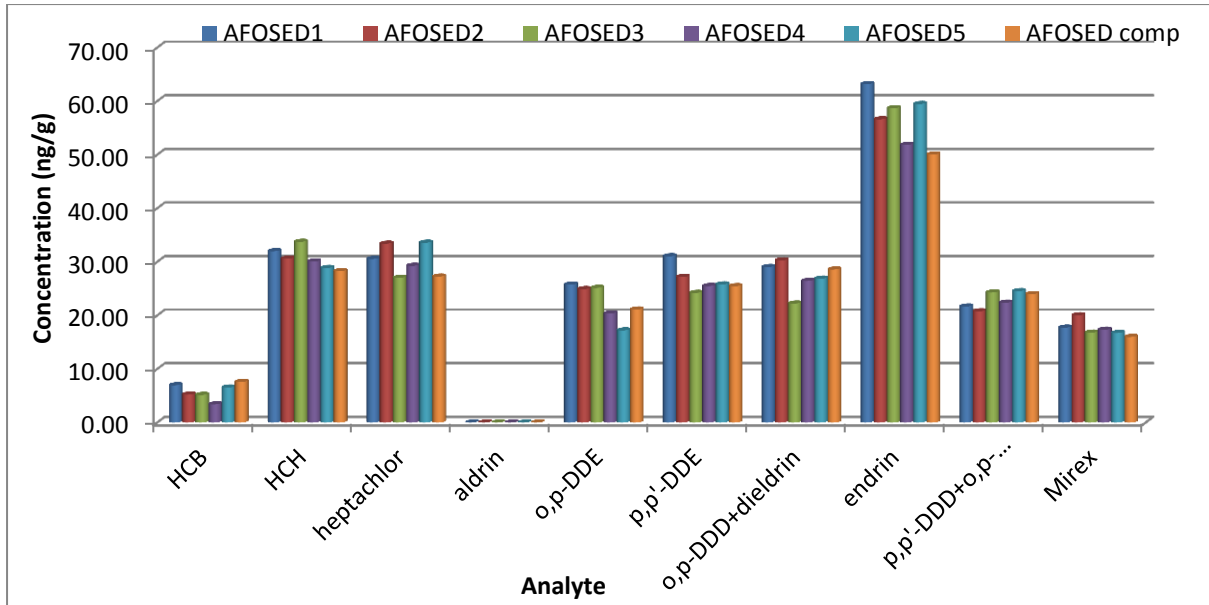
Figure 3.2 Variability of the concentration of OCP analytes at the Albert Falls outlet sampling site (n=3).

Table 3.3 and Figure 3.2 above show minimum variability of OCP concentrations at different points within the same site. The standard deviations of the concentrations of the same analyte at 5 different sampling points at a distance of 1 m from each another and the composite sample vary within 1.40 to 4.93 (Table 3.3 and Figure 3.3). The lowest variability was recorded for mirex (SD = 1.40) and the highest for endrin (SD = 4.93). The concentration of aldrin for all the 5 sampling points and the composite subsample was below the limit of detection.
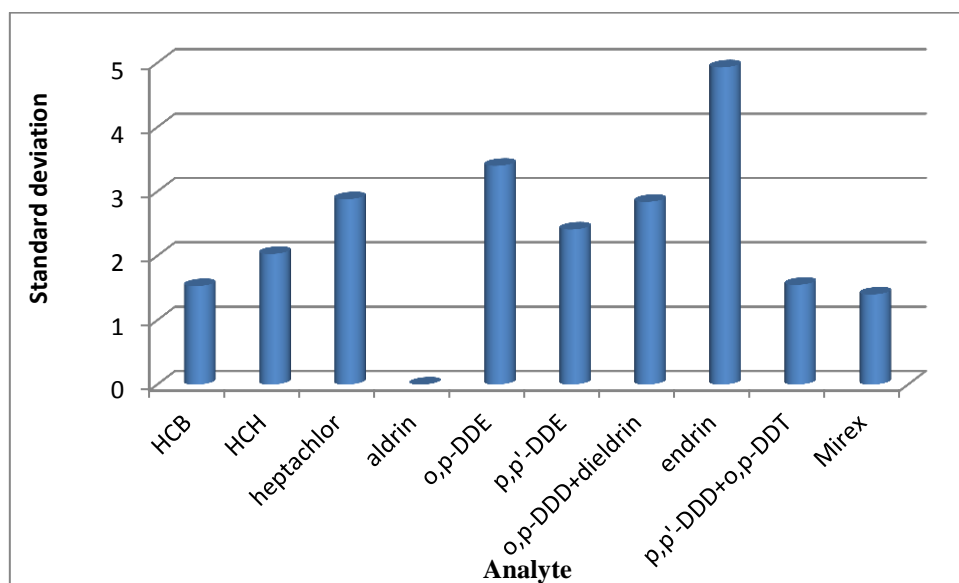
Figure 3.3 Standard deviation of OCP measured in six subsamples collected at the same site.

Table 3.4 Variability of concentrations of PCBs (ng/g) in surface sediment within site

Subsample code	Concentration (in ng/g, dw)							
	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180
AFOSED1	19.76	11.87	8.44	6.86	28.13	12.81	17.45	47.71
AFOSED2	20.53	10.9	10.17	5.31	29.58	14.81	17.7	45.86
AFOSED3	21.21	11.58	7.03	5.34	31.15	14.32	17.9	49.28
AFOSED4	21.58	11.41	9.35	5.79	33.54	15.64	18.06	45.89
AFOSED5	18.96	11.55	8.93	6.14	30.23	14.46	18.35	46.08
AFOSED comp	18.7	10.48	10.13	6.33	32.51	13.04	19.59	44.37
SD	1.18	0.51	1.18	0.60	1.97	1.08	0.76	1.71
Mean AFOSED(1-5)	20.41	11.46	8.78	5.89	30.53	14.41	17.89	46.96
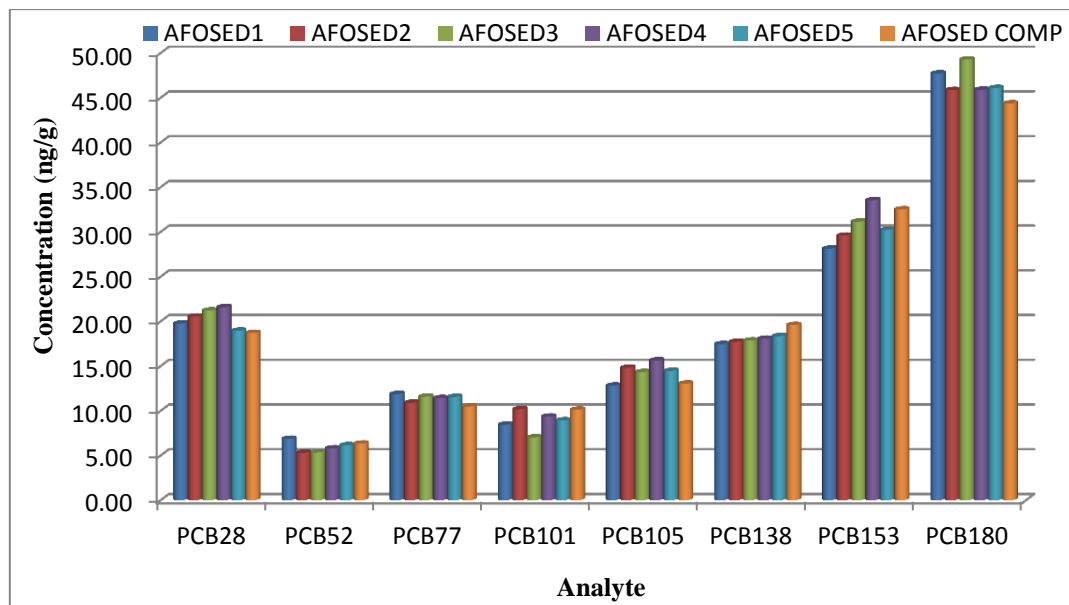
Figure 3.4 Variability of the concentration of PCB analytes the Albert Falls outlet sampling site (n=3)

Table 3.4 and Figure 3.4 show that the difference between concentrations of the same analyte in different subsamples is not high. The standard deviations of the concentrations of individual PCBs in the 5 subsamples and the composite sample vary from 0.51 for PCB77 to 1.97 for PCB153 (Figure 3.5). Generally the variability of both OCPs and PCBs within the site investigated was low between individual samples as well as the composite sample across a 1 m^2 surface area and any one of the individual samples were found to be representative of the sampling site. Therefore the grab sampling method was chosen to collect samples from

the different sampling sites along the Umgeni River and the choice of one sample per site was adopted.
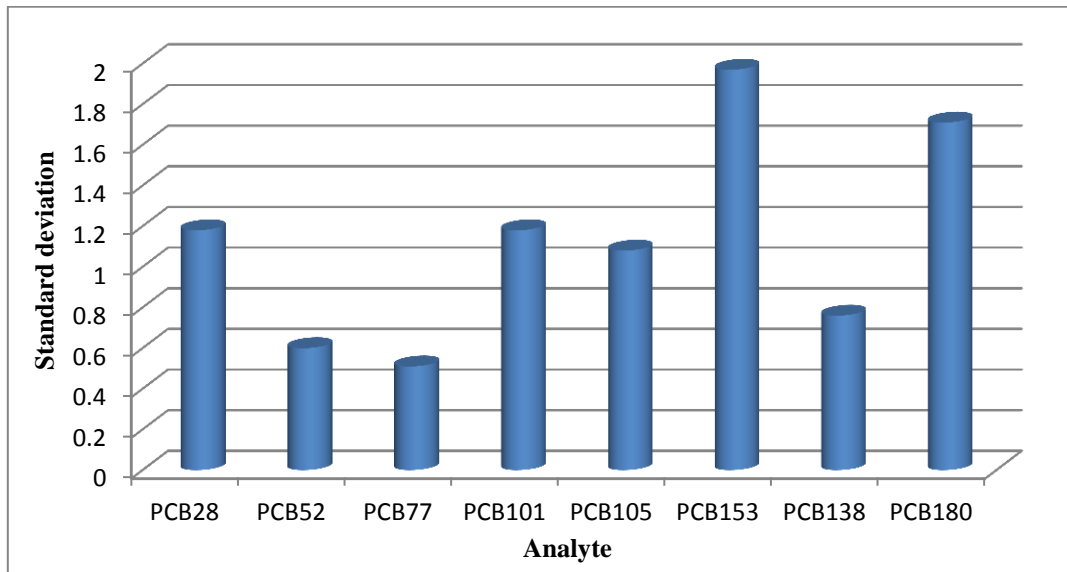
Figure 3.5 Standard deviation of PCBs measured in six subsamples collected at the same site.

3.2. GENERAL EXPERIMENTAL

This section highlights the general experimental procedure followed and the different techniques used as well as their significance for each phase of the research work performed in this project.

3.2.1. Sampling Protocol

3.2.1.1. Sampling sites

Fifteen sampling sites were chosen based on activities in the area around them such as agricultural activities, industrial activities or residential area but some of the sites had a combination of all these activities. Apart from these activities, sites were also chosen considering their accessibility in order to be able to collect a representative sample. These sampling stations included 12 sites chosen along the river from the source at Midmar Dam to the mouth where the river empties into the Indian Ocean at Blue Lagoon; as well as 3 sites around the Northern Wastewater Treatment Works which empties its treated water into the Umgeni River. The map in Figure 3.6 shows the study area location.
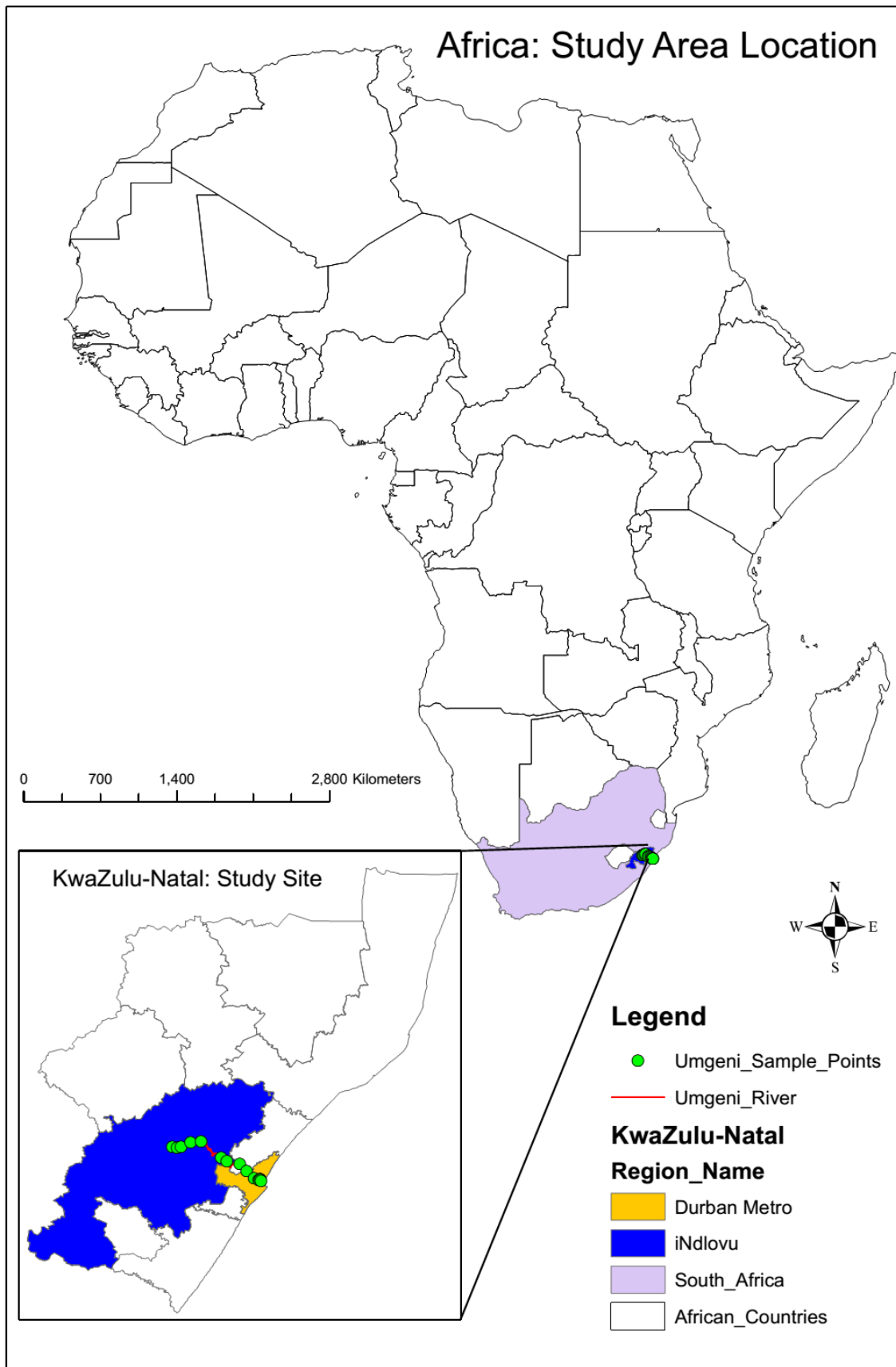
Figure 3.6 Map showing the study area locations (map was generated from GPS coordinates using ArcGIS 10.2).

3.2.1.2. Water sampling

Water samples were collected in 2.5 L amber Winchester bottles previously washed with hot water and detergent and rinsed three times respectively with deionised water and sulfuric acid. At the site, the bottles were rinsed 3 times with the river water to be sampled. The bottles were filled to overflowing leaving no headspace. Bottle caps were lined with aluminium foil to prevent contamination with phthalates and plasticisers from the lids. All the samples were kept in a cooler box containing ice and transported to the lab. A 1 mL aliquot of H_2SO_4 (50 %) was transferred to each water sample for the purpose of preservation and the samples were stored in a fridge at 4 ^oC until extraction which was carried out within 5 days.

3.2.1.3. Sediment sampling

Sediment samples were collected using a grab sampler and were stored in glass bottles with the caps lined with aluminium foil. The bottles were then kept in a coolant box containing ice and were transported to the laboratory and stored in the fridge at 4 ^oC. Sediment samples were subsequently centrifuged to extract its pore water which was also acidified and kept in a fridge until extraction which was carried out within 5 days. After removal of pore water, the sediment was immediately transferred onto aluminium foil for air drying. Note that every season two bio-solid samples were taken from wastewater at NWTI and from treated water at NWTT and treated as sediment samples.

3.2.1.4. River bank soil sampling

Soil samples were collected from the banks of the Umgeni River close to the water edge at each sampling site. A metal spade or auger was used to transfer soil samples to glass bottles. The bottles were sealed with caps lined with aluminium foil and the samples were kept in a cooler box containing ice before being transported to the laboratory. At the laboratory, the soil samples were immediately transferred onto aluminium foil and air dried in the drying room. For every seasonal sampling one bio-solid sample was taken out of water at NWTT and was treated as river bank soil.

3.2.2. Actual Sample Treatment

After the samples were collected and transported to the laboratory, they underwent various treatment steps. Preservation, extraction, concentration and clean-up and analysis were the

main treatment steps for water and pore water, while drying, grinding, sieving, extraction, concentration and clean-up were the key steps for sediment and soil samples. The details for these steps for each matrix are mentioned in chapters 4, 5, 6, 7, 8 and 9.   Figure 3.7 shows a summary of the experimental procedures used for sample treatment for surface water, sediment pore water, surface sediment and river bank soil.
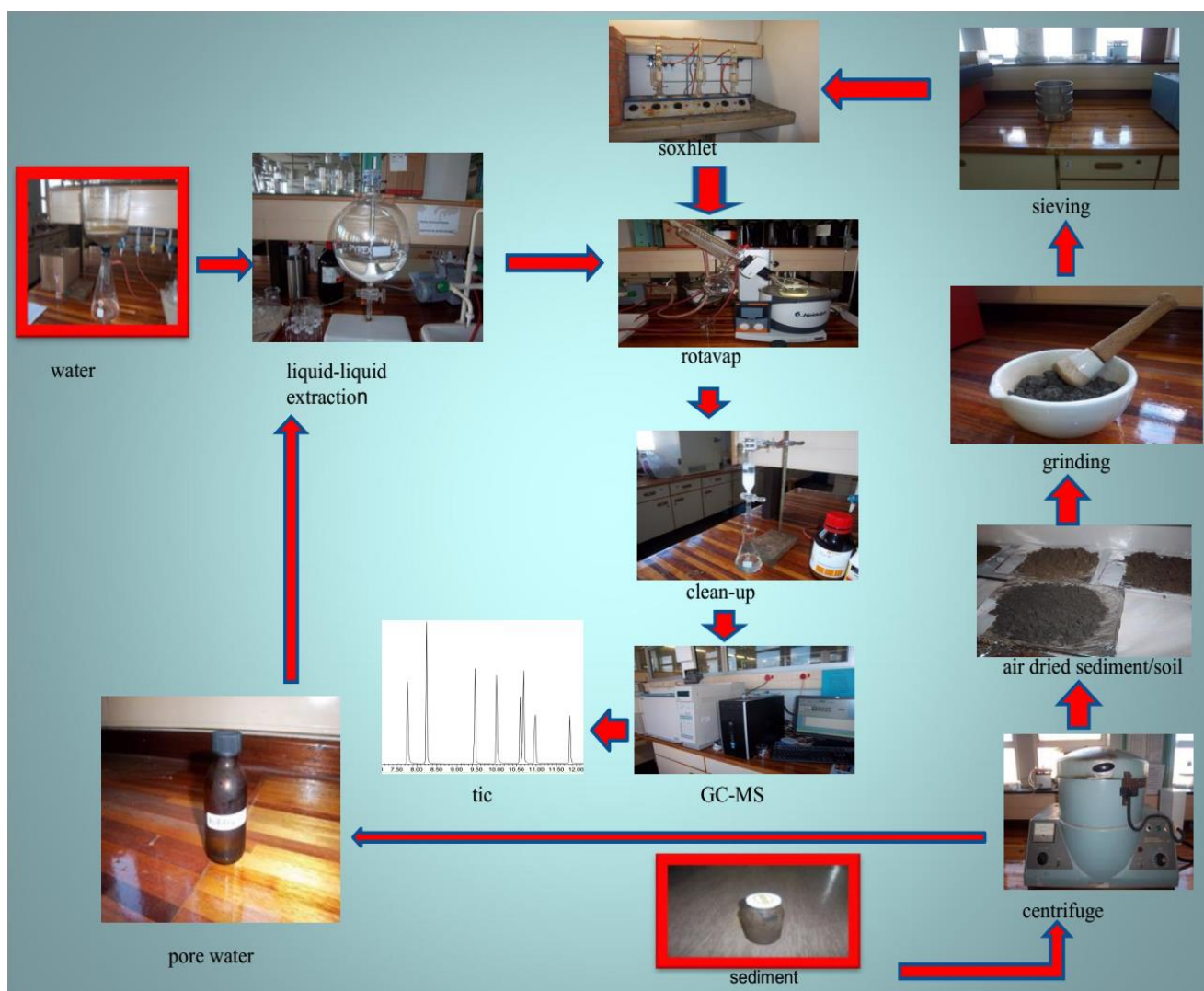
Figure 3.7 Summary of experimental procedures used for water, pore water, sediment and river bank soil sample preparation.

3.2.3. Actual Sample Analysis

After the clean-up step (Figure 3.7), the extracts were concentrated to exactly 2 mL and analysed. Sample analyses were carried out in triplicate using an Agilent 6890 series gas chromatography system attached to a mass spectrometer detector (MSD5973). The GC

system was equipped with a ZB-5MS capillary column, 0.25 mm i.d., 0.25 μm film thickness and 30 m length (Hewlett Packard; Houston, TX). The MS was operated using the selective ion monitoring acquisition mode (SIM). The carrier gas was purified helium. Splitless mode was used to inject 2 μL of sample into the GC-MS with injector and detector temperatures set at 250 and 280 ^{o}C respectively.

To enhance peak resolution and avoid confusion of analyte peak and baseline noises, before the GC-MS analysis, the cleaned and concentarated extract was spiked with 0.25 mL of standard mixture with concentration of 6 μg/mL, making a total volume of 2.25 mL and a spiking level of 0.67 μg/mL. A 2 μL aliquot of the above-mentioned mixture (extract + standard) was injected onto the GC column. At the end of the analysis, the spiked concentration was substracted from the total concentration (analyte + spiked) to obtain the actual sample concentration.

Note that due to the hardware problems of the instrument used for analysis of pilot samples (Shimadzu GC-MS-QP2010 SE), the actual samples were analysed using (Agilent 6890 series GC-MSD5973). Before any analysis was performed, the method parameters used for analysis of pilot samples were used to run analyte standatds on the new instrument (GC-MSD5973) to check for any variations. The calibration curves were ploted for each analyte and there were no differences from the calibration graphs obtained from the first instrument (Shimadzu GC-MS-QP2010 SE). Therefore all the analyses for all seasons were performed on the Agilent 6890 series GC-MSD5973.

Before sample analysis, a standard mixture was run through the column and the fragmentation pattern of each compound compared to that provided by the National Institute of Standards and Technology (NIST) library. This was done primarily to determine the fragment ions of the analyte of interest so that three of the most frequent fragment ions could be chosen for selected ion monitoring (SIM) in the GC-MS system. Secondly this was done to ensure the chromatograms and spectra of the standards agreed with the NIST library and allowed easy identification. Figure 3.8 shows a sample mass-spectrum for hexachlorobenzene standard with the three most abundant fragment ions being *m/z* 284, *m/z* 249 and *m/z* 142. These ions/fragments were monitored using the SIM mode (Figure 3.9) for all sample analysis. The same procedure was used for all analytes in this study.

RawMode:Averaged 6.935-6.945(388-390) BasePeak:283.70(48317)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan
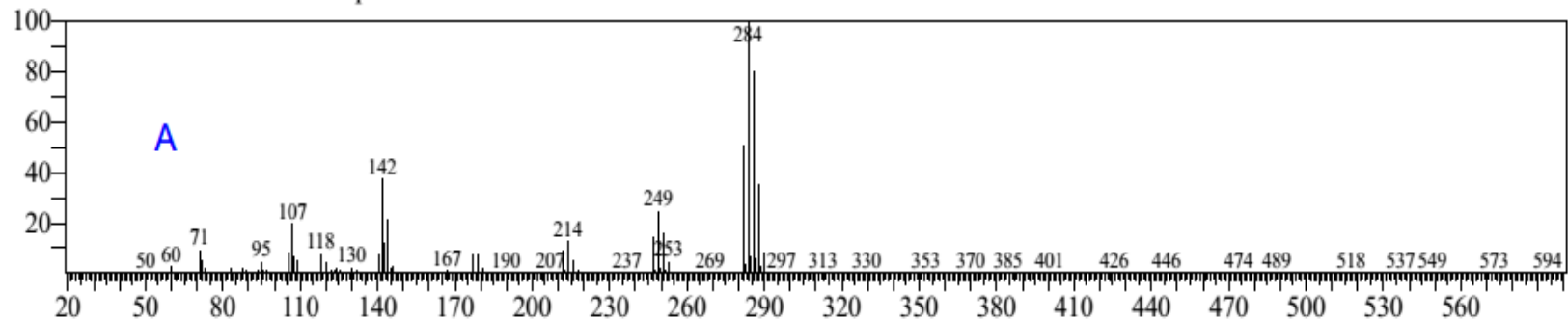
Hit#:1 Entry:24978 Library:NIST11s.lib
SI:97 Formula:C6Cl6 CAS:118-74-1 MolWeight:282 RetIndex:1760
CompName:Benzene, hexachloro- $$ Perchlorobenzene $$ Amatin $$ Anticarie $$ Bunt-cure $$ Bunt-no-more $$ Co-op Hexa $$ HCB $$ Julin's car
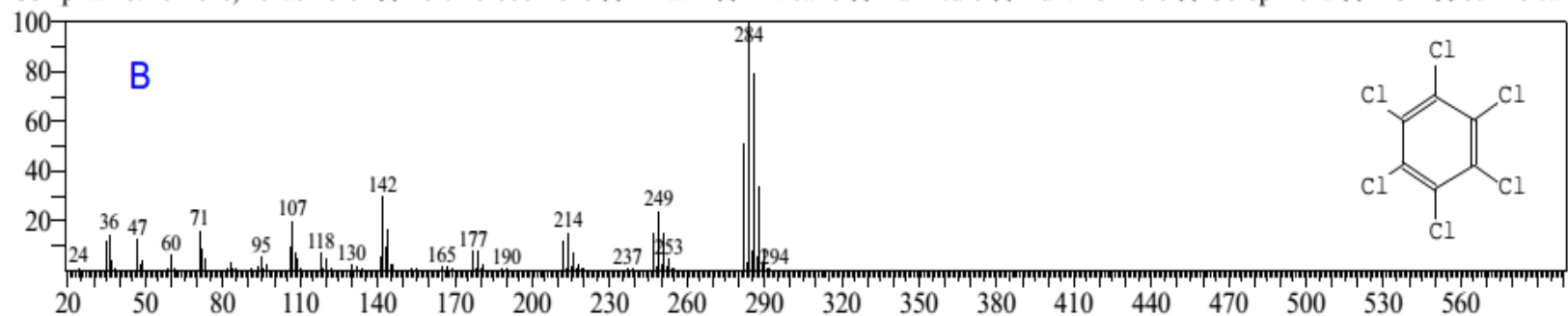
Figure 3.8 A- Mass-spectrum of hexachlorobezene standard obtained in scan mode, B- NIST library mass spectrum of hexachlorobenzene.
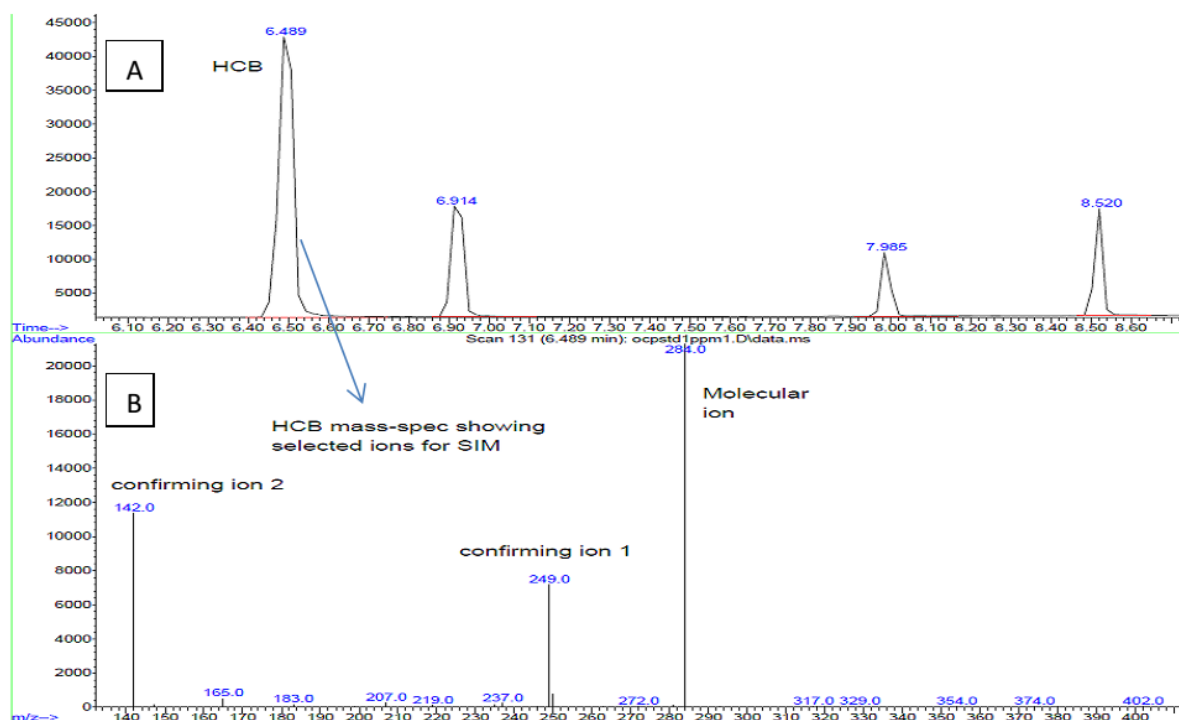
Figure 3.9 A – Total ion chromatogram of standard mixture showing analyte HCB at 6.489 mins. B – SIM mass spectrum for HCB showing the three selected confirming ions.

The oven temperature for analysis of OCPs and PCBs was initially 120 $^{\circ}$C and then increased to 290 $^{\circ}$C at a ramping rate of 14°C/min and held for 2 min. The total run time was 14.14 min. The MS source was operated at 250 $^{\circ}$C and the quad at 200 $^{\circ}$C. A 2 µL sample was injected in splitless mode with injection port set at 250 $^{\circ}$C. The electron ionisation energy was 70 eV.

Target analytes were quantified based on peak areas and by using an external calibration technique with the following six calibration concentrations: 0.25; 0.5; 1; 2, 4 and 8 µg/mL. These standard concentrations were obtained by serial dilution of a stock solution of 32 µg/mL. The identification of analytes of interest was achieved by comparison of retention times of sample analytes with those of reference standards and by using the NIST library. Note that the analysis of OCPs was carried out separately from that of PCBs to avoid overlapping of peaks and to allow for good resolution.
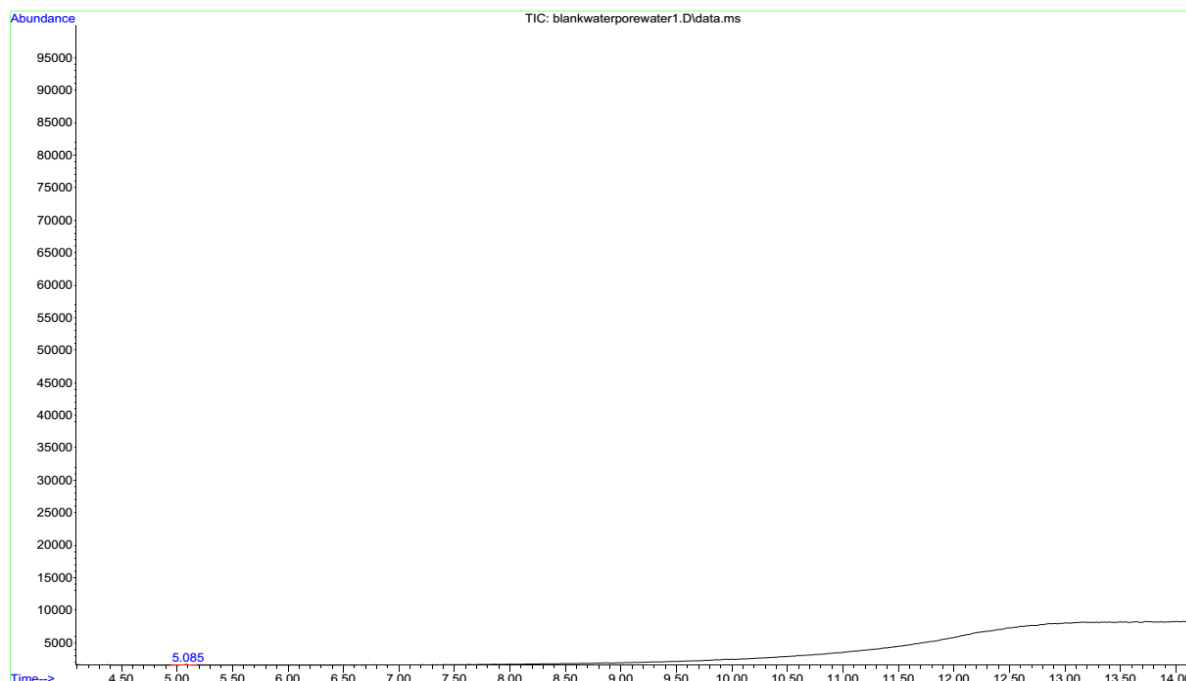
Figure 3.10 Chromatogram for blank sample (extraction solvent treated and analysed using the above method).

The above chromatogram (Figure 3.10) shows that there were no analytes of interest in the blank sample (solvent extracted and analysed, using all the steps used for actual samples). Therefore the concentrations of analyte calculated were exclusively from the samples collected and not from the experimental procedure or solvents used during sample treatment and analysis. Figure 3.11 shows an example of a PCB standard mixture chromatogram and a fortified sediment cleaned extract chromatogram.
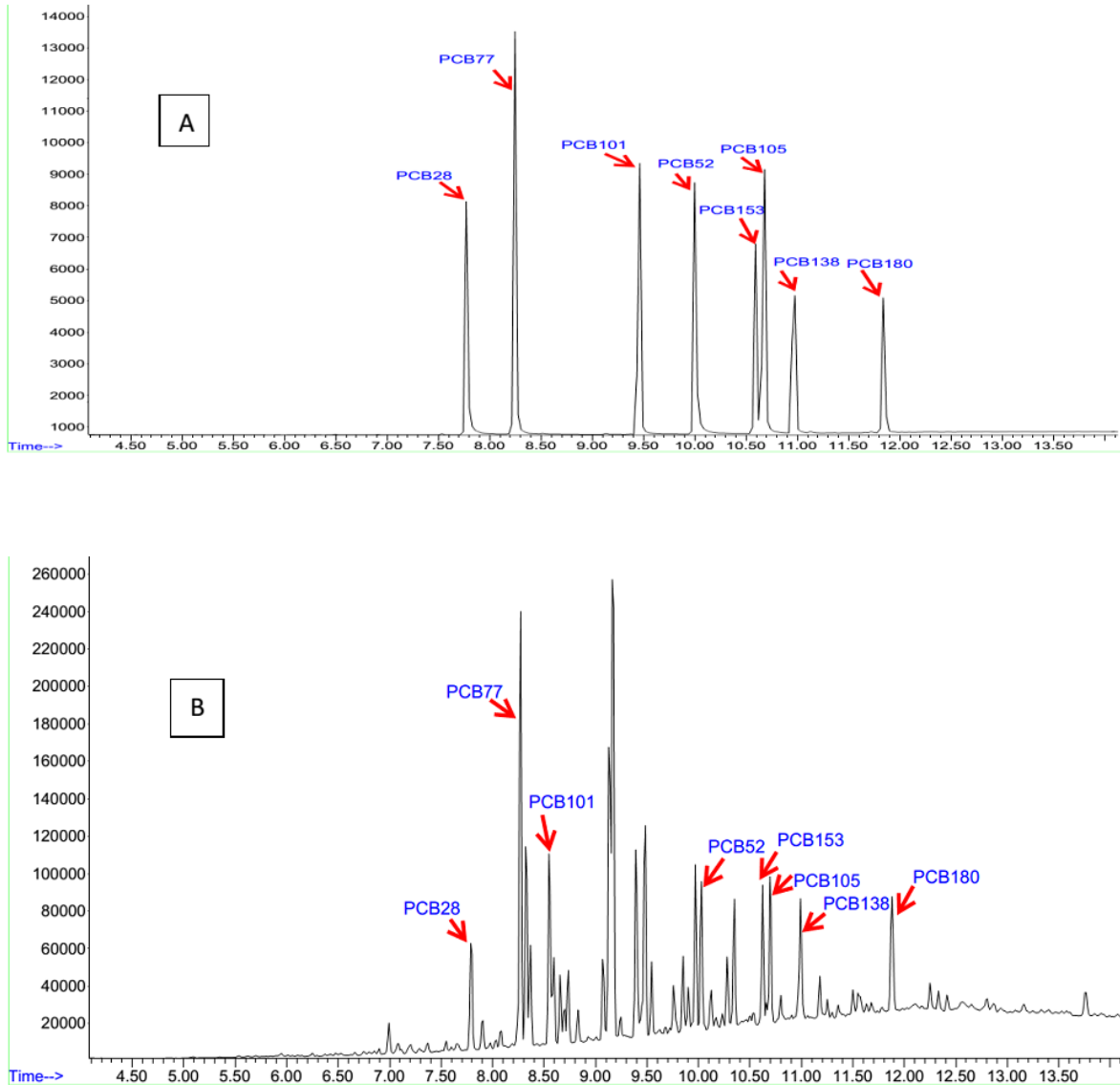
Figure 3.11 A-Chromatogram of a 0.125 ppm mixture of 8 PCB. B: standards B- Chromatogram of a clean-up sediment extract spiked with 0.125 ppm of PCB standard mixture and analysed using the SIM mode.

The analyte standards were run in triplicate and the three calibration curves obtained were combined and averaged to obtain an overall equation from which the anayte concentrations were calculated. The actual samples were run in triplicate. Each peak area from each of the triplicate analysis was used to calculate the concentrations of the analytes which was then averaged and the mean reported together with the standard deviation from the triplicate analysis (sample calculations shown in Appendix B). Table 3.5 shows the different analytes investigated, their retention times, correlation coefficients (R^2) and overall calibration equations for winter samples.

Table 3.5 Retention times, overall calibration equations and R^2 values for each analyte for winter samples.

Analyte	Retention time (min)	Overall calibration equations	R^2
PCB28	7.776	y = 75529x - 10772.6	0.9994
PCB52	8.250	y = 110017x - 25568	0.9985
PCB77	9.460	y = 1118815.3x - 16980	0.9993
PCB101	10.005	y = 117649.7x - 22998.3	0.9987
PCB105	10.598	y = 133702.6x - 28238.7	0.9988
PCB138	10.681	y= 95212.6x - 20438	0.9986
PCB153	10.966	y = 75269x - 16340	0.9985
PCB180	11.843	y = 69561.3x - 17016.7	0.9979
HCB	6.544	y = 101236.3x - 2089	0.9917
HCH	6.969	y = 40349.7x - 3929.9	0.9906
Heptachlor	8.002	y = 21733.7x - 6750.6	0.9947
Aldrin	8.557	y = 25370.3x - 3497.5	0.9978
o,p'-DDE	9.444	y = 83028.7x - 11718.7	0.9975
p,p'-DDE	9.887	y = 86629.3x - 14438.7	0.9970
o,p'-DDD+Dieldrin	9.98	y = 170087x - 38213	0.9968
Endrin	10.312	y = 19229x - 6331.2	0.9951
p,p'-DDD+*o,p'*-DDT	10.478	y = 266705x - 79865.3	0.9965
Mirex	12.528	y = 82334x - 10043.2	0.9976

The calculation of the concentrations of various native OCPs and PCBs in water and pore water was computed by using the concentration of the target analyte in the cleaned extract and the volume of water extracted as follows (USEPA, 2008):

$$Concentration \left(\frac{ng}{mL}\right) = \frac{C_{ex} * V_{ex}}{V_s} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots . (3.6)$$

Where:

C_{ex} = the concentration of the compound in the extract in ng/mL

V_{ex} = the extract volume in mL.

V_s = the sample volume in mL.

The calculation of the concentrations of native OCPs and PCBs in the soil and sediment samples involved the use of the concentration of the compound in the cleaned extract and the weight of the dried, ground and sieved soil and sediment as follows (USEPA, 2008):

$$Concentration\ \left(\frac{ng}{g}\right) = \frac{C_{ex}\ * V_{ex}}{W_S} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3.7)$$

Where:

C_{ex} = the concentration of the compound in the extract in ng/mL

V_{ex} = the extract volume in mL

W_S = the sample weight (dw) in g

Sample calculations are shown in Appendix B.

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CHAPTER FOUR
MANUSCRIPT ONE

OCCURRENCE AND SIGNIFICANCE OF POLYCHLORINATED BIPHENYLS IN WATER, SEDIMENT PORE WATER AND SURFACE SEDIMENT OF UMGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

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ABSTRACT

The Umgeni River is one of the main sources of water in KwaZulu-Natal, South Africa; however there is currently a lack of information on the presence and distribution of organic pollutants in its sediment, sediment pore water and surface water. This study aims to determine the occurrence and significance of selected polychlorinated biphenyls (PCBs) in the surface water, sediment pore water and surface sediment samples from the Umgeni River. Liquid-liquid and soxhlet extractions were used for water or pore water, and sediments respectively. Extracts were cleaned-up using a florisil column and analysed by gas chromatography-mass spectrometry. The total concentrations of 8 polychlorinated biphenyls were 6.910-21.69 ng/mL, 40.67-252.3 ng/mL and 102.6-427.8 ng/g (dw), in unfiltered surface water, unfiltered sediment pore water and surface sediments respectively. The percentage contributions of various matrices were 4, 36 and 60% for unfiltered surface water, unfiltered pore water and sediment respectively. The highest concentrations of PCBs were found in water, pore water and sediment collected from sampling sites close to the Northern Waste Water Treatment Works. The highest chlorinated biphenyl, PCB180, was the most abundant at almost all sampling sites. To our knowledge, this is the first report on occurrence of polychlorinated biphenyls in the Umgeni River water, pore water

and sediment system and our results provide valuable information regarding the partitioning of the PCBs between the water and sediment systems as well as the organic chemical quality of the water.

Keywords: *Umgeni River, sediment, pore water, polychlorinated biphenyls, gas chromatography-mass spectrometry*

4.1 INTRODUCTION

Polychlorinated biphenyls (PCBs) constitute a group of organic pollutants characterized by their persistence, bioaccumulation and bioamplification in biota, toxicity and long-range transport (Pennington, 2001, Sapozhnikova et al., 2004). PCBs are primarily industrial in origin and were intentionally produced and globally used in transformers and condensers; as flame resistant dielectric insulating fluids; in mining as hydraulic oils; in printing ink, glues, resins, plasticisers, etc. (Manz et al., 2001, Samara et al., 2006). However, their emission also results from domestic waste incineration plants and rubbish dumps; plants processing industrial waste; waste-oil incineration plants and extensive application in agriculture (sewage, sludge) (Manz et al., 2001). They have carcinogenic, mutagenic as well as teratogenic effects (Lauby-Secretan et al., 2013). PCBs have been the subject and focus of extensive research and monitoring in the environment, due to their potential of deleterious effects in development and reproduction in all biological species, fish behaviour and wild life (Daouk et al., 2011, Cohn et al., 2011, Katarzyńska et al., 2015). PCBs have been detected in fresh water, wastewater and sediments in different parts of the world (Zhang et al., 2003, Sapozhnikova et al., 2004, Katsoyiannis and Samara, 2004, Zhang et al., 2010). Due to their various environmental hazards, they were banned by the United States congress and the Stockholm convention in 2001 and are included in the list of priority pollutants to be regularly analysed and monitored (USEPA, 1996). Although, they were restricted, their residues can still be found in different environmental matrices such as water, sediment, soil, air, bio-solids etc. due to their persistence.

In South Africa less than a half of the rural population do not have access to clean and safe drinking water and about 12 million people who do not have access to clean water are left to access water from other sources such as rivers (Thwala, 2010). Therefore, investigations into the quality of available water resources such as lakes, rivers, and other water bodies are very important for protection of a scarce resource. Until now many studies have focused on the investigation of heavy metals (Binning and Baird, 2001, Fatoki and Awofolu, 2003a, Pegram and Bath, 1995) and only a few on organic pollution (Fatoki and Awofolu, 2003b, Fatoki et al., 2010) in South African rivers.

The Umgeni River is one of the major rivers found in the province of KwaZulu-Natal in South Africa and is one of the main water sources, but the water is of poor quality due to dumping of domestic waste from informal settlements, seepage of industrial wastes, use of agricultural pesticides, etc. that make their way into this river. Studies showed that more than 85% of contaminants in the Umgeni River basin were from non-point sources (Pegram and Bath, 1995). However, some metals such as mercury have been found in this river; their source being identified as Thor Chemicals (mercury reprocessing plant) which is thought to have discharged them into the Mngceweni River which is a tributary of the Umgeni River (Pegram and Bath, 1995). In 2002, a survey of some persistent organic pollutants in major South African waters revealed the presence of some PCBs congeners such as PCB28, PCB52, PCB 101, PCB138 and PCB153 in a sediment sample collected from the mouth of the Umgeni River (Vosloo and Bouwman, 2005). No other information about the occurrence and significance of persistent organic pollutants such as PCBs in the Umgeni River has been found. Therefore the aim of this work was to determine the occurrence, concentrations and significance of eight selected PCBs in water, pore water and sediment samples collected from 15 different sites along the Umgeni River. The water and pore water were analysed without being filtered in order to determine the total concentration of PCBs in water (freely dissolved + dissolved organic carbon + total suspended solids). The Umgeni River water is used by informal settlements along the river for various household activities such as washing, bathing, cleaning and irrigating, as well as a source of drinking water for livestock. In order to determine the concentrations that the residents of the informal settlements and the livestock are exposed to, it was necessary to investigate the unfiltered water. The structures of the 8 selected PCBs are shown in Figure 4.1. These particular PCBs were chosen because some of them are among the most toxic congeners and are recommended by World Health Organisation for monitoring (PCB77, PCB105) while other PCBs were chosen for the study because they are indicator PCBs (PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180) and are recommended by the European Union for assessing PCB pollution (EC, 1999). This work aimed to determine their presence and quantity in the Umgeni River catchment area.
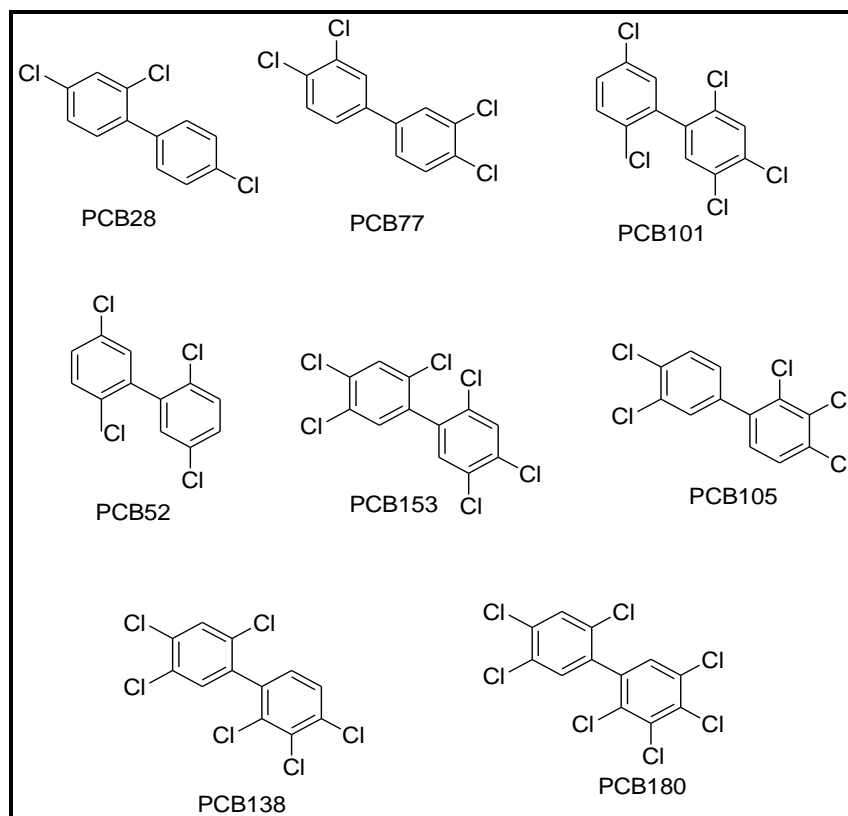
Figure 4.1 Structures of investigated polychlorinated biphenyl (PCB) congeners.

4. 2 MATERIALS AND METHODS

4.2.1. Physical Parameters of the Sampling Sites

Ambient and water temperature, pH of water (model IQ150, handheld pH/mv/ temperature meter), conductivity and total dissolved solids (TDS) (portable conductivity meter, Schott handylab LF12) were determined for each sample at the sampling site. Table 4.1 shows the physical parameters that were recorded at the different sampling sites during winter 2013.

4.2.2. Reagents and Standards

High performance liquid chromatography (HPLC) grade solvents, namely hexane, dichloromethane (DCM) and toluene, and florisil (MgO$_3$Si residue analysis grade, mesh 60-100, pore size 60Å), as well as the following PCB standards: PCB28 (2,4,4'-trichlorobiphenyl), PCB52 (2,2',5,5'-tetrachlorobiphenyl), PCB77 (3,3',4,4'-tetrachlorobiphenyl), PCB101 (2,2',4,5,5'-pentachlorobiphenyl), PCB105 (2,3,3',4,4'-pentachlorobiphenyl), PCB138 (2,2',3,4,4',5'–hexachlorobiphenyl), PCB153 (2,2',4,4',5,5'-hexachlorobiphenyl) and PCB180 (2,2',3,4,4',5,5'-heptachlorobiphenyl), were purchased from Sigma Aldrich (South Africa).

Table 4.1 Physical parameters at the sampling sites during the winter 2013 sampling season.

Sampling site (code)	Ambient Tᵒ (°C)	Water Tᵒ (°C)	pH	Conductivity (μs/cm)	TDS (mg/L)	Coordinates South	Coordinates East
Midmar Dam inlet (MDI)	12.3	11.6	5.54	83.7	49	29° 29′16.05"	30° 09'23.10"
Midmar Dam outlet (MDO)	12.3	13.2	5.69	75.5	44	29° 29'34.02"	30° 12'09.13"
Howick Falls (HOF)	17.8	13.8	5.99	89.7	53	29° 29'18.18"	30° 14'19.70"
Albert Falls inlet (AFI)	18.6	13.5	5.78	111.5	65	29° 26'31.94"	30° 19 47.10"
Albert Falls outlet (AFO)	19.2	15.4	6.04	93.8	55	29° 26'01.81"	30° 25'55.76"
Nagle Dam (NAD)	18.4	15.4	5.00	114.0	66	29° 35'08.42"	30° 37'23.94"
Joining point Umgeni-Msunduzi Rivers (JUM)	15.6	15.7	5.56	367.0	214	29° 37'16.61"	30° 40'46.59"
Inanda Dam inlet (IDI	17.2	16.6	4.98	278.0	160	29° 39'05.20"	30° 48'06.24"
Inanda Dam outlet (IDO)	15.1	15.9	4.53	257.0	149	29° 42'55.74"	30° 52'07.69"
Reservoir Hills (REH)	21.4	17.9	5.63	305.0	176	29° 47'08.05"	30° 56'25.51"
Umgeni business park (UBP)	21.4	17.6	4.90	334.0	194	29° 48'19.05"	30° 58'58.08"
Northern wastewater treatment works influent (NWTI)	22.8	21.9	4.70	970.0	568	29° 47'47.08"	30° 59'50.01"
Northern wastewater treatment works after treatment (NWTT)	19.8	19.9	4.64	1238	719	29° 47'47.02"	30° 59'50.06"
Northern wastewater treatment works effluent (NWTE)	21.0	19.8	4.94	674	392	29° 48'27.01"	30° 59'51.05"
Blue Lagoon (BLA)	21.4	20.0	5.12	[8]	[9]	29° 48'41.03"	31° 02'12.05"

[8] Blue lagoon is at the mouth of the river close to the Indian Ocean. Conductivity was higher than the maximum value the instrument could measure.
[9] The TDS at blue lagoon was higher than the maximum value the instrument could measure
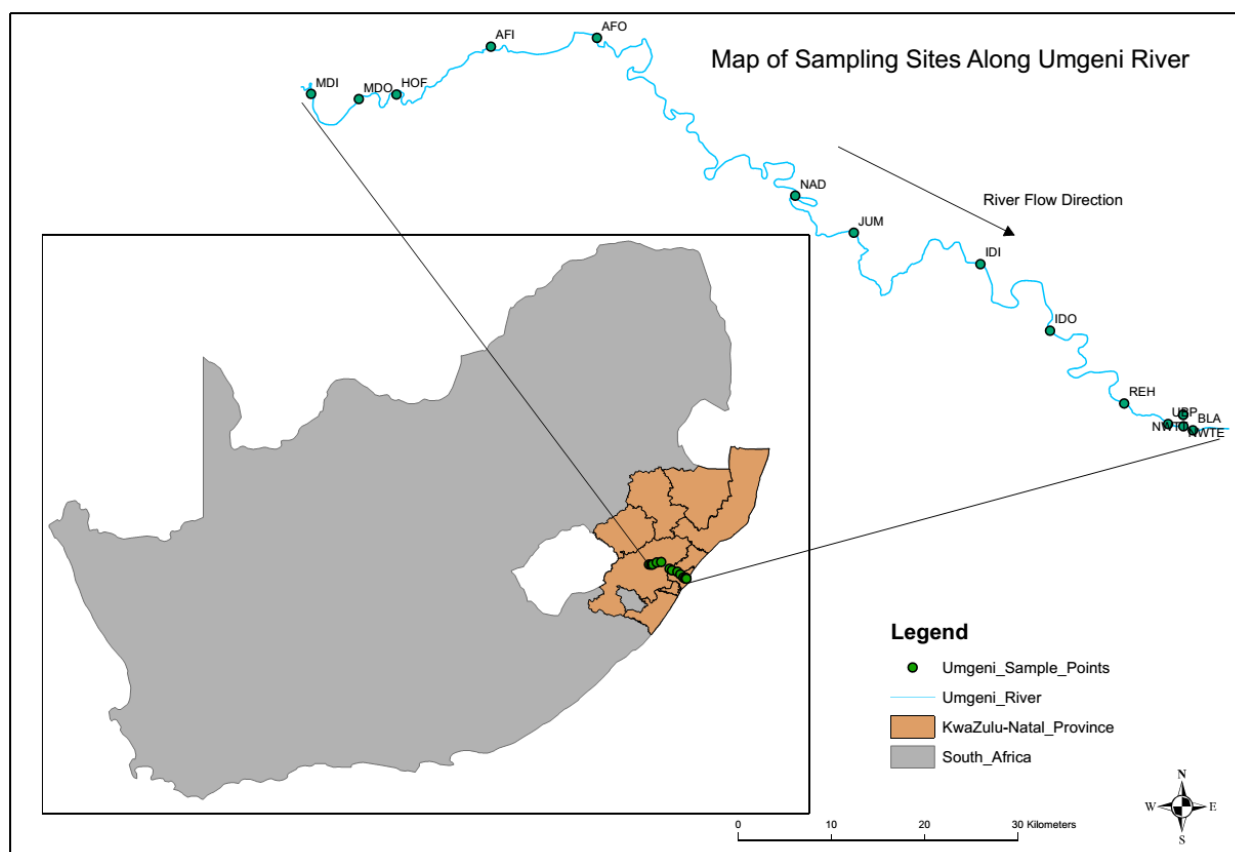
Figure 4.2 Map of sampling sites with the sample collection locations (map was generated from GPS coordinates using ArcGIS 10.2).

Anhydrous sodium sulfate (Na_2SO_4) gold line (CP) and silicon carbide boiling stones (CSi) were obtained from Associated Chemical Enterprises (ACE, South Africa) and sulfuric acid (98%) was obtained from Promark Chemicals (USA).

4.2.3. Sample Collection

Sampling was carried out during the winter period from 15th to 17th July 2013 and targeted 15 sampling sites including 12 sites selected along the Umgeni River and 3 sites at the Northern Wastewater Treatment Works and discharge point into the Umgeni River. Sampling sites were selected based on the close proximity of industrial, residential or agricultural activities along the river. The sampling locations and coordinates are shown in Table 4.1 and Figure 4.2. Water and sediment samples were collected at the same sites. The pore water samples were obtained from the sediment after centrifugation (DuPont instruments[R] SS-automatic centrifuge).

Water samples were collected in 2.5 L amber Winchester bottles previously washed with hot water and detergent and rinsed three times respectively with deionised water and sulfuric acid. At the site, the sampling bottles were rinsed three times with the river water to be collected. The bottles were then filled to overflowing, leaving no headspace. After water collection, the bottles were closed with caps that were lined with aluminium foil to prevent contamination with phthalates and plasticisers from the lids. A 1 mL aliquot of H_2SO_4 (50%) was transferred to each water sample to reduce microbial activity. Sediment was collected using a grab sampler and transferred to glass bottles that had been previously washed and rinsed as mentioned above. All the samples were kept in a cooler box containing ice and transported to the laboratory where they were kept in a fridge at 4 ^{o}C until extraction which was carried out within five days.

4.2.4. Sample Preparation and Clean-up

The water samples were extracted using liquid-liquid extraction (EPA method 3510-C) (EPA, 1996a). One litre of water was transferred to a separatory funnel and extracted with a 50 mL aliquot of HPLC-grade DCM. This process was repeated 6 times for each sample with fresh aliquots of DCM each time to increase recovery. All fractions were then combined and transferred into a round-bottom flask and concentrated using rotary evaporation (Heidolph Instruments GmbH & Co.kG) to approximately 5 mL. The concentrated extract was then transferred to a florisil (activated at 130°C for 12 hours) column containing 5 g of anhydrous sodium sulfate as a top layer, and eluted sequentially with 5 mL of hexane:DCM (94:6), (85:15), (50:50) and DCM (100%) (modified EPA method 3620-C) (EPA, 2007). The increasing polarity of the hexane-DCM solvent system allowed elution of different PCBs having different polarity indexes and solubilities with respect to hexane and DCM. All fractions were combined and concentrated with a rotary evaporator and finally air-dried and stored in a fridge at 4 °C until analysis.

After sampling, the sediment samples were subjected to centrifugation using 10 x 1000 rpm (revolutions per minute) for 15 min to separate the pore water (Zhang et al., 2003, Ankley and Schubauer-Berigan, 1994). The pore water samples were treated as per water samples, extracting 100 mL of pore water with 10 mL of DCM. The centrifuged sediment was transferred onto aluminium foil and air–dried before being ground with a mortar and pestle and sieved (laboratory test sieves: ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm purchased from DLD Scientific) for homogenisation and to increase the surface area. The sieved sediment (60 g, dw) underwent soxhlet extraction for 24 hours with 300 mL of toluene (EPA method 3540-C) (EPA, 1996b). The obtained extracts were concentrated with a rotary evaporator

to nearly 5 mL. The clean-up and concentration procedures were carried out as mentioned above with a florisil column containing 10 g of anhydrous Na_2SO_4 as a top layer and eluting with 4 aliquots of 20 mL of hexane-DCM solvent system. The extracts were air-dried and made up to 2 mL with DCM for analysis using gas chromatography-mass spectrometry (GC-MS).

4.2.5. Sample Analysis

Sample analyses were carried out in triplicate using an Agilent 6890 series gas chromatography system attached to a mass spectrometer detector (MSD5973). The GC system was equipped with a ZB-5MS capillary column, 0.25 mm i.d., 0.25 μm film thickness and 30 m length (Hewlett Packard; Houston, TX). The MS was operated using the selective ion monitoring acquisition mode (SIM). The carrier gas was purified helium. A 2 μL injection volume was used on a splitless mode with injector and detector temperatures set at 250 and 280 ^{o}C respectively. The oven temperature for analysis of PCBs was initially 120 ^{o}C and then increased to 290 ^{o}C at a ramping rate of 14 ^{o}C/min and held for 2 min. The total run time was 14.14 min. The MS source was operated at 250 ^{o}C and the quad at 200 ^{o}C. The electron ionisation energy was 70 eV.

Target analytes were quantified based on peak areas and by using an external calibration technique with the following six calibration concentrations: 0.25, 0.5, 1, 2, 4 and 8 μg/mL. The identification of analytes of interest was achieved by comparison of retention times of sample analytes with those of reference standards and by using the NIST library mass spectral data by monitoring 3 ions for each analyte (See Appendix A.1).

4. 3 QUALITY ASSURANCE

For water and pore water samples, the extraction recoveries were obtained by spiking tap water (three samples) (Meharg et al., 2003, Hellar-Kihampa et al., 2013) with known concentrations of standards and percentage recoveries were calculated (APHA et al., 1999, USEPA, 2008). For sediment sample recoveries, real sediment samples (three samples from three different sites) were subdivided into two subsamples whereby one was spiked with known concentrations of standards before extraction and the other was left unspiked. The recoveries were obtained by subtracting non spiked subsample concentrations from spiked subsample concentrations (Harry et al., 2008). The recovery samples were analysed at the same time with the actual samples. Procedural lab blanks (3–5) were used throughout all extractions and analyses for all matrices.

Table 4.2 Ions monitored limits of detection and quantification and percentage recoveries for the analysis of PCBs in water, pore water and sediment by GC-MS.

Analyte	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180
	150	220	254	150	145	184	145	162
Ions monitored	186	255	291	220	290	254	290	324
	256	292	326	292	360	326	360	394
LOD (ng/mL) in water	0.045	0.055	0.02	0.015	0.02	0.015	0.015	0.01
LOQ (ng/mL) in water	0.15	0.19	0.06	0.045	0.06	0.055	0.045	0.04
LOD (ng/mL) in pore water	0.455	0.55	0.18	0.13	0.185	0.17	0.135	0.115
LOQ (ng/mL) in pore water	1.51	1.835	0.595	0.43	0.625	0.56	0.445	0.39
%Recovery in water and pore water[10]	74.54 ±0.37	79.27 ±0.83	71.18 ±0.59	76.99 ±0.67	77.83 ±0.86	73.88 ±0.45	74.67 ±0.40	82.36 ±0.41
LOD (ng/g in sediment)[11]	0.76	0.92	0.30	0.21	0.31	0.28	0.22	0.19
LOQ (ng/g in sediment)[12]	2.52	3.06	0.99	0.71	1.03	1.12	0.75	0.66
%Recovery in sediment	69.53 ±1.75	73.67 ±1.22	79.77 ±2.03	80.74 ±2.94	82.87 ±2.50	78.46 ±1.27	79.39 ±1.05	84.39 ±1.15

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[10] ± number = Standard deviation; this means that the recovery experiments were carried out in triplicate and the mean recovery calculated as well as the standard deviation.

[11] The limit of detection was calculated as three times the signal-to-noise ratio using three calibration intercepts divided by the slope.

[12] The limit of quantification was calculated as ten times the signal-to-noise ratio using three calibration intercepts divided by the slope.

There were no detectable levels of analytes of interest in the extracted blank samples. The solvent blanks and standards were regularly analysed on the GC-MS to monitor the presence of interferences and as well as the condition of the column and instrument. To ensure minimal variation from the initial calibration standards, a calibration standard (0.5 μg/mL) was analysed after each batch of sample to ensure consistency of results. The identification of all analytes was possible using the base peak and two other confirming fragments including molecular ion. The limits of detection and quantification were calculated as three times and ten times respectively the signal-to-noise ratio using the standard deviation of the three calibration intercepts divided by the slope (Table 4.2). All data were processed using Microsoft excel (Version 2010).

4.4 RESULTS AND DISCUSSION

4.4.1. Polychlorinated Biphenyls in Surface Water

The concentrations of different PCB congeners investigated are shown in Table 4.3. All investigated PCBs were detected in all sites. The concentration of PCB180 (Log K_{ow} = 6.82) was highest in all sites while that of PCB28 (Log K_{ow} = 5.71) was lowest (See Appendix C.1). The relatively high Log K_{ow} value for PCB180 corresponds to low solubility in water and it was therefore expected to be present in lower concentrations in water. However, the higher concentrations of PCB180 that were found in water may be explained by the strong affinity of this high molecular weight PCB with total suspended solids (TSS) and dissolved organic carbon (DOC) in the water. The water samples were unfiltered in order to determine the concentrations that animals and humans are exposed to when they directly consume it. The Umgeni River water samples may possibly contain high TSS and DOC to which PCB180 would partition to resulting in high PCB180 concentrations in water (Aparna et al., 2014, Matyas et al., 2015, Zhang et al., 2011b). Furthermore, PCB180 has a higher number of chlorine atoms (7) compared to other investigated congeners, and consequently was more difficult to degrade, lasting longer in the aquatic environment (de Voogt et al., 1990, Nhan et al., 2001). This suggests that its presence in the environment was due to accumulation over time rather than point source entry. This is in contrast to PCB28 which has 3 chlorine atoms and was found to be present in the lowest concentration. The lowest concentration for PCB28 was observed at Howick Falls (HOF) (0.42 ng/mL) and the highest concentration of PCB180 was observed at Northern Wastewater Treatment Works influent (NWTI) (7.34 ng/mL).

Table 4.3 Concentrations of PCBs in the surface water (ng/mL) of the Umgeni River.

	Concentrations of Congeners (ng/mL)								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCBs
MDI	0.73 ±0.16	0.87 ±0.10	1.15 ±0.11	1.33 ±0.12	1.26 ±0.12	1.13 ± 0.15	1.15 ±0.14	2.19 ±0.18	9.81 ±1.08
MDO	0.74 ±0.13	0.90 ±0.11	1.15 ±0.09	1.35 ±0.09	1.26 ±0.09	1.15 ±0.09	1.17 ±0.10	2.21 ±0.20	9.92 ±0.91
HOF	0.42 ±0.23	0.70 ±0.15	0.80 ±0.10	0.97 ±0.09	0.90 ±0.10	0.80 ±0.07	0.81 ±0.09	2.26 ±0.04	7.67 ±0.86
AFI	0.85 ±0.11	0.90 ±0.15	1.25 ±0.03	1.44 ±0.04	1.38 ±0.02	1.26 ±0.04	1.27 ±0.04	2.37 ±0.04	10.70 ±0.47
AFO	0.71 ±0.10	0.82 ±0.08	1.11 ±0.06	1.29 ±0.04	1.23 ±0.03	1.13 ±0.07	1.13 ±0.06	2.53 ±0.03	9.96 ±0.49
NAD	0.83 ±0.05	0.96 ±0.06	1.26 ±0.04	1.46 ±0.03	1.37 ±0.06	1.26 ±0.03	1.28 ±0.04	2.53 ±0.01	10.95 ±0.29
JUM	1.02 ±0.05	1.24 ±0.02	1.50 ±0.01	1.68 ±0.01	1.62 ±0.03	1.49 ±0.01	1.50 ±0.03	2.08 ±0.02	12.12 ±0.17
IDI	0.84 ±0.10	1.01±0.11	1.24 ±0.07	1.41 ±0.07	1.36 ±0.02	1.25 ± 0.05	1.25 ±0.06	1.54 ±0.04	9.89 ±0.55
IDO	0.98 ±0.07	1.09 ±0.09	1.40 ±0.06	1.57 ±0.06	1.53 ±0.06	1.40 ± 0.06	1.41 ±0.05	1.77 ±0.06	11.15 ±0.50
REH	0.94 ±0.12	1.12 ±0.05	1.37±0.07	1.50 ±0.06	1.40 ±0.06	1.25 ±0.06	1.26 ±005	2.74 ±0.01	11.59 ±0.50
UBP	0.81 ±0.03	0.96 ±0.03	1.21 ±0.02	1.38 ±0.03	1.31 ±0.02	1.16 ±0.01	1.16±0.01	2.48 ±0.07	10.47 ±0.22
NWTI	1.09 ±0.05	2.94 ±0.28	4.01 ±0.04	1.61 ±0.02	1.54 ±0.03	1.51 ±0.04	1.39 ±0.03	7.34 ±0.02	21.43±0.50
NWTT	0.66 ±0.11	1.31 ±0.07	1.11 ±0.08	1.27 ±0.08	1.19 ±0.04	1.06 ±0.05	1.05 ±0.02	1.74 ±0.02	9.39 ±0.47
NWTE	0.72 ±0.12	0.92 ±0.09	1.15 ±0.05	1.39 ±0.06	1.26 ±0.03	1.14 ±0.06	1.13 ±0.04	1.51±0.02	9.21 ±0.47
BLA	0.60 ±0.04	1.11 ±0.03	1.03 ±0.04	1.20 ±0.02	0.90 ±0.87	1.01 ±0.02	1.02 ±0.04	2.30 ±0.02	9.16 ±1.06
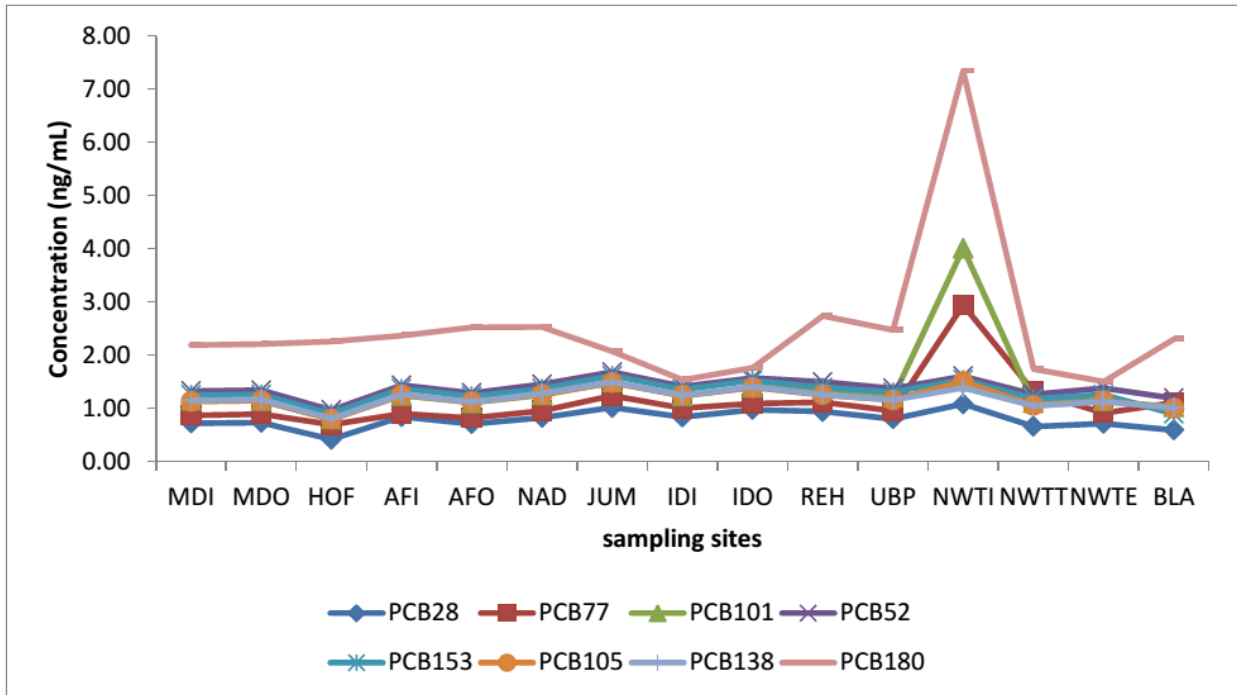
Figure 4.3 Trend of concentration of PCB congeners in water from the source to the mouth of the Umgeni River.

The mean concentration of individual PCBs in water was 1.36. ±0.07 ng/mL. The high concentration at NWTI was expected because this plant receives residential and industrial waste from the surrounding area which may contain high levels of PCBs. The conductivity was 970.00 µs/cm (Table 4. 1) at this site, which is the second highest observed, and indicates content high in dissolved ions and the TDS value was also high at this site (568 mg/L) (Table 4.1). This suggests a highly contaminated site which again provides organic content in the water onto which PCB180 can adsorb resulting in its high concentration at this site (ter Laak Thomas et al., 2009). In addition, oxygen is required for the proliferation of water-dwelling animals and microorganisms. A high TDS content interferes with oxygen transfer (Pophali et al., 2003), leading to a reduced growth of microbes. As a result, the reduction in microbial growth results in little or no microbial degradation of PCBs which may also contribute to the high levels of PCBs observed at this sampling site (Rein et al., 2007, Chang et al., 2001). The total concentration of PCBs in water samples varied from 6.910 - 21.69 ng/mL with a mean concentration of 10.90 ±0.56 ng/mL (Table 4. 4).

Table 4.4 PCB concentrations in water (ng/mL), pore water (ng/mL) and sediment (ng/g, dw) of Umgeni River.

Analytes	Water			Pore water			Sediment		
	range	mean	SD	range	mean	SD	range	mean	SD
PCB28	0.42-1.09	0.80	0.10	nd-17.73	8.36	0.55	11.41-93.74	28.54	1.76
PCB77	0.70-2.94	1.12	0.09	nd-52.30	14.64	1.03	11.09-88.73	28.28	1.93
PCB101	0.80-4.01	1.38	0.06	5.00-26.09	13.26	0.83	18.43-44.89	24.56	0.97
PCB52	0.97-1.68	1.39	0.05	5.63-29.25	15.08	0.91	14.17-39.42	22.04	0.49
PCB153	0.90-1.62	1.30	0.11	5.49-27.76	14.44	0.91	12.70-43.36	20.73	0.76
PCB105	0.80-1.51	1.20	0.05	4.83-25.09	12.74	0.79	10.16-26.67	17.95	0.55
PCB138	0.81-1.50	1.20	0.05	4.90-25.42	12.77	0.83	11.24-31.69	17.77	0.90
PCB180	1.51-7.34	2.51	0.05	8.86-48.72	25.47	0.60	13.42-59.34	34.62	1.43
∑PCBs	6.91-21.69	10.90		40.67-252.37	116.77		102.62-427.83	194.50	

This high level of PCBs in this river water may also be explained partly by the leaching of PCBs from urban activities at Durban as was demonstrated by Chevreuil and Granier who showed that the main cause of high levels of PCBs in the basin of river Seine in France was leaching (Chevreuil and Granier, 1985, Kim et al., 2007). Note that the levels of PCBs in this river water were higher than the maximum allowed by US EPA for fresh water (0.014 ng/mL) (US EPA, 1984) and European Union Council (0.010 ng/mL) (EU, 1998). However in this study, the water was unfiltered and contained much total suspended solids on which PCBs adsorb and this may have increased the PCB concentrations in water sample extract.

The wastewater treatment process showed some reduction in the concentrations of the PCBs in the water when it reached the NWTT (after treatment) compared to the influent (NWTI) (Table 4.5, Figure 4.3). Table 4.5 shows that the treatment process was most able to reduce PCB180, PCB101 and PCB77 by 76.29, 72.32 and 55.44% respectively of the amount received by the plant at the influent. This reduction may be attributed to either the actual chemical treatment used in the plant process or the hydrophobic PCBs partitioning itself into the phase containing the organic particles which then settle in the sedimentation step, during the wastewater treatment process. In a study on activated sludge treatment process, Katsoyiannis and Samara found that WWTP sludge contains between 39 and 98% of POPs and the fraction remaining in treated water was due to adsorption of these pollutants onto non-settleable solids (Katsoyiannis and Samara, 2005). Concerning the Northern Wastewater Treatment Works (NWWTW), mentioned in this study, more investigation is needed to determine the annual loading of POPs, their accumulation in the sludge and their remaining fraction in treated water or if the addition of a chemical coagulation agent affects the partitioning of POPs between the water and bio-solids. Studies on wastewater treatment plants also showed that in general, persistent organic pollutants were in higher concentrations in the influent than effluent (Mowery and Loganathan, 2007).

Table 4.5 Percentage reduction of PCB concentrations in water by the Northern Wastewater Treatment Works.

Congeners	Concentrations (ng/mL)			
	NWTI	NWTT	Difference	%
PCB28	1.09	0.66	0.43	39.45
PCB52	1.61	1.27	0.34	39.00
PCB77	2.94	1.31	1.63	55.44
PCB101	4.01	1.11	2.90	72.32
PCB105	1.51	1.06	0.45	29.80
PCB138	1.39	1.05	0.34	24.46
PCB153	1.54	1.19	0.35	22.73
PCB180	7.34	1.74	5.68	76.29

4.4.2. Polychlorinated Biphenyls in Sediment Pore Water

The concentrations of PCBs in pore water ranged from not detectable level for PCB28 at MDO to 52.30 ng/mL for PCB77 at UBP (Table 4.6) with an average concentration of 14.60 ±0.81 ng/mL. The concentrations were generally lower towards the source of the river and increased towards the mouth (Table 4.6 and Figure 4.4). This may be due to the increase of industrial activities as the river flows down towards Howick and the city of Durban or also an accumulation effect of the PCBs as the river flows downstream towards the mouth carrying with it TSS and DOC with PCBs partitioned to it. PCB180 was again the most abundant PCB in pore water in almost all sampling sites (Table 4.6 and Figure 4.4) confirming its strong affinity with TSS and DOC whose concentrations were greater in unfiltered pore water than unfiltered surface water (Aparna et al., 2014, Matyas et al., 2015, Zhang et al., 2011b). Another possible reason is its highly chlorinated structure which makes it less volatile and lipophilic allowing it to be preferentially retained in the sediment pore water (de Voogt et al., 1990).

The total concentrations of congeners at each site (Table 4.6) showed that the levels of PCBs were highest at NWTT and NWTE due to the accumulation of contaminants from different sources that make their way to the treatment plant. The higher levels of total PCBs at sites IDO and UBP were attributed to the low water flowrate at these sites, allowing time for the TSS onto which the pollutants were partitioned, to settle in sediment and therefore be extracted in its pore water. PCB77 was in high concentrations at UBP (Table 4. 6, Figure 4.4) (See appendix C.2) which suggested a possible input of

this congener at this site from sources such as transformer liquids, incineration of waste or from construction material (this site is currently under construction and is being used by heavy machinery).

The total PCB levels in pore water varied from 40.67 to 252.37 ng/mL with a mean of 116.77 ng/mL (Table 4.4), which is higher than in water. The higher concentrations in pore water is expected because PCBs are hydrophobic and tend to associate with organic materials found in sediments rather than dissolve in water (Julia et al., 2012). However the hydrophobic PCBs, in sediment tend to re-suspend from sedimentary phase to the pore water (Zhang et al., 2003) which may be the case for the present study. Studies on sediment-pore water distribution models of POPs have also confirmed higher POP concentrations in pore water than in water (Perssona et al. 2005).

Table 4.6 Concentration of PCB congeners in the pore water of the Umgeni River.

	Concentrations of PCBs in pore water in ng/mL±SD								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCBs
MDI	3.42 ±0.26	8.30 ±0.41	6.39 ±0.18	7.29 ±0.24	7.17 ±0.22	5.98 ±0.26	6.31 ±0.21	23.17 ±0.50	68.02 ±2.30
MDO	nd	8.41 ±4.84	5.00 ±2.92	5.63 ±3.28	5.49± 3.35	4.83 ±2.89	4.90 ±2.92	22.47 ±0.58	59.17 ±21.35
HOF	4.71 ±0.06	5.48 ±0.46	6.78 ±0.12	6.84 ±0.15	6.81 ±0.10	6.06 ±0.16	5.84 ±0.24	21.91 ±0.20	64.43 ±1.50
AFI	5.20 ±0.07	6.24 ±0.19	7.72 ±0.19	8.78 ±0.13	8.47 ±0.13	7.47 ±0.28	5.62 ±0.11	11.10 ±0.15	60.60 ±1.25
AFO	nd	nd	5.13 ±0.60	6.05 ±0.74	5.69 ±0.76	4.88 ±0.70	5.04 ±0.66	8.86 ±0.09	42.08 ±4.27
NAD	8.21 ±1.11	8.92 ±1.35	12.60± 1.46	14.69 ±1.73	13.95 ±1.52	12.35 ±1.32	12.48 ±1.54	15.33 ±0.35	98.52 ±10.38
JUM	6.71 ±0.75	10.05 ±1.42	11.89 ±1.69	14.07 ±2.15	13.50 ±1.98	11.76 ±1.64	11.67 ±1.60	25.22 ±0.50	104.86 ±11.71
IDI	9.30 ±0.50	10.09 ±0.33	14.67 ±0.34	17.31 ±0.48	16.27 ±0.43	14.56 ±0.34	14.57 ±0.18	18.98 ±0.45	115.75 ±3.06
IDO	15.44 ±1.27	17.72 ±1.09	23.84 ±0.89	27.39 ±0.54	26.17 ±0.82	22.99 ±0.70	23.82 ±0.87	33.79 ±1.00	191.15 ±7.19
REH	8.48 ±0.67	14.22 ±0.52	15.47 ±0.57	18.00 ±0.53	17.30 ±0.52	15.03 ±0.48	15.23 ±0.28	48.72 ±0.73	152.47 ±4.30
UBP	10.82 ±0.54	52.30 ±1.32	17.64 ±0.84	19.99 ±0.58	18.64 ±0.71	16.26 ±0.51	16.70 ±0.57	35.37 ±0.86	187.72 ±5.92
NWTT	14.38 ±0.99	27.92 ±1.32	21.73 ±0.94	23.61 ±0.66	23.32 ±0.68	20.77 ±0.71	20.70 ±0.64	45.26 ±1.05	197.69 ±7.00
NWTE	17.73 ±0.34	20.33 ±0.54	26.09 ±0.66	29.25 ±1.16	27.76 ±1.29	25.09 ±0.85	25.42 ±1.55	32.10 ±1.63	203.78 ±8.02
BLA	7.36 ±0.28	11.41 ±0.28	10.71 ±0.24	12.28 ±0.30	11.66 ±0.29	10.35 ±0.23	10.46 ±0.26	14.35 ±0.34	88.57 ±2.22

nd = not detected
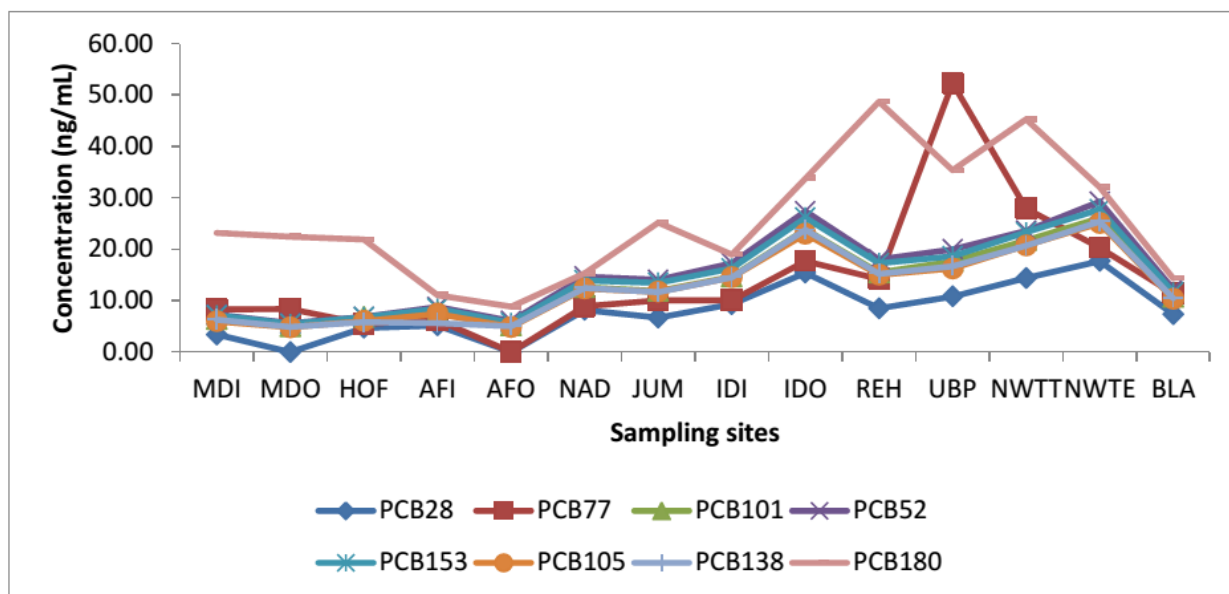
Figure 4.4 Trend of PCB concentrations in pore water from the source to the mouth of the Umgeni River.

4.4.3. Polychlorinated Biphenyls in Surface Sediments

The concentrations along the river ranged from 10.16 ng/g (PCB105 at IDO) to 93.74 ng/g, (PCB28 at NWTT) with an average of 24.31 ±1.10 ng/g of dry weight (dw) (Table 4.7). All the PCB congeners investigated were detected in all sediment samples. This may be attributed to the strong affinity that exists between the hydrophobic pollutants and sediment organic carbon (Kookana, 2011). As in water and pore water, the level of PCB180 was highest in all sediment samples (Table 4.4) due to its hydrophobicity in the aquatic environment which is related to its K_{ow} value and therefore its sorption to the organic matter in sediment (Zhou et al., 2005). The distribution of PCB congeners in the aquatic systems may also be assigned to losses of less chlorinated congeners through volatilisation, sedimentation and degradation by microbial activity as well as thermal and UV light degradation (Brown et al., 1987b, Quensen et al., 1988, MacDonald et al., 1992, De et al., 2006). PCBs 28 and 77 were in unusually high concentrations at NWTT (See appendix C.3). This suggested that apart from the waste received by the plant there may be another input of these two congeners at that site such as industrial effluent received by the plant (Gioia et al., 2014). The lowest total concentrations of PCBs were observed at IDO while the highest was recorded at NWTT.

Table 4.7 Concentrations of PCBs (ng/g, dw) in the sediment at each site across Umgeni River.

Site	Concentrations of PCBs in sediment (ng/g ±SD)
	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	$\sum$PCBs
MDI	16.70 ±0.60	19.85 ±1.43	18.43±0.52	18.41±0.03	16.64±0.33	15.04±0.08	15.07±0.68	36.69±0.83	156.83±4.51
MDO	30.57 ±3.10	24.58 ±1.91	22.50±0.59	19.93±0.15	18.38±0.03	17.32±0.07	15.73±0.36	35.64±2.12	184.66±8.02
HOF	31.18 ±0.83	29.91 ±1.27	26.40±1.78	21.44±0.51	23.51±0.65	24.11±0.17	18.75±0.26	55.78±4.83	231.07±10.30
AFI	15.49 ±0.85	20.47 ±1.00	19.91±1.34	18.83±0.32	17.73±0.68	13.46±0.56	16.41±1.92	30.75±1.66	153.05±8.32
AFO	18.09 ±0.95	34.45 ±2.35	19.82±1.01	19.58±0.20	17.30±0.16	15.28±0.13	14.38±0.59	43.73±5.14	182.64±10.53
NAD	16.40 ±1.22	19.61 ±1.14	18.51±0.72	18.97±0.55	16.59±0.32	15.76±0.62	13.70±0.41	34.66±0.43	154.20±5.41
JUM	33.81 ±1.97	31.73 ±6.47	28.34±0.08	21.49±0.55	19.16±0.30	18.11±0.84	15.63±0.55	43.15±0.79	211.42±12.55
IDI	23.33 ±0.82	24.89 ±1.60	24.86±0.56	24.99±1.30	22.43±1.21	22.12±1.43	23.49±2.89	25.97±1.90	192.09±11.72
IDO	11.41 ±1.66	11.09 ±1.87	19.46±1.86	14.17±0.10	12.70±0.47	10.16±0.23	11.24±0.33	13.42±0.26	103.65±6.78
REH	18.74 ±1.62	19.01 ±1.76	21.15±1.23	21.48±0.66	19.97±0.82	17.55±0.23	16.11±0.67	21.16±0.48	155.17±8.31
UBP	26.23 ±1.43	25.47 ±1.35	28.48±0.97	27.31±0.93	24.75±0.63	22.51±1.06	22.21±0.36	27.32±0.82	204.28±6.97
NWTI	31.86 ±4.74	26.37 ±1.78	26.84±0.35	24.16±0.30	21.12±0.20	18.82±0.48	18.48±0.91	27.70±0.78	195.35±9.47
NWTT	93.74 ±2.79	88.73 ±2.11	44.89±1.05	39.42±0.69	43.36±3.49	26.67±0.41	31.69±1.04	59.34±0.33	427.83±12.14
NWTE	24.41 ±1.24	26.01 ±0.66	22.66±0.57	21.53±0.48	20.29±1.48	18.05±0.64	19.31±2.08	29.35±0.21	181.61±7.74
BLA	36.17 ±2.56	22.01 ±2.21	26.19±1.31	18.92±0.60	17.02±0.61	14.25±0.48	14.40±0.46	34.61±0.83	183.58±9.06

The relatively low concentrations at the IDO sampling site could be because most of the PCBs had already been extracted from the sediment in the pore water (Table 4. 6).

Zhao and his co-workers showed that high PCBs levels occur in the fraction of sediment with grain size of 31 to 63 μm (Zhao et al., 2010b). In addition, studies on sorption of hydrophobic pollutants on natural sediment demonstrated that the sand fraction (>50 μm) is considerably less effective in adsorption of hydrophobic pollutants (Karickhoff et al., 1979, Ke-xin et al., 2003, Carro et al., 2002). Therefore since more than 52% of IDO sediment size was higher than 300 μm (particle sizes determined during grinding and sieving steps of sample preparation), it could not retain much pollutant and hence pore water was more concentrated than the sediment itself at this site. For the NWTT, the high concentration of PCBs in its bio-solid was expected since this site continually receives treated water before being discharged. Table 4.5 shows that even the treated water still has considerable amounts of PCBs which eventually partition itself in the bio-solid sampled at the NWTT site resulting in its increased concentration. The levels of PCBs in the bio-solids of NWTI were generally lower than those in the bio-solids of NWTT. This was because the bio-solid at NWTI was fresh and occasional while the bio-solid at NWTT accumulated over time at that sampling point. Note that in all matrices the levels of PCB concentrations at sites close to and exiting the Northern Wastewater Treatment Works (NWWTW) were high. Other studies have also found that wastewater treatment plants are important point sources of POP contamination (Samara et al., 2006).
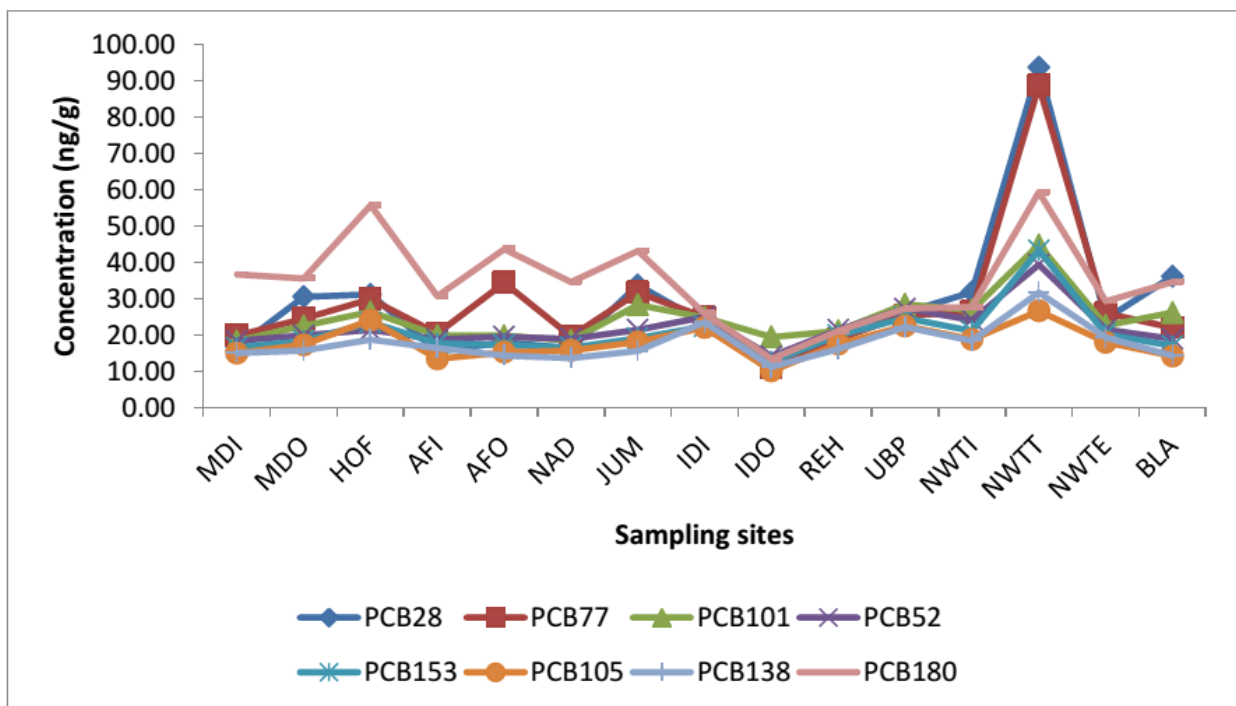
Figure 4.5 Trend of PCB concentrations in sediment across the Umgeni River.

4.4.4. Comparison of Sediment Total PCBs With Levels Found Elsewhere in the World

The total concentration of PCBs congeners in sediment fluctuated between 102.62–427.83 ng/g with a mean concentration of 194.50 ±8.79 ng/g, dry weight (Table 4.4). Concentrations of PCBs in sediment were higher than in pore water and much higher than in water (See appendix C.4). This was expected because PCBs are hydrophobic and tend to be adsorbed onto solid organic particles and sediment (Bazzanti et al. 1997). Compared to PCBs detected elsewhere, this level was higher than that detected in the sediments obtained from Yamuna River in Dehli in India (0.20-21.16 ng/g) with a mean of 6.63 ±0.69 ng/g (Kumar et al., 2013a). The levels in this study were also found to be higher than those found in Vietnam (Hanoi region) (0.47-28.1 ng/g, dw) (Nhan et al., 2001) or that in Bahlui River, in Eastern Romania (24–158 ng/g with mean: 59 ng/g) (Dragan et al., 2006). However, the present results were in the same range as those obtained in surface sediments of an industrialised urban river (Huveaune) in France (2.8-435 ng/g) having an average concentration of 148 ±64 ng/g (Kanzan et al., 2014) and lower than PCB levels found in the Keelong River in Taiwan (mean: 230 ng/g, dw) (Iwata et al., 1994), Minjiang Estuary (985.2 ng/g), Pearl Estuary (635.7 ng/g) Jiaozhou Bay (273.3 ng/g) (Xing et al., 2005), upper Sheboygan River, Winsconsin in United States (1000-104000 ng/g) (Li et al., 2005). No comparison could be made on the temporal PCB concentration trends, as no data were available on the past PCB levels for the investigated river in this study. Note that the current study revealed that the total average PCB level in the Umgeni River sediment was very much lower than the interim fresh water sediment quality guidelines (ISQG) of 21 500 ng/g (dw) and probable effect level (PEL) of 189 000 ng/g (dw) permitted by the Canadian quality sediment guidelines (CCME, 2002). According to Ontario sediment quality guidelines, however, the total average of PCBs in the sediment of Umgeni River, was found to be higher than the lowest effect level (LEL) (70 ng/g, dw) and far less than the severe effect level (SEL) (530000 ng/g, dw) (Persaud et al., 1993).

4.5 CONCLUSION

The present study has provided data on the levels of PCBs in water, pore water and sediments from 15 sampling sites along the Umgeni River. All 8 selected PCB congeners were found in all 15 sites investigated and in all matrices. The concentrations of PCBs increased clearly at

the sites of the Wastewater Treatment Works. The total concentrations of 8 polychlorinated biphenyls were 6.910-21.69 ng/mL, 40.67-252.3 ng/mL and 102.6-427.8 ng/g (dw), in surface water, pore water and surface sediments respectively. The PCB levels were higher in sediment than in water and pore water. In general, PCB180 is the most abundant PCB in water, pore water and sediment samples which was expected because PCB 180 has the highest molecular weight in this study's set of investigated analytes and has a K_{ow} value that shows its preference to adsorb onto organic particles which was present in high amounts in the unfiltered samples. Our results suggest that the Umgeni River water quality is poor with regard to pollution by PCBs and may represent a risk to human health and aquatic environment. The findings of this study indicate that there is a need to establish a reliable system of monitoring polychlorinated biphenyls and other organochlorinated compounds in order to take appropriate action to maintain environmental water quality standards in the Umgeni River. Further research is needed on levels of organochlorines in aquatic biota such as fish and aquatic plants in the Umgeni River to allow a complete assessment of the risks these contaminants have on aquatic life and human health.

ACKNOWLEDGEMENTS

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CHAPTER FIVE
MANUSCRIPT TWO

PARTITION DISTRIBUTION OF SELECTED ORGANOCHLORINE PESTICIDES IN WATER, SEDIMENT PORE WATER AND SURFACE SEDIMENT FROM UMGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

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ABSTRACT

Organochlorine pesticides (OCPs) were analysed in surface water, pore water and surface sediment samples collected from the Umgeni River which is one of the largest rivers in the province of KwaZulu-Natal, South Africa. Liquid-liquid extraction was used to extract the analytes from water and pore water samples and soxhlet extraction was used to extract sediment samples with subsequent florisil clean-up and gas chromatography-mass spectrometry (GC-MS) analysis. Twelve selected OCPs were analysed and their total concentrations were found to range between 8.04-21.06 ng/mL, 36.06-188.43 ng/mL and 148.17-554.73 ng/g in unfiltered surface water, unfiltered pore water and surface sediment (dry weight) respectively. The results indicated that the concentrations of these selected pesticides were far higher in sediment (72%) than in pore water (25%) and water (3%). The most polluted sites were Northern Wastewater Treatment influent (NWTI) for water ($\sum^{12}$OCP $= 19.41 \pm 1.43$ ng/mL) and Northern Wastewater Treatment effluent (NWTE) for pore water ($\sum^{12}$ OCP $= 166.23 \pm 7.16$ ng/mL) and sediment ($\sum^{12}$ OCP $= 495.21 \pm 32.38$ ng/g, dw). The most abundant individual OCPs and their average concentrations in general in the river were

p,p-DDE in unfiltered water (1.62 ±0.22 ng/mL) and unfiltered sediment pore water (17.09 ±7.96 ng/mL) and endrin in surface sediment (55.57 ±19.01 ng/g, dw)

5.1 INTRODUCTION

Pesticides are agrochemicals extensively used in agriculture and public health sectors to control or mitigate pests causing crop damage and diseases. Their main properties include low polarity, low aqueous solubility and high lipophilicity. As a result, they bioaccumulate and bioamplify through the food chain and are hence a threat to the environment and to human health (Afful et al., 2010, Zhao et al., 2013, Zhao et al., 2009). Researchers have found that organochlorine pesticides and their metabolites may cause chronic toxicity to humans and animals through air, water and food intake (Dong-hui and Guang-xing, 2012, Rachid et al., 2012). Many of them are agents of reproduction and birth defects (Edwards, 1987, Ghuman et al., 2013, Tadevosyan et al., 2012), immune system dysfunction, endocrine disruptions and cause cancer (Adeyemi et al., 2008, Cockburn et al., 2011, Rull and Ritz, 2003). OCPs have been banned in many countries since the 1970s but are still detected in water, sediments, air and aquatic biota today, because of their persistence in the environment (Fox et al., 2001, Albaiges et al., 1987, Iwata et al., 1994, Hogarh et al., 2014). Even though only 3% of pesticides sold worldwide per year is purchased by Africa, South Africa alone forms about 60% of the pesticide market and is the leading agricultural power in sub-Saharan Africa (Naidoo and Buckley, 2003). Therefore monitoring of the presence of OCPs in the South African environment is necessary.

The Umgeni River has a surface area of 4416 km^2 and spans a length of 225 km from source to mouth. It is the main source of water for many people in this province; both urban and rural and particularly for people living in squatter camps along this river who use its untreated water for bathing, cooking, washing etc. This river is also interrupted by many dams which store water for different uses such as irrigation, recreation and fish farming apart from its main use of drinking water. However, the quality of the Umgeni River water is poor due to pollution by people residing in these informal settlements and pesticides used by

farmers which make their way into the waterway by runoff. In addition there is also seepage of untreated industrial waste into this river and its tributaries which pass through urban, agricultural and industrialized areas. Limited studies have been done on the qualitative and quantitative analysis of pesticides in this river and this study aims to provide important information on the levels of selected pesticides (Figure 5.1) in the Umgeni River as well identify the most highly contaminated sites along the river. In order to know the total concentrations of pesticides (freely dissolved + organic carbon + suspended solids) to which animals and people using this water are exposed, the water was treated unfiltered. To the best of our knowledge, this is the first study that has investigated the qualitative and quantitative levels of these selected OCPs from the source to the mouth of the Umgeni River. The reported results provide much needed information on the presence of these OCPs which may contribute to the health risk of animals and humans who consume the water from the Umgeni River.
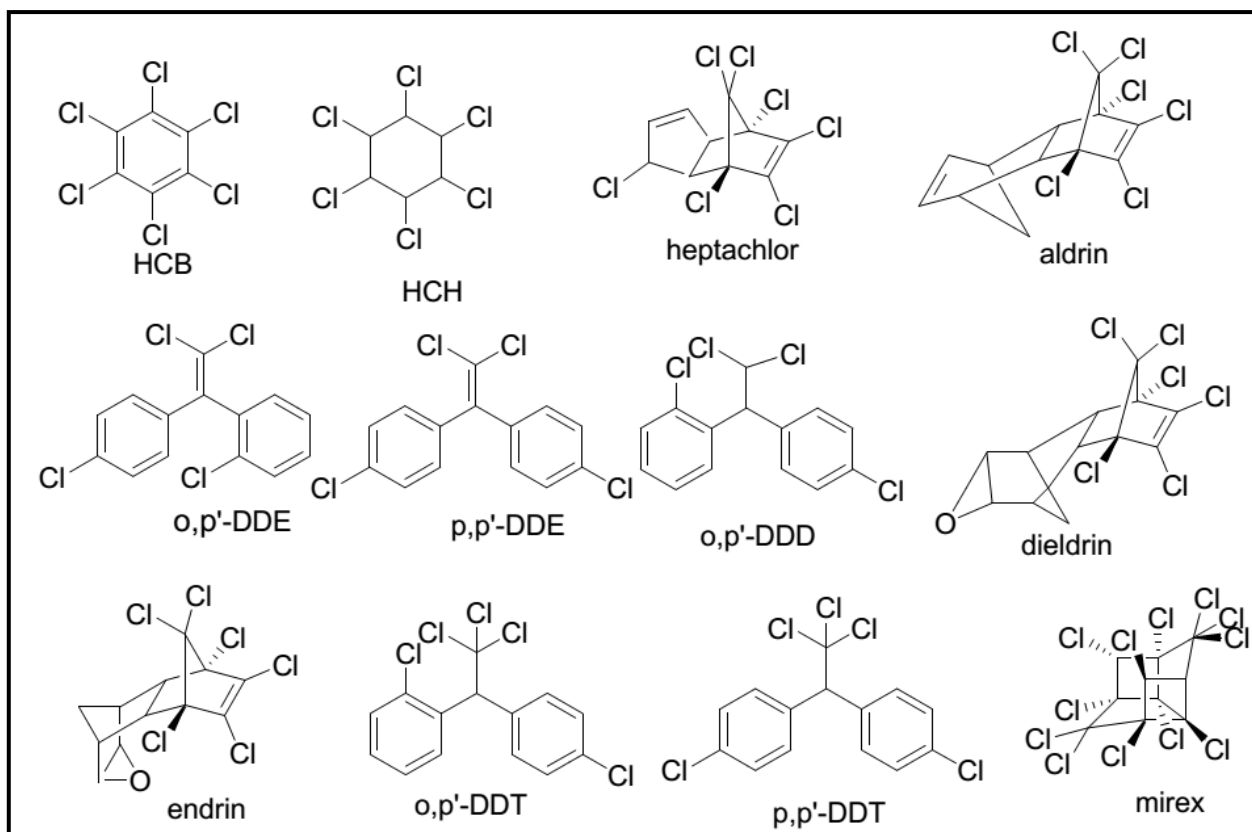
Figure 5.1 Structures of investigated organochlorine pesticides (OCPs) in the Umgeni River.

5.2 MATERIALS AND METHODS

5.2.1. Chemicals and Apparatus

The solvents including high pressure liquid chromatography (HPLC) grade solvents, namely hexane, dichloromethane (DCM) and toluene, and florisil (MgO_3Si residue analysis grade, mesh 60-100, pore size 60Å), as well as OCP standards (HCB, HCH, heptachlor, aldrin, *o,p*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, dieldrin, endrin, and mirex) were purchased from Sigma Aldrich. Anhydrous sodium sulfate (Na_2SO_4) gold line (CP) and silicon carbide boiling stones (CSi) were obtained from Associated Chemical Enterprises (ACE) and sulfuric acid (98%) was obtained from Promark Chemicals. The test sieves (ss 200 mm ϕ x 100 µm to ss 200 mm ϕ x 600 µm) were obtained from DLD Scientific in South Africa. Also separatory funnel, pestle and motar and a column were used.

5.2.2. Study Area

The Umgeni River is the main river in the province of KwaZulu-Natal and starts from the lower mountains of Spioenkop and Lionskop on either side of Nottingham (Van der Zel, 1975) and ends at the mouth at the Blue Lagoon in Durban which empties into the Indian Ocean. Water and sediment samples were collected during the winter period, from 15th to 17th July, 2013 from fifteen sampling stations including 12 sites selected along the Umgeni River and 3 sites around the Northern Wastewater Treatment Works (NWWTW), which discharges its treated water back into the Umgeni River a few kilometers downstream. Sampling stations were selected based on their location and activities around them, such as, agricultural, industrial or residential. The environmental physical parameters, coordinates and map of the sampling area are shown in Table 5.1, Figure 5.2 and Figure 5.3.

5.2.3. Physical and Chemical Parameters of the Study Area

The physical parameters of a given area influences the chemistry of the environment, such as the partition of pollutants between the various environmental matrices (water, pore water and surface sediment) and the concentration of pollutants. The physical parameters of each sampling site were measured. These were water temperature, ambient temperature, pH, conductivity and total dissolved solids (TDS).

Table 5.1 Physical and chemical parameters and geographical coordinates of the sampling sites along the Umgeni River during winter 2013.

Sampling site	Ambient T° (°C)	Water T° (°C)	pH	Conductivity (µs/cm)	TDS (mg/L)	Coordinates	
						South	East
Midmar Dam inlet (MDI)	12.3	11.6	5.54	83.7	49	29 29′ 16.05″	30 09′ 23.10″
Midmar Dam outlet (MDO)	12.3	13.2	5.69	75.5	44	29 29′ 34.02″	30 12′ 09.13′
Howick Falls (HOF)	17.8	13.8	5.99	89.7	53	29 29′ 18.18″	30 14′ 19.70″
Albert Falls inlet (AFI)	18.6	13.5	5.78	111.5	65	29 26′ 31.94″	30 19 47.10″
Albert Falls outlet (AFO)	19.2	15.4	6.04	93.8	55	29 26′ 01.81″	30 25′ 55.76″
Nagle Dam (NAD)	18.4	15.4	5.00	114.0	66	29 35′ 08.42″	30 37′ 23.94″
Joining point Umgeni-Msunduzi Rivers (JUM)	15.6	15.7	5.56	367.0	214	29 37′ 16.61″	30 40′ 46.59″
Inanda Dam inlet (IDI	17.2	16.6	4.98	278.0	160	29 39′ 05.20″	30 48′ 06.24″
Inanda Dam outlet (IDO)	15.1	15.9	4.53	257.0	149	29 42′ 55.74″	30 52′ 07.69″
Reservoir Hills (REH)	21.4	17.9	5.63	305.0	176	29 47′ 08.05″	30 56′ 25.51″
Umgeni business park (UBP)	21.4	17.6	4.90	334.0	194	29 48′ 19.05″	30 58′ 58.08″
Northern Wastewater Treatment works influent (NWTI)	22.8	21.9	4.70	970.0	568	29° 47′ 47.08″	30° 59′ 50.01″
Northern Wastewater Treatment works after treatment (NWTT)	19.8	19.9	4.64	1238	719	29° 47′ 47.02″	30° 59′ 50.06″
Northern Wastewater Treatment works effluent (NWTE)	21.0	19.8	4.94	674	392	29° 48′ 27.01″	30° 59′ 51.05″
Blue Lagoon (BLA)	21.4	20.0	5.12	-[13]	-	29 48′ 41.03″	31 02′ 12.05″

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[13] Blue lagoon is located at the mouth of the river where it empties in Indian ocean, the conductivity and TDS were higher than the maximum the instrument could measure
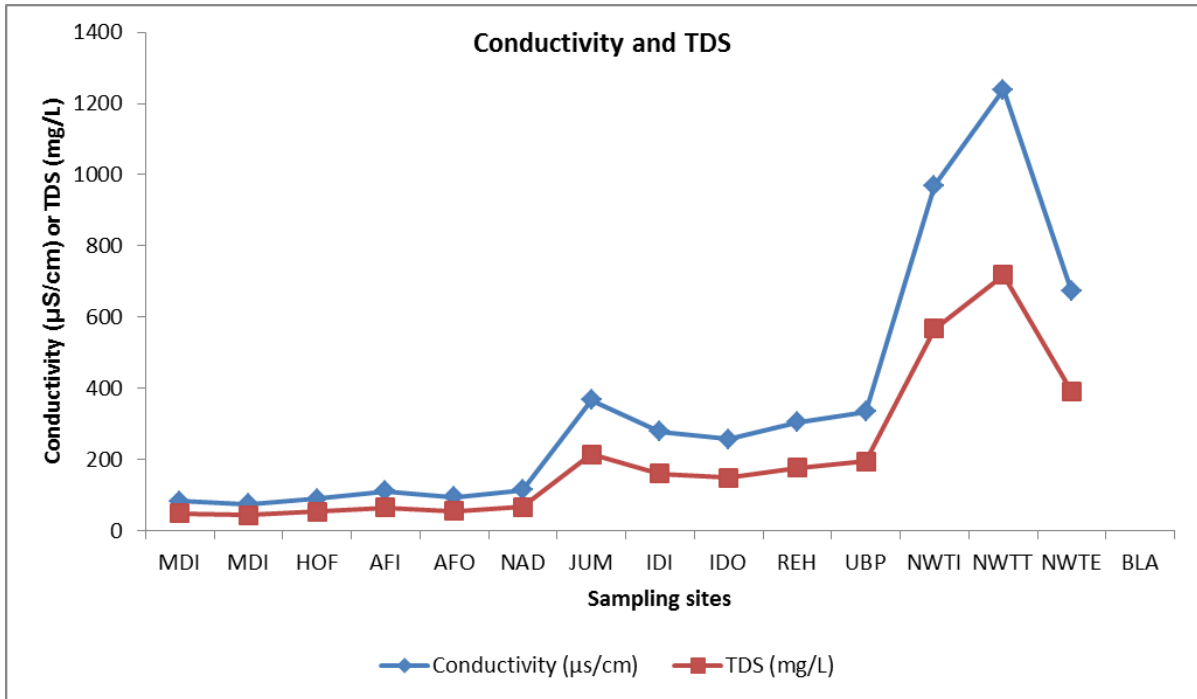
Figure 5.2 Conductivity and TDS in the water of Umgeni River at eah site.
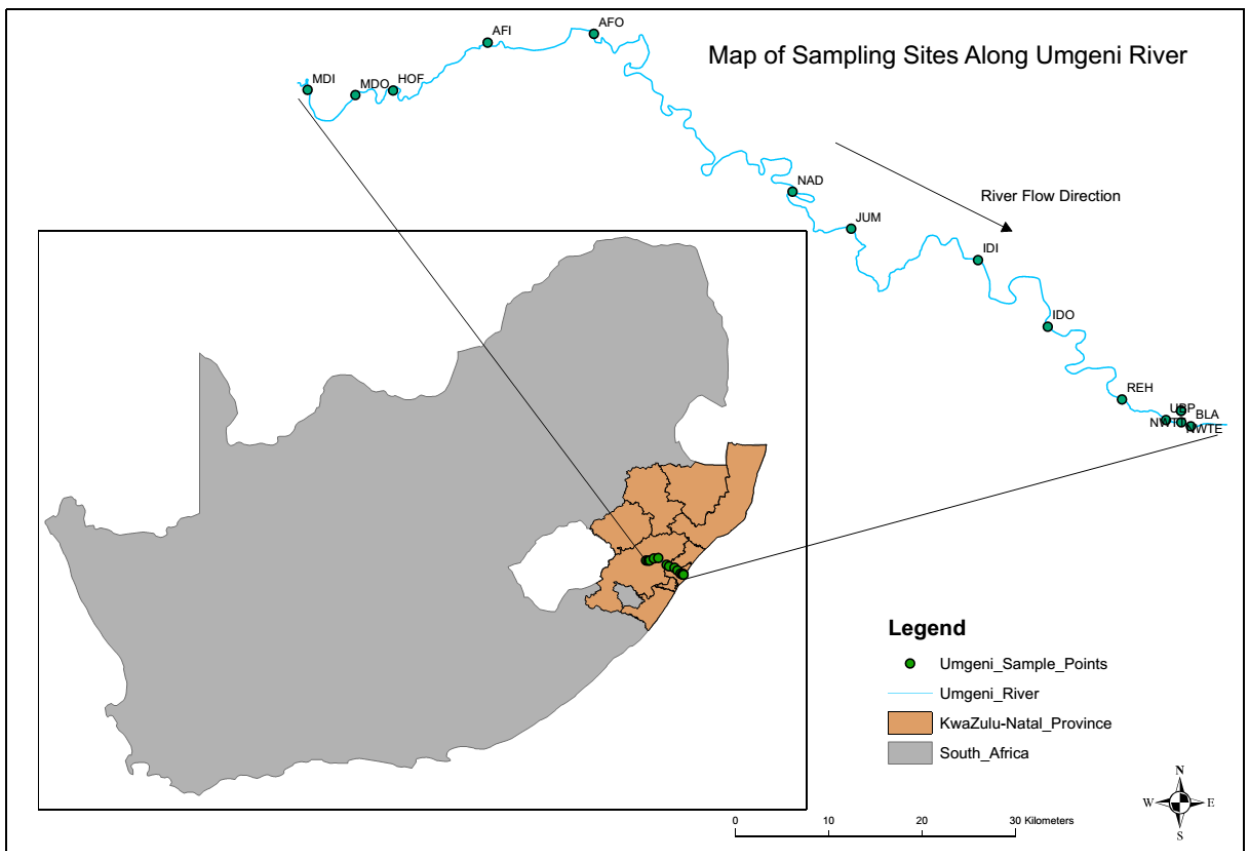
Figure 5.3 Map of sampling sites with the sample collection locations along the Umgeni

River (map was generated from GPS coordinates using ArcGIS 10.2).

5.2.4. Sampling

Water samples were collected in 2.5 L Winchester amber bottles previously washed with hot water and detergent and rinsed three times with sulfuric acid and deionized water respectively. At the site, the bottles were washed three times with the river water to be sampled. After sample collection, the bottles were sealed with caps lined with aluminium foil. Sediment samples were collected at the same sites as the water samples using a grab sampler and stored in glass bottles washed and capped as aforementioned. Water and sediment sample bottles were kept in a cooler box containing ice while they were transported to the laboratory. Water samples were acidified with 1 mL of H_2SO_4 (50% v/v) to prevent microbiological degradation and stored in a refrigerator at 4 ^{o}C until extraction which followed within three days. The sediment samples were centrifuged (Du pont instruments[R] SS-automatic centrifuge) using 10 x 1000 rpm for 15 min to separate it from the pore water (Ankley and Schubauer-Berigan, 1994, Zhang et al., 2003) and thereafter transferred onto aluminium foil for air drying. The pore water obtained was treated as per surface water samples.

5.2.5. Sample Extraction and Clean-up

Water samples were extracted using liquid-liquid extraction as per EPA method 3510C (EPA, 1996a). A 1 L aliquot of the water sample was transferred to a separatory funnel and extracted with 50 mL of DCM. The organic layer was removed and the process repeated six times for the same sample using fresh DCM aliquots each time in order to increase recovery. The six fractions of extracts were combined and concentrated to approximately 5 mL using a rotavap (Heidolph Instruments GmbH & Co.kG). The concentrated extract was quantitatively transferred onto a florisil (activated at 130 °C for 12 hours) column containing anhydrous Na_2SO_4 (5 g) on top for clean-up. The column was eluted with increasing polarity mixtures of hexane:DCM (5 mL each) (94:6), (85:15), (50:50) and 100% DCM (modified EPA method 3620-C) (EPA, 2007) in order to elute different OCPs with varying polarity indices. The four fractions were combined and concentrated using rotary evaporation to nearly 5 mL, then air-dried and reconstituted to 2 mL (concentration factor = 1000 mL/2mL = 500) and analysed using GC-MS. The pore water obtained after centrifugation of the sediment was treated as the water samples above using 100 mL of the sample and 10 mL of DCM. The sediment samples were air-dried, ground and sieved for homogenization and to increase the surface area. A 60 g (dw) sample of dry sediment was extracted with 300 mL of toluene in a soxhlet

extraction unit for 24 hours. Toluene is a suitable solvent for aromatic compounds such as organochlorine pesticides because of its similar polarity and research has shown it to be one of the most efficient solvents for extraction of these compounds (Oleszek-Kudlak et al., 2007). The resulting extract was concentrated using a rotavap for subsequent clean-up. The clean-up procedure was carried out as described for the water and pore water samples using a 20 mL mixture of hexane and DCM. The sediment extract was concentrated to 2 mL and analysed with GC-MS.

5.2.6. Sample Analysis

Sample analyses were carried out in triplicate using an Agilent 6890 series gas chromatography system attached to a mass spectrometer detector (MSD5973). The GC system was equipped with a ZB-5MS capillary column, 0.25 mm i.d., 0.25 μm film thickness and 30 m length (Hewlett Packard; Houston, TX). The MS was operated using the selective ion monitoring acquisition mode (SIM). The carrier gas was purified helium. Splitless mode was used to inject 2 μL of sample onto the GC column with injector and detector temperatures set at 250 and 280 ^{o}C respectively. The oven temperature was programmed from 120 ^{o}C, increased to 290 ^{o}C with a ramping rate of 14 ^{o}C/min and held for 2 min. The MS source was operated at 250 ^{o}C and quad at 200 ^{o}C. The electro energy was 70 eV.

Target analytes were quantified based on peak areas and by using an external calibration technique with the following six calibration standards: 0.25; 0.5; 1; 2; 4; 8 μg/mL. The identification of the analytes of interest was achieved by using mass spectral data compared to that found in the National Institute of Standard (NIST) library and comparison of retention times of analytes with those of reference standards. The identification was also carried out using the base peak and two other confirming ions (Table 5.2).

5.3 QUALITY CONTROL

The extraction recoveries (R) and limits of detection (LOD) and quantification (LOQ) for each analyte in each matrix were calculated (Table 5.2). Recoveries (R1) were obtained by spiking tap water (Agunbiade and Moodley, 2014, Meharg et al., 2003) with pesticide standards which were extracted using the method described above for water and pore water

samples, and percent recoveries ($\%R_1$) were obtained by calculating the ratio between the concentration found (C_f) and the concentration spiked (C_S), multiplied by 100 (Equation 5.1) (APHA et al., 1999, USEPA, 2008). For sediment sample analyte recoveries (R2), real sediment samples were subdivided into two subsamples whereby one was spiked with OCP standards before extraction, while the other was left unspiked and both extracted and analysed. The %R2 was obtained by subtracting the concentration of unspiked subsample (C_u) from the concentration of the spiked subsample (C_S), divided by the known concentration spiked (C_k) and the result was multiplied by 100 (Equation 5.2) (Harry et al., 2008). The recovery studies were carried out in triplicate and the mean recovery and the standard deviation were calculated for each analyte. The actual samples were also analysed in triplicate to measure the reproducibility and precision of the method used. The limit of detection and quantification were calculated as three times and ten times respectively the signal-to-noise ratio, using the standard deviation of three calibration intercepts divided by the slope. Procedural blanks were used through all phases of extraction and analysis. The analytes of interest were not detected in the blank samples. The solvent blanks and pesticide standards were regularly run on the GC-MS to ensure that there were no interferences in the GC system. A check was done, by running a calibration standard of 0.5 mg/mL after each batch of sample, to ensure that the variation from the initial calibration standards was minimal. All data were processed using Microsoft excel (version 2010).

$$\%R_1 = \frac{C_f}{C_S} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5.1)$$

$$\%R_2 = \frac{C_S - C_u}{C_k} * 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots (5.2)$$

Table 5.2 Ions monitored, limits of detection and quantification and percentage recoveries (%R) in the analysis of OCPs in water pore water and sediment by GC-MS.

Analyte	HCB	HCH	heptachlor	aldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD/dieldrin[14]	endrin	*p,p'*-DDD/*o,p*-DDT[15]	mirex
Ions monitored (m/z)	284	219	374	327	318	318	320/380	317	320/235	402
	249	183	272	293	284	281	235/263	263	235/199	272
	142	147	237	263	246	246	165/147	207	165/165	237
LOD (ng/mL) in water	0.025	0.06	0.03	0.045	0.06	0.07	0.035	0.06	0.075	0.07
LOQ (ng/mL) in water	0.58	0.10	0.10	0.155	0.19	0.125	0.205	0.205	0.245	0.23
LOD (ng/mL) in pore water	0.24	0.295	0.295	0.465	0.06	0.37	0.06	0.615	0.74	0.69
LOQ (ng/mL) in pore water	0.795	0.35	0.975	1.55	0.19	1.24	0.205	2.05	2.47	0.235
%R in water and pore water	51.90±0.47	64.38±0.28	32.66±0.67[16]	69.66±0.36	84.36±1.39	87.42±0.68	103.43±0.97	61.08±0.87	75.27±0.19	65.31±0.33
LOD (ng/g) in sediment	0.50	0.50	0.50	0.78	0.96	0.62	1.04	1.02	1.23	1.15
LOQ (ng/g) in sediment	1.66	1.66	1.62	2.59	3.20	2.07	3.45	3.41	4.11	3.83
%R in sediment										
	79.14±3.64	98.22±3.81	99.15±10.0.3	116.97±5.36	95.60±12.15	52.73±1.35	90.02±3.59	94.19±14.81	96.68±2.71	109.28±6.19

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[14] *o,p*-DDD and dieldrin could not be resolved on the GC and were reported as a single peak.
[15] *p,p*-DDD and *o,p*-DDT could not be resolved on the GC and were reported as a single peak.
[16] Heptachlor was in contact with tap water for some days to allow its contact with matrix before extraction. It may have degraded into heptachlor epoxide by oxidation, photolysis and can also volatilise in air (Callahan, M. A., 1979) and consequently its recovery was low during extraction.

5.4 RESULTS AND DISCUSSION

The present paper reports results obtained from a comprehensive study of the Umgeni River situated in the province of KwaZulu-Natal in South Africa, This work aims to report on levels of selected persistent organic pollutants, and serves to provide an understanding of these pollutants from non-point sources. The results presented are for twelve selected organochlorine pesticides in surface water, sediment pore water and surface sediment.

5.4.1. Levels of Organochlorine Pesticide Residues in Surface Water

The distribution of the OCPs in water from the fifteen sampling sites revealed a broad and diverse range of fluctuations (Table 5.3). The concentrations of individual pesticides ranged from a non-detectable level for aldrin at Reservoir Hills (REH) to 3.48 ng/mL for endrin at Northern Wastewater Treatment works influent (NWTI). The levels of pesticides were higher at the sites surrounding the wastewater treatment works and the point of discharge into the Umgeni River. This was expected because the wastewater treatment plant receives residential waste which may contain residues of pesticides from food sold in supermarkets, such as fish, fruits and vegetables in which they are known to accumulate (Gómez-Pérez et al., 2015, Asensio-Ramos et al., 2014, Vuković et al., 2012, Barnhoorn et al., 2015a). Researchers have found that wastewater treatment plants can be considered as a source point of persistent organic pollutants (Samara et al., 2006).

The results showed that *o,p*-DDE and *p,p'*-DDE were among the main OCPs in the Umgeni River water with average concentrations of 1.50 and 1.62 ng/mL, respectively. The presence of these DDT degradation products suggest that DDT was the common pesticide in use before it was banned in 1983 in South Africa. Thereafter, DDT was allowed to be used in a controlled manner only by government, for the purpose of malaria control (Rother and Jacobs, 2008) and therefore may be present in food stuff such as meat, fish, vegetables transported from DDT-affected areas (McHugh et al., 2011) such as Limpopo and Mpumalanga (Dalvie et al., 2004c, Dalvie et al., 2004b, Naudé and Rohwer, 2012a, Van Dyk et al., 2010) to the area investigated in this study. A study by Batterman and coworkers found that many of the OCPs investigated in this study were also found in air samples collected in the Durban city area close to where the Umgeni River passes before it reaches the

mouth at the Indian Ocean (Batterman, 2008) Their study confirmed that these OCPs had local as well as regional or even global sources and may travel from far areas of input because of trans boundary effects. Furthermore, during cooler temperatures they have the ability to re-condense from air and enter water ways especially during the winter period when these samples were collected (Scheringer et al., 2004, Lohmann et al., 2007b, Valle et al., 2007).

The present study found no significant difference in total concentrations of pesticides at each site (Figure 5.4), from the source of the river at MDI (10.99 ng/mL) downstream to NAD (9.73 ng/mL), however JUM, the joining point of the Msunduzi River (tributary) with the Umgeni River, showed a slightly higher concentration (12.69 ng/mL) compared to upstream sites. This could be due to an added effect of the pollutants from the Msunduzi River now mixing with the Umgeni River thus increasing the total concentration. After JUM, the total concentration of OCPs decreased to 10.31 ng/mL at IDI (Table 5.3, Figure 5.4). The decrease in concentration of OCPS in water was attributed to low flow rates of the dam water, allowing contaminants partitioned to the organic matter to settle down into the sediment instead of being transported in the water column *via* suspended particles. Similarly, the high flow rates observed at the JUM sampling site also meant that the organic matter with the partitioned OCPs did not have sufficient time to settle into the pore water and sediment and hence were present in higher concentrations in the unfiltered water matrix (Figure 5.5B) (Voice and Walter J. Weber, 1983).

Table 5.3 Concentration of OCPs in Umgeni River surface water.

site code	HCB	HCH	heptachlor	aldrin	*o,p*-DDE	*p,p'*-DDE	*o,p*-DDD/dieldrin	endrin	*p,p'*-DDD/*o,p*-DDT	mirex	∑OCPs
						Concentration (ng/mL ±SD)					
MDI	0.41±0.12	0.65±0.21	0.48±0.11	1.21±0.21	1.37±0.11	1.52±0.11	1.64±0.04	1.52±0.28	1.41±0.14	0.79±0.06	10.99±1.39
MDO	0.48±0.17	0.69±0.29	0.47±0.17	1.16±0.12	1.37±0.13	1.48±0.07	1.61±0.12	1.28±0.26	1.36±0.09	0.90±0.15	10.80±1.56
HOF	0.70±0.09	0.53±0.23	0.36±0.10	1.02±0.19	1.21±0.13	1.34±0.08	1.41±0.11	1.42±0.25	1.25±0.10	0.74±0.13	9.97±1.41
AFI	0.53±017	0.73±0.24	0.43±0.10	1.17±0.11	1.40±0.15	1.53±0.11	1.64±0.12	1.14±0.18	1.36±0.09	0.94±0.13	10.87±1.40
AFO	0.74±0.06	0.50±0.13	0.34±0.06	1.02±0.16	1.21±0.13	1.35±0.13	1.43±0.08	0.88±0.08	1.23±0.13	0.78±0.19	9.47±1.13
NAD	0.43±0.16	0.59±0.20	0.35±0.11	1.05±0.18	1.31±0.15	1.41±0.15	1.47±0.10	1.06±0.11	1.25±0.10	0.79±0.07	9.73±1.31
JUM	0.69±0.16	0.81±0.21	0.53±0.11	1.43±0.21	1.67±0.19	1.84±0.05	1.84±0.11	1.30±0.08	1.52±0.04	1.06±0.07	12.69±1.34
IDI	0.50±0.05	0.60±0.05	0.40±0.03	1.20±0.16	1.37±0.05	1.55±0.05	1.54±0.21	0.92±0.04	1.31±0.04	0.90±0.03	10.31±0.62
IDO	0.56±0.04	0.69±0.05	0.41±0.1	1.20±0.03	1.48±0.03	1.64±0.07	1.65±0.17	1.06±0.02	1.46±0.01	0.98±0.02	11.12±0.45
REH	0.53±0.03	1.57±0.40	0.81±0.21	nd	1.61±0.01	1.80±0.06	1.87±0.10	1.00±0.02	1.44±0.16	1.06±0.02	11.69±1.03
UBP	0.730.08	1.97±0.43	0.71±0.20	0.67±0.02	1.82±0.06	1.97±0.04	1.99±0.05	1.11±0.02	1.56±0.16	1.24±0.10	13.76±1.18
NWTI	1.04±0.21	1.26±0.29	1.91±0.42	2.73±0.08	2.32±0.09	2.01±0.04	1.92±0.07	3.48±0.07	1.72±0.09	1.02±0.06	19.41±1.43
NWTT	0.49±0.11	0.64±0.10	2.07±0.13	1.37±0.11	1.58±0.03	1.81±0.02	1.82±0.08	1.53±0.10	1.32±0.06	1.74±0.07	14.36±0.80
NWTE	0.77±0.06	0.53±0.13	0.32±0.08	1.35±0.02	1.37±0.08	1.49±0.04	1.79±0.11	1.90±017	1.35±0.07	1.38±0.05	12.26±0.81
BLA	0.80±0.03	0.53±0.05	0.35±0.08	1.40±0.10	1.41±0.10	1.54±0.03	1.78±0.09	1.24±0.18	1.36±0.14	0.96±0.06	11.38±0.85
∑OCPs	9.40±0.55	12.27±3.00	9.95±1.92	17.98±1.60	22.51±1.43	24.29±1.11	25.41±1.57	20.83±1.86	20.88±1.45	15.29±1.21	178.80±16.71
min	0.41±0.12	0.50±0.13	0.32±0.08	nd	1.21±0.13	1.34±0.08	1.41±0.11	0.88±0.08	1.23±0.13	0.74±0.13	9.47±1.13
mean	0.63±0.10	0.82±0.20	0.66±0.13	1.20±0.11	1.50±0.10	1.62±0.07	1.69±0.04	1.39±0.12	1.39±0.10	1.02±0.08	11.92±1.11
max	1.04±0.21	1.97±0.43	2.07±0.13	2.73±0.08	2.32±0.09	2.01±0.04	1.99±0.05	3.48±0.07	1.72±0.09	1.74±0.07	19.41±1.43

nd= not detected
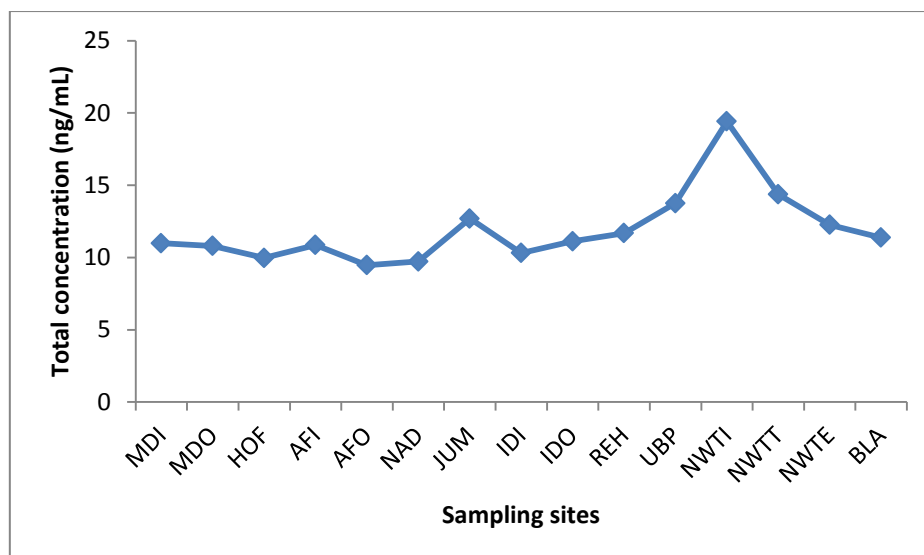
Figure 5.4 Trend of total concentration of OCPs in surface water across the sampling sites (n= 3).

As the river flowed from IDI towards the mouth of the river, the concentration rose to 19.41 ng/mL at NWTI. The high concentration at NWTI was expected because it receives untreated wastewater and has a content high in organic matter to which the OCPs partition which results in high OCP concentrations (Kile et al., 1995). The Northern Wastewater Treatment works (NWWTW) does reduce the concentrations of the analysed pesticides to some extent as relatively lower concentrations were found for the water sample collected after treatment (NWTT). Table 5.4 shows the extent to which the individual OCPs were removed from wastewater during the treatment process. Another phenomenon which may have reduced the concentrations of OCPs in water at NWTT is their settling into the bio-solids. This was probably due to a very low flow rate of water in the collecting well area, before being sent to the point of discharge to the river allowing the organic matter to settle into the sediment, thus the reason for the high total concentrations in sediment pore water (Figure 5.6B) and sediment than in water. After NWTT the concentration decreases due to dilution of OCPs as they are discharged into the river.
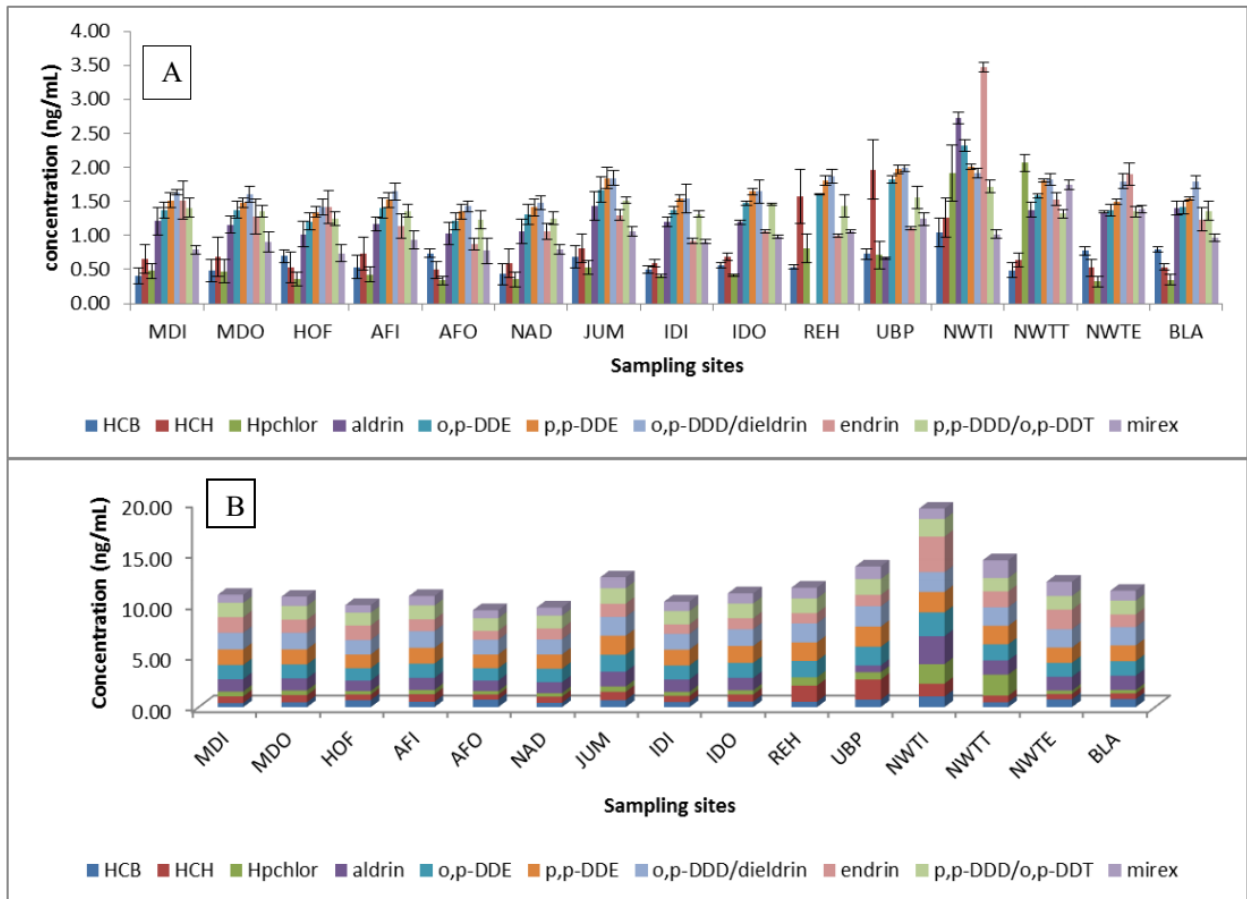
Figure 5.5 A- Individual OCP concentrations and B- Total concentration of OCPs in surface
water samples at each site of the Umgeni River (n=3).

The increase in total concentration of OCPs may also be explained by the physical parameters
that were recorded during the sampling trip. The higher concentration in total suspended
solids and total dissolved solids is an indication of pollution (Mahananda et al., 2010) and the
higher the conductivity, the higher the TDS. Figures 5.2 and 5.4 and Tables 5.1 and 5.3,
showed very little increase in total dissolved solids and conductivity from the source at MDI
(TDS = 49 mg/L, conductivity = 83.7 μs/cm) to NAD (66 mg/L, 114.0 μs/cm), with the
corresponding total OCP concentrations ranging from 9.47±1.13 to 10.99±1.39 ng/mL.
However, at JUM, the values of TDS and conductivity increased considerably to 214.0 mg/L
and 367.0 μs/cm respectively. The significant increase in TDS and conductivity corresponded
to the large increase in OCP concentration at that site (12.69 ng/L) which could be explained
by the high preference of the OCPs to adsorb onto the dissolved organic matter (high TDS) at
this site. Furthermore, the total OCP concentration at this site was increased by the joining of
the tributary (Msunduzi river) and may be contributing to the pollution load at that site. The
second portion of the river from IDI to NWTI had the highest values in TDS (568.0 mg/L)

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and conductivity (970.0 µs/cm) and corresponded to the highest total OCP concentrations (19.41 ng/mL) at NWTI. Figures 5.4 and 5.5B showed a decrease in total concentration of OCPs in the NWTI to BLA which is attributed to dilution effects because the treated water is discharged into the Umgeni River at NWTE. Moreover, Waziri and Ogugubuaja demonstrated a positive correlation between levels of pollution indicators in River Yobe-Nigeria, such as total organic carbon (TOC) and biochemical oxygen demand (BOD) on one hand and between BOD and TDS on the other hand; therefore there was a positive correlation between levels of TOC and TDS in the river (Waziri and Ogugbuaja, 2010). Samples with high TDS values (Figure 5.2) are therefore expected to have corresponding high TOC values as shown by Waziri and Ogugbuaja (Waziri and Ogugbuaja, 2010). Research has also shown that there is a strong affinity between organic carbon and hydrophobic compounds that have high Log K_{ow} values such as organochlorine pesticides (Luo et al., 2009). Since the present study analysed water samples that were unfiltered in order to determine the concentrations of OCPs that humans and animals were exposed to by direct consumption, it was expected to contain high levels of organic carbon and hence the reason for the presence of high concentrations of total OCPs observed at AFI, JUM and NWTI (Figure 5.4).

Table 5.4 Reduction of OCP concentrations in wastewater by the treatment process in the NWWTW (Northern Wastewater Treatment Works).

OCPs	Influent conc. (ng/mL)	conc. after treatment (ng/mL)	difference	% reduction
HCB	1.04	0.49	0.55	52.88
HCH	1.26	0.64	0.62	49.21
heptachlor	1.94	2.07	-0.13	-6.70
aldrin	2.73	1.37	1.36	49.82
o,p-DDE	2.32	1.58	0.74	31.90
p,p'-DDE	2.01	1.81	0.2	9.95
o,p-DDD/Dieldrin	1.92	1.82	0.1	5.21
endrin	3.48	1.53	1.95	56.03
p,p'-DDD/*o,p*-DDT	1.73	1.32	0.41	23.70
mirex	1.02	1.74	-0.72	-70.59

Table 5.4 showed that most OCP concentrations were reduced, with the highest reduction observed for endrin at 56.03% and the lowest reduction for DDD/dieldrin at 5.21%. The concentrations of heptachlor and mirex were not reduced at all but instead their concentrations were increased through the water treatment process (6.70% increase for heptachlor and up to 70.59% for mirex). This may also suggest that the NWWTW pollutant concentrations vary considerably throughout the day depending on the type of effluent received. A further detailed investigation is needed of the NWWTW water purification process in order to understand how, why and to what extent the treatment procedure selectively reduces some OCP concentrations and not others. Previous studies on wastewater treatment plants have shown that POPs are generally present in higher concentrations in the influent than effluent (Mowery and Loganathan, 2007). Also, it was confirmed that WWTP sludge contains between 39 to 98% of POPs, and the remaining portion in water after treatment is due to their adsorption onto non-settleable solids (Katsoyiannis and Samara, 2005).

5.4.2. Levels of Organochlorine Pesticide Residues in Pore Water

The results obtained for OCP concentrations in pore water are shown in Table 5.5 and Figures 5.6 and 5.7. The levels of individual OCPs varied from 0.76 ±0.01 to 34.92 ±4.01 ng/mL. The total concentration of OCPs in pore water was ten times higher than in surface water. This may be explained by the low solubility of these OCPs in surface water and preference for adsorption onto organic matter because of the strong affinity that exists between OCPs and colloids in sediment pore water. The high Log K_{ow} values for these selected OCPs range from (5.46-6.89) (shen and Wania, 2005) which also indicates its preference to partition itself to organic matter rather than dissolve in water and hence is the reason for the higher concentrations of OCPs in pore water than in surface water. As a result these OCPs tend to have long-term deposition and accumulation in sediment (Josefsson, 2011).
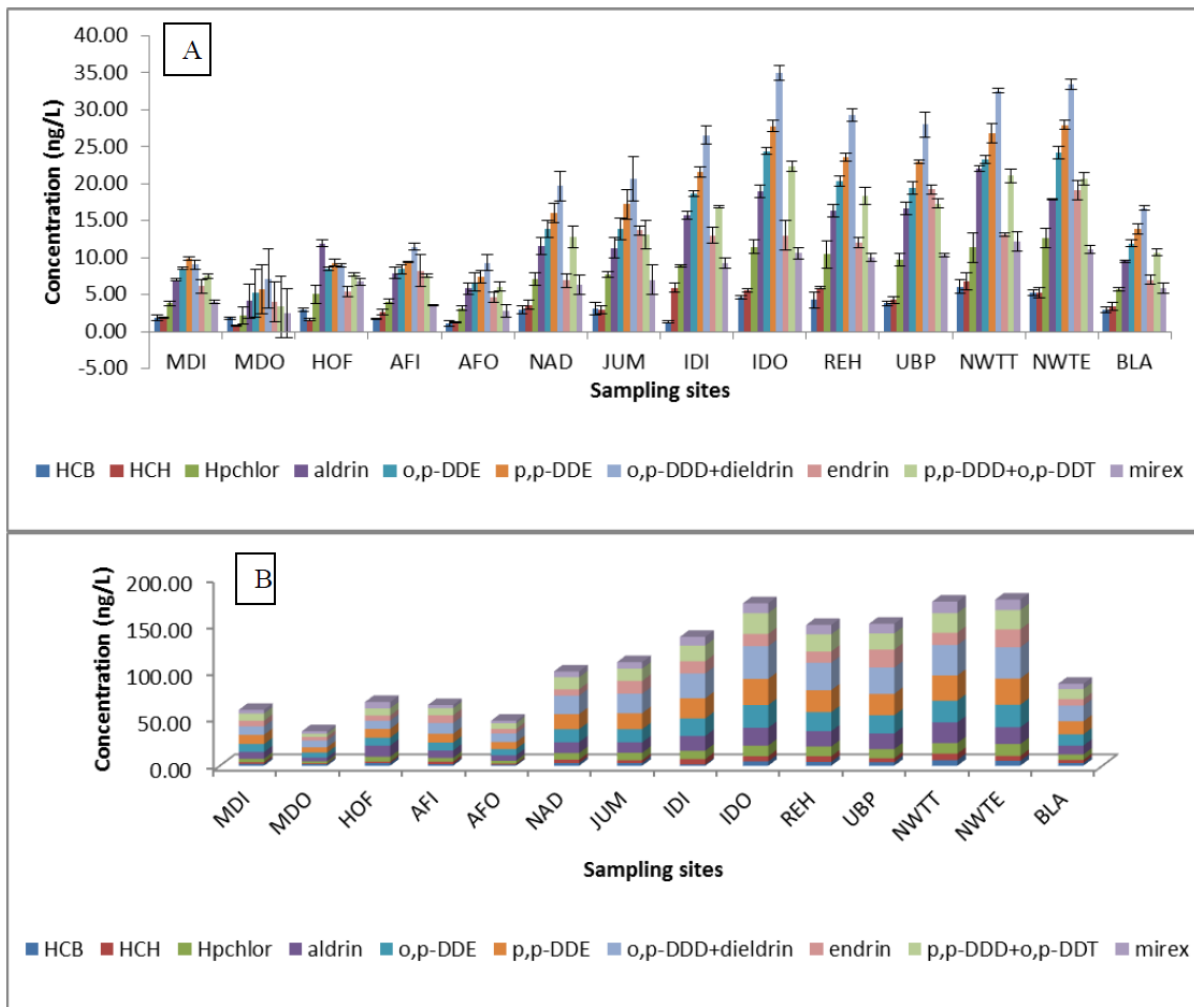
Figure 5.6 A-Concentrations of individual OCPs in pore water. B-Total concentrations of OCPs at each site of the Umgeni River (n=3).

There was a general increase in concentration of OCPs in pore water from the source to the mouth of the river. This corresponded to an increase in TDS and conductivity in water in the same direction (Mahananda et al., 2010). Once again the increase of TDS downstream implies an increase of TOC (Waziri and Ogugbuaja, 2010) which allowed the pesticides to partition to it and hence resulted in their increased concentrations downstream as well. In addition, there is also an increase in urban and residential activities towards the mouth of the river which could possibly be a source for solid particles including plastics, paints, plastic packets etc. OCPs could possibly suspend themselves on these types of solid particles in water and may sink down to the sediment and re-suspended themselves in sediment pore water (Zhang et al., 2003). Research has shown that solid particles such as plastic resin pellets and broken bits of plastics from consumers are good carriers of persistent organic pollutants which are sorbed onto them in waterways (Moore et al., 2004, Mato et al., 2001). The downstream organic pollutant accumulation effect observed in pore water in this study resembles that reported by Marie-Jeanne and her team, who found the same effect for organic contaminants such as PCBs, PBDs and phthalates in sediment of the Seine River in France. The downstream Seine River concentrations increased 69-fold, 25-fold and 11-fold respectively for BDE 209, $\sum$ tri-hexa BDE and $\sum$ 7 PCBs, compared to upstream concentrations (Marie-Jeanne et al., 2014).
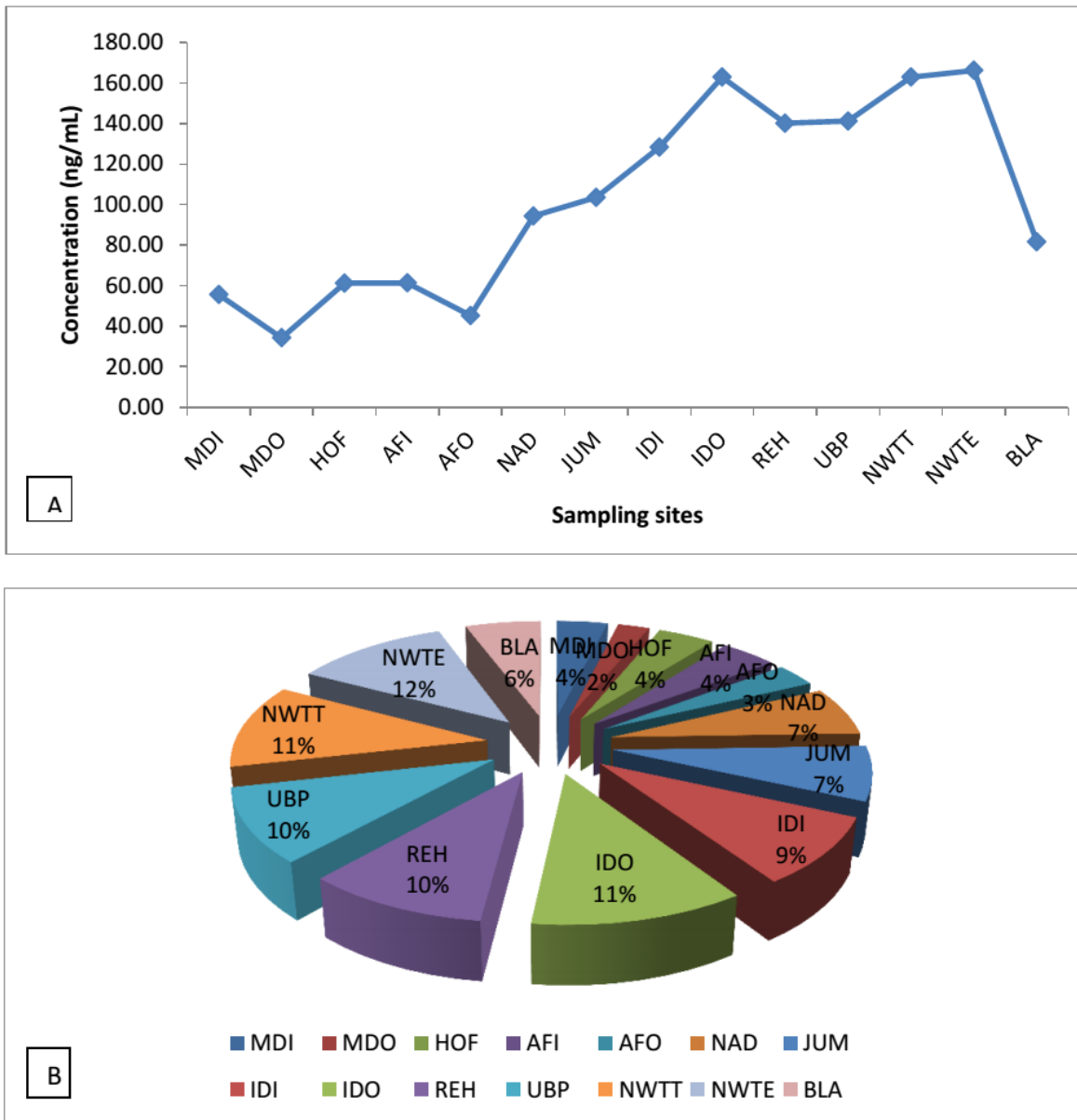
Figure 5.7 A- Trend of total concentrations of OCPs in pore water across the sites B- Percent contribution of total concentration for sites for sediment pore water samples.

Table 5.5 Concentrations of OCPs (ng/mL) in sediment pore water of the Umgeni River.

							o,p-DDD+dieldrin		p,p-DDD+o,p-DDT		
				Concentration (ng/mL + SD) of OCPs in winter pore water							
site code	HCB	HCH	heptachlor	aldrin	o,p-DDE	p,p-DDE	o,p-DDD+dieldrin	endrin	p,p-DDD+o,p-DDT	mirex	∑OCPs
MDI	1.90±0.41	1.92±0.07	3.81±0.33	6.99±0.16	8.52±0.16	9.88±0.21	9.02±0.64	6.10±0.90	7.50±0.34	3.99±0.12	55.63±3.34
MDO	1.78±0.08	0.76±0.11	2.19±1.13	4.11±2.32	5.18±3.22	5.73±3.28	7.15±4.01	4.17±2.71	5.37±4.16	2.47±1.33	34.32±22.36
HOF	2.93±0.19	1.62±0.12	5.04±1.26	11.87±048	8.47±0.19	9.30±0.43	8.91±0.28	5.41±0.70	7.73±0.19	6.71±2.66	61.28±6.53
AFI	1.69±0.10	2.61±0.43	4.07±0.35	7.91±0.78	8.45±0.60	9.41±0.05	11.42±0.48	8.22±2.10	7.57±0.19	3.54±0.20	61.35±5.29
AFO	1.60±0.25	1.24±0.01	3.13±0.29	5.79±0.71	6.67±1.27	7.44±0.83	9.30±1.09	4.61±0.72	6.06±0.58	2.74±0.35	45.29±6.24
NAD	2.94±0.49	3.56±0.62	7.08±0.84	11.56±1.17	13.89±1.18	16.07±1.29	19.64±1.95	6.86±0.88	12.79±1.53	6.28±0.82	94.40±10.78
JUM	3.08±0.89	2.97±0.51	7.69±0.32	11.31±1.37	13.87±1.41	17.20±2.01	20.69±3.01	13.68±0.63	13.11±1.97	6.97±1.12	103.61±13.24
IDI	1.59±0.19	5.93±0.61	8.92±0.17	15.69±0.58	18.61±0.41	21.53±0.67	26.53±1.28	13.01±1.10	16.82±0.12	9.22±0.55	128.30±5.64
IDO	4.61±0.20	5.55±0.27	11.43±0.93	18.89±0.85	24.39±0.51	27.76±0.76	34.92±1.05	13.00±1.93	22.34±0.71	10.59±0.24	162.88±7.47
REH	4.24±1.13	5.88±0.14	10.41±1.79	16.33±0.87	20.32±0.70	23.50±0.55	29.27±0.83	11.98±0.72	18.26±1.16	10.03±0.37	140.18±8.27
UBP	3.84±0.30	4.25±0.41	9.72±0.86	16.65±0.81	19.43±0.82	22.87±0.23	27.96±1.66	19.21±0.60	17.28±0.62	10.27±1.19	141.22±7.50
NWTT	6.08±0.94	6.80±1.11	11.35±1.97	21.96±0.37	23.27±0.49	26.75±1.31	32.54±0.30	13.10±0.29	21.02±0.96	12.18±0.90	162.88±8.65
NWTE	5.28±0.37	5.20±0.69	12.63±1.37	17.90±0.10	24.16±0.87	27.93±0.57	33.38±0.71	19.08±1.30	20.66±0.86	11.11±0.34	166.23±7.16
BLA	2.91±0.39	3.43±0.55	5.71±0.21	9.53±0.16	11.89±0.49	13.93±0.69	16.70±0.26	6.95±0.61	10.64±0.48	5.84±0.58	81.69±4.41
∑OCPs	43.61±6.04	51.72±5.64	103.18±11.84	176.49±10.74	207.12±12.33	239.29±12.89	287.44±17.54	145.27±15.21	185.14±13.88	101.95±10.76	1541.22±116.89
min	1.59±0.19	0.76±0.11	2.19±1.13	4.11±2.32	5.18±3.22	5.73±3.28	7.15±4.01	4.17±2.71	5.37±4.16	2.47±1.33	34.32±22.36
mean	3.11±0.43	3.69±0.40	7.37±0.85	12.61±0.77	14.79±0.88	17.09±0.92	20.53±1.25	10.38±1.09	13.22±0.99	7.28±0.77	102.80±8.35
max	6.08±0.94	6.80±1.11	12.63±1.37	21.96±0.37	24.39±0.51	27.93±0.57	34.92±1.05	19.21±0.60	22.34±0.71	12.18±0.90	166.23±7.16

The highest mean concentration of individual contaminants across all sampling sites include *o,p*-DDE (14.79 ±0.88 ng/mL), *p,p'*-DDE (17.09 ±0.92 ng/mL), endrin (10.38 ±1.09 ng/mL) and aldrin (12.61 ±0.77 ng/mL) in pore water samples.

It was observed that the concentration of OCPs decreased at Blue Lagoon (mouth of the river) which may be attributed to dilution effects because of the close proximity of the Indian Ocean at that site. The highest total concentration of OCPs was observed at NWTE (166.23 ng/mL, 12%), NWTT (162.88 ng/mL, 11%), IDO (162.88 ng/mL, 11%), UBP (141.22 ng/mL, 10%), REH (140.18 ng/mL, 10%) and IDI (128.30 ng/mL, 9%) (Figures 5.7A and B). The high OCP concentrations at the REH site is of concern as this sampling site is a few kilometres upstream of an informal settlement whose residences may be exposed to these OCPs if they collect their drinking water too close to the sediment, as the OCPs can re-suspend into the water column (Chau, 2006, Elena et al., 2011).

5.4.3. Levels of Organochlorine Pesticide Residues in Sediments

The OCPs investigated were detected in the sediment samples from all sites. The total concentrations of pesticides at each site are shown in Table 5.6 and Figure 5.8B and varied from 183.63-495.21 ng/g, with an average concentration of 308.70 ng/g, dw. The highest concentrations of pesticides were obtained at NWTT (495.21 ±32.38 ng/g, 11%), BLA (417.49 ±23.58 ng/g, 9%) and HOF (353.39 ±41.71 ng/g, 8%).The highest individual mean concentration in sediment was obtained for indrin (55.57±7.11ng/g) probably due to its High octanol-water coefficient (Log K_{ow} = 5.6) and its persistence since it can persist up to 14 years or more (USEPA,2009). The analysis of bio-solids collected from NWTT (post-chlorination) (11%) showed a higher concentration than that collected from NWTI (before process treatment) (7%). A possible explanation could be that at NWTT, the pollutants from the WWTW accumulated over years in the bio-solid at the bottom of the pit where treated water is held before being discharged, while at NWTI, the bio-solid collected was not allowed to accumulate over long periods but were occasional since it is periodically removed from influent water. The levels of OCPs in sediments were higher than in water and in pore water. This was expected since POPs are known to prefer partitioning to organic material in sediment rather than dissolving in water (Zhou and Rowland, 1997).

Table 5.6 Concentrations of OCPs in sediment (ng/g, dw) of the Umgeni River.

| | | | | | | | o,p- | | p,p'-DDD/o,p- | | |
Site code	HCB	HCH	heptachlor	aldrin	o,p-DDE	p,p'-DDE	DDD/dieldrin	endrin	DDT	mirex	∑OCPs
MDI	6.23±0.93	4.34±0.91	26.67±2.85	21.52±0.04	17.78±0.11	20.61±0.13	23.60±1.14	36.86±2.23	19.17±0.01	6.83±0.52	183.63±8.87
MDO	4.51±1.24	30.36±4.02	26.70±2.93	22.70±2.29	26.38±2.11	26.45±2.50	23.96±0.46	44.43±6.61	27.58±0.64	48.86±2.28	281.93±25.07
HOF	10.75±1.69	37.49±5.06	30.06±2.22	19.59±7.55	25.56±4.12	34.40±4.50	29.94±1.16	73.84±8.69	33.44±3.77	58.31±2.94	353.39±41.71
AFI	6.81±1.32	23.49±3.17	26.38±8.10	17.45±7.90	22.34±2.08	27.23±2.69	29.93±2.54	63.70±7.76	21.98±0.77	61.22±1.38	300.53±34.93
AFO	7.41±1019	34.81±6.84	30.06±4.54	8.27±4.94	24.33±1.60	27.60±2.37	29.80±1.22	60.50±9.06	22.78±0.98	22.00±6.58	267.58±39.25
NAD	9.06±1.23	8.68±2.16	30.30±7.71	23.48±0.29	27.07±1.03	29.25±1.19	32.57±1.65	38.77±8.33	24.78±0.90	70.50±7.35	294.45±31.45
JUM	14.12±3.99	4.40±1.23	34.60±8.26	30.96±5.71	27.13±2.50	32.45±0.76	30.49±1.05	59.25±6.47	27.56±0.52	31.07±0.79	292.04±32.55
IDI	7.30±2.38	39.52±4.05	32.35±6.50	13.81±2.61	23.20±2.92	29.12±3.36	24.06±3.08	78.51±2.99	24.05±1.77	45.13±1.39	317.06±30.13
IDO	2.29±0.57	25.04±1.82	18.50±3.08	19.18±7.01	25.80±6.31	23.43±5.52	23.46±0.48	67.20±10.67	20.67±0.85	44.34±1.03	269.91±39.64
REH	5.49±1.58	16.83±3.83	18.46±3.67	23.9±77.68	18.52±1.19	20.95±1.56	23.79±0.94	32.74±9.38	19.18±3.14	56.35±4.83	236.28±35.37
UBP	11.35±0.48	41.94±4.31	43.31±1.68	13.80±2.34	23.78±1.43	21.20±0.20	22.97±0.97	28.10±1.05	18.51±0.71	50.32±2.82	275.30±15.55
NWTI	7.07±1.15	87.87±4.25	37.15±9.15	14.32±6.63	27.33±2.07	28.68±0.77	25.64±1.68	33.90±3.72	20.47±0.27	22.29±7.45	304.74±37.04
NWTT	49.44±2.45	82.96±3.13	26.83±3.78	37.80±6.91	50.70±1.40	38.72±2.44	26.40±1.81	75.84±9.60	27.84±0.18	78.66±0.20	495.21±32.38
NWTE	10.57±0.49	93.02±3.50	24.25±3.66	36.42±1.29	19.10±0.87	25.80±1.22	34.46±1.07	52.11±7.02	18.91±0.67	26.38±3.04	341.01±23.58
BLA	45.26±2.24	83.47±2.73	50.77±3.32	31.12±2.84	35.10±1.09	27.59±1.36	24.98±0.75	87.72±13.14	20.22±0.92	11.27±1.44	417.49±30.07
∑OCPs	197.68±23.32	614.24±51.02	456.38±71.44	334.40±64.04	394.12±30.82	413.49±29.57	406.06±20.01	833.51±106.72	347.14±16.51	633.52±44.03	4630.55±457.57
min	2.29±0.57	4.34±0.91	18.46±3.67	8.27±4.94	17.78±0.11	20.61±0.13	22.97±0.97	28.10±1.05	18.51±0.71	6.83±0.52	183.63±8.87
mean	13.18±1.56	40.95±3.40	30.43±4.76	22.29±4.27	26.27±2.05	27.57±1.97	27.07±1.33	55.57±7.11	23.14±1.10	42.23±2.94	308.70±30.50
max	49.44±2.45	93.02±3.50	50.77±3.32	37.80±6.91	50.70±1.40	38.72±2.44	34.46±1.07	87.72±13.14	33.44±3.77	78.66±0.20	495.21±32.38

Concentration (ng/g, dw) of OCPs in sediments
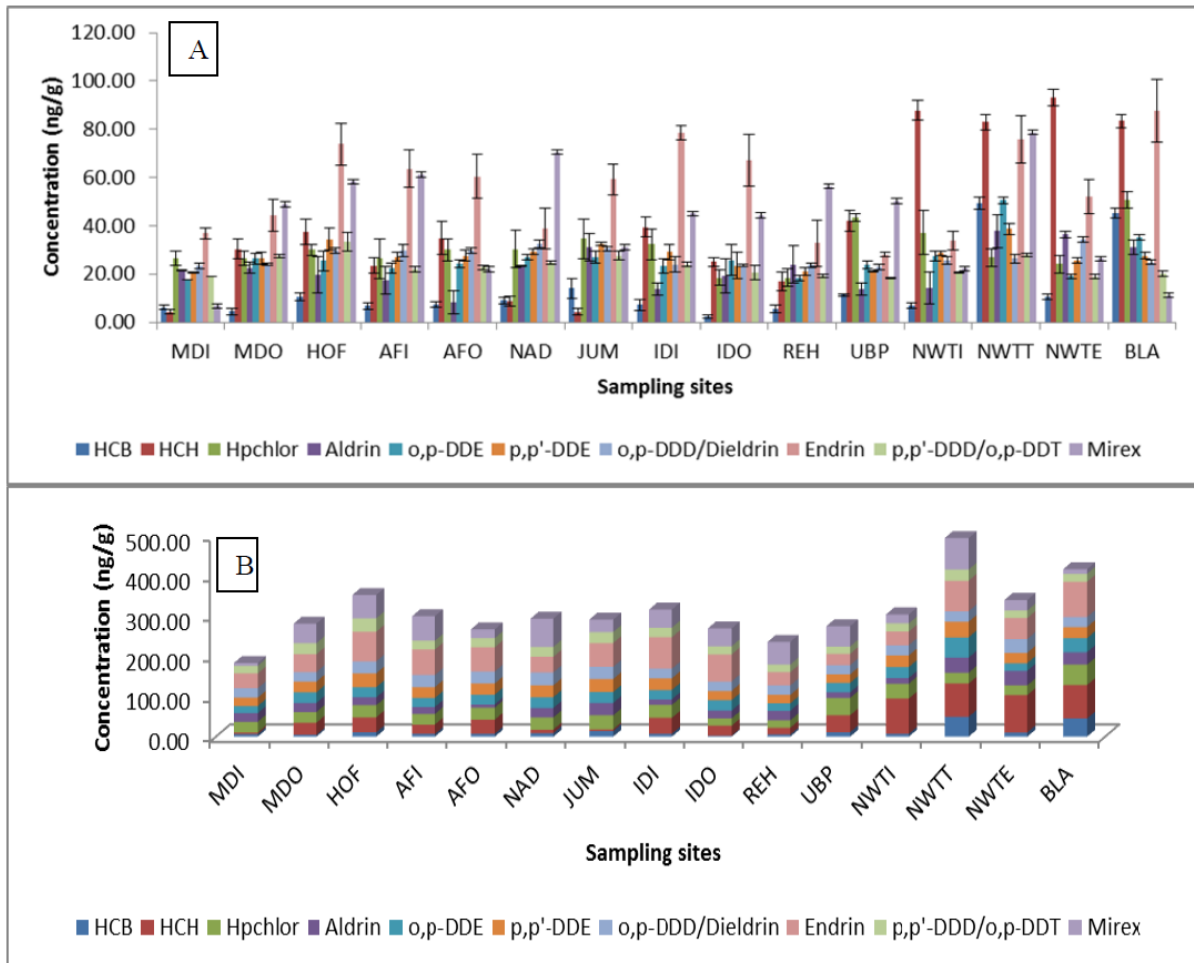
Figure 5.8 A- Individual OCP concentrations in sediment at different sites along the Umgeni River. B-Total concentrations (ng/g,dw) of OCPs in sediments (n=3).

The sediment pore water distribution model of POPs has shown that they occur in high concentrations in sediment than in pore water (Perssona et al., 2005). As the treated water flows towards the point of discharge (NWTE), the total concentration of pesticides decreased from NWTT to NWTE. This can be attributed to the increased volume of water at the discharge point into the river resulting in dilution of the pesticide concentration (Figure 5.9A). The concentration of HCH in the sediment of the Umgeni River (4.34-93.02 ng/g, dw) was higher than levels of HCH observed in the sediments of Qinhe River (nd-13.72 ng/g) in China (Fei et al., 2013) and in the sediment samples collected from the Old Yellow River estuary in China (0.001-14.85 ng/g,dw) (Da et al., 2014). However, the individual levels of OCPs in Umgeni River sediment (2.29–93.02 ng/g), were comparable to individual levels in four rivers running through an intensive agricultural area in Kilimanjaro in Tanzania (nd–132 ng/g) (Hellar-Kihampa, 2011). The levels in this study were below the results obtained from

water (0.1-48.6 ng/mL) and sediment (0.10-163.00 ng/g) collected from the Densu River basin in Ghana (Kuranchie-Mensah et al., 2012).
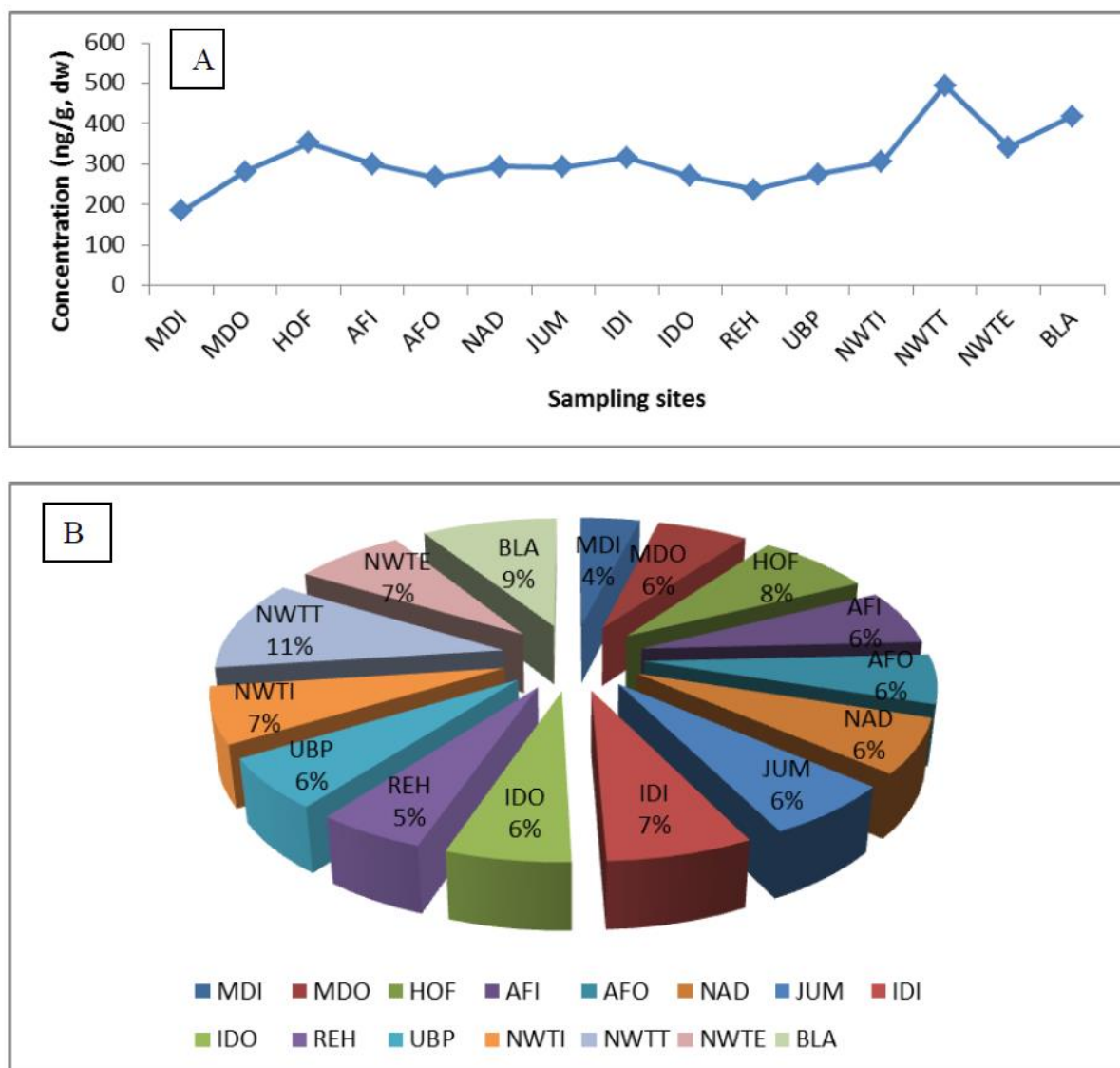
Figure 5.9 A- Trend of the total concentration across sites for sediment samples B- Percentage contribution of the total concentrations in sediment at each site.

5.4.4. Total Mean Concentration of OCPs in Water, Pore Water and Sediment

The total concentrations and mean values of 12 pesticides investigated in surface water, sediment pore water and surface sediment are shown in Table 5.7. The total concentrations ranged from 8.04 to 21.06 ng/mL with a mean of 11.92 ±1.12 ng/mL for water and 36.06 to 188.43 ng/mL with a mean of 110.09 ±8.35 ng/mL for sediment pore water. The overall concentration of the pesticides in surface sediment varied from 148.17 to 554.73 ng/g, with a

mean concentration of 308.07 ±3.05 ng/g, dw (Table 5.7). These total concentrations of OCPs observed in the sediment of Umgeni River were higher than those found in in surface sediment from River Yamuna in Dehli, India ($\sum^{20}$ OCPs 157.71-307.66 ng/g) in pre-monsoon season (Pandey et al., 2011), however results of the present study were similar to those obtained by Pandey for sediment of the Yamuna River (195.86-577.74 ng/g) in monsoon season and lower than those obtained during post monsoon (306.9-844.45 ng/g,dw) (Pandey et al., 2011). The Umgeni River sediment was also more polluted with OCPs than sediment collected from Nanshan underground river in China (51-3 842.0 ng/g) (Jahangir et al., 2014). The comparison of the results of the present study with other results obtained elsewhere in South Africa showed that the levels of OCPs in the Umgeni River sediment were higher than the levels detected in sediment (trace-184 ng/g) of fresh water systems in the Eastern Cape (Fatoki and Awofolu, 2003b). However, the Umgeni River was much less polluted by OCPs than the Jukskei River catchment area in Gauteng, where the OCPs levels varied from 0.895 to 9089 ng/mL in unfiltered water and from 0.266 to 22 914 ng/g, dw in sediment (Sibali et al., 2008).
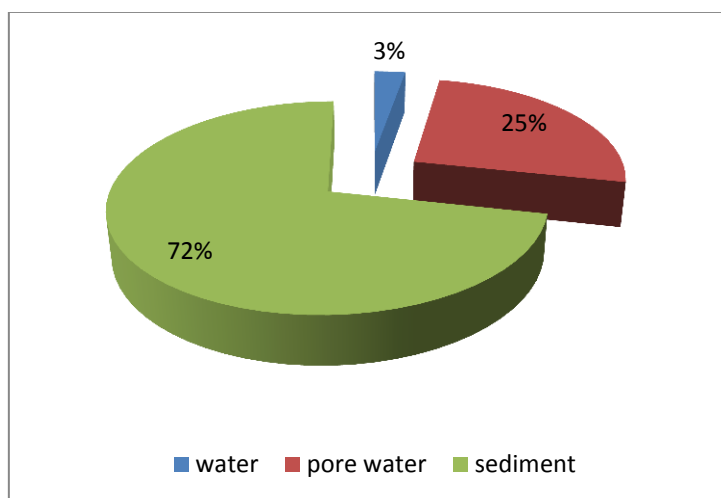
Figure 5.10 Percent contribution of each matrix to the total average levels of OCPs analysed in the Umgeni River.

Table 5.7 Total concentrations of OCPs in water, pore water and sediment of the Umgeni River.

Analyte	water (ng/mL)			porewater (ng/mL)			sediment (ng/g,dw)		
	range	mean	SD	range	mean	SD	range	mean	SD
HCB	0.41-1.04	0.63	0.1	1.06-6.08	3.11	0.43	2.29-49.44	13.18	1.56
HCH	0.50-1.97	0.82	0.2	0.76-6.80	3.69	0.4	4.34-93.02	40.95	3.4
heptachlor	0.32-2.07	0.66	0.13	2.19-12.63	7.37	0.85	18.46-50.77	30.43	4.76
aldrin	0.01-2.73	1.2	0.11	4.11-21.96	12.61	0.77	8.27-37.80	22.29	4.27
o,p'-DDE	1.21-2.32	1.5	0.1	5.18-24.39	14.79	0.88	17.78-50.70	26.27	2.05
p,p'-DDE	1.34-2.01	1.62	0.07	5.73-27.93	17.09	0.92	20.61-38.72	27.57	1.97
o,p-DDD/dieldrin	1.41-1.99	1.69	0.1	7.15-34.92	20.53	1.25	22.97-34.46	27.07	1.33
endrin	0.88-3.48	1.39	0.12	4.07-19.21	10.38	1.09	28.10-87.72	55.57	4.27
p,p'-DDD/*o,p'*-DDT	1.23-1.72	1.39	0.1	3.37-22.34	13.22	0.99	18.51-33.44	23.14	1.1
mirex	0.74-1.74	1.02	0.08	2.47-12.18	7.28	0.77	6.83-78.66	42.23	2.94
∑OCPs	8.04-21.06	11.92	1.12	36.06-188.43	110.09	8.35	148.17-554.73	308.7	3.05
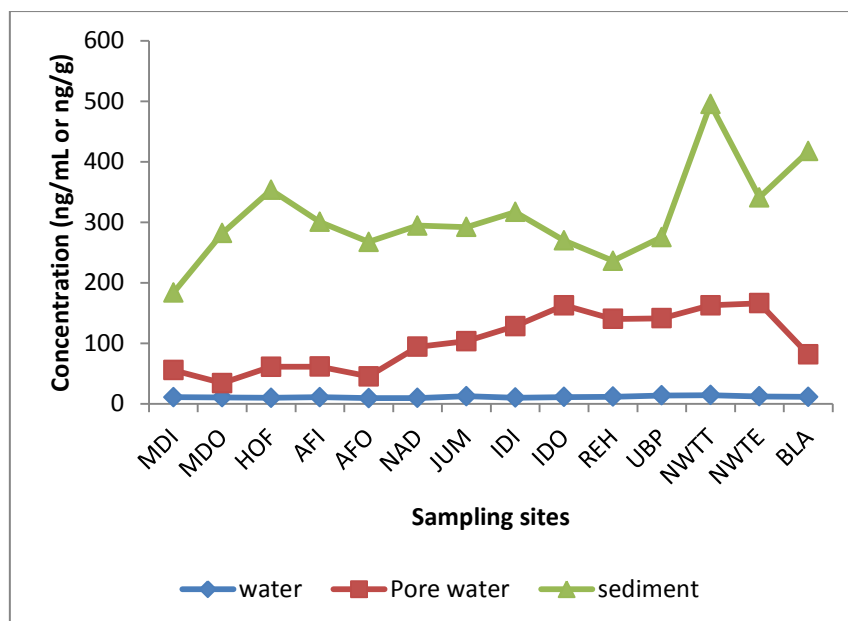
Figure 5.11 Trend of the total concentrations in water, pore water and sediment (n =3).

Figures 5.10 and 5.11 show that the concentrations of OCPs in water were less than in pore water and much less than in sediment. The total mean concentrations of OCPs in sediment pore water and in surface sediment were 9 times and 25 times respectively higher than in surface water (Table 5.7). This was expected because the organochlorine pesticides are non-polar and hydrophobic and may only dissolve partially in water while sediment is considered as a sink for them (Noegrohati et al., 2008, Houde et al., 2008, Miglioranza et al., 2004). Currently, there are no South African guidelines or regulations to direct the environmental POPs levels in South Africa. Compared to Canadian Sediment Quality guidelines, the levels of HCB (2.29-49.44 ng/g), HCH (4.34-93.02 ng/g), *o,p*-DDE (17.78-50.70 ng/g), *p,p´*-DDE (20.61-38.72), in this study of the Umgeni River, they were higher than the interim freshwater sediment quality guidelines (ISQG) (HCB: 0.940 ng/g), (HCH: 0.600 ng/g), (*o,p*-DDE and *p,p´*-DDE: 1.420 ng/g) and Probable Effect Level (PEL) (HCB:1.380 ng/g), (HCH: 2.740 ng/g), (*o,p*-DDE and *p,p´*-DDE: 6.750 ng/g) (CCME, 2002). Compared to Ontario Sediment Quality Guidelines, the HCB level in this study was lower than its Lowest Effect Levels (LEL) (20 ng/g) except at NWTT (49.44 ng/g) and BLA (45.26 ng/g) sites. The other above-mentioned OCPs levels were higher than their LEL values (HCB: 20 ng/g). However, the levels of the aforesaid OCPs at all sites, in the current study, were far below their severe effect level (SEL) (HCB: 24000 ng/g), HCH (12000 ng/g), (*o,p*-DDE and *p,p´*-DDE: 19.000 ng/g) according to Ontario Sediment Quality Guidelines (Persaud et al., 1993). A review done by Borton on the sediment guidelines in use around the world showed that PEL in

sediment for *p,p*-DDE, *p,p'*-DDD and endrin are 6.8. 8.51 and 1.38 ng/g (Burton, 2002) which are lower than results obtained in this study.

5.5 CONCLUSION

The present study has provided data on levels of organochlorine pesticides in surface water, sediment pore water and sediment of the Umgeni River in KwaZulu-Natal, South Africa. All 12 selected pesticides investigated were detected in all sites, in water, pore water and sediment, except aldrin which was below the limit of detection in water at the Reservoir Hills sampling site. The levels of organochlorine pesticides in sediment were higher than in pore water and much higher than in surface water. The present study showed that the discharge from the wastewater treatment plant increased the concentrations of organochlorine pesticides in the river, for water, pore water and sediment samples collected at the sites close to the NWWTW. Hence discharges from this WWTP may be considered as one of the sources of pollutants such as OCPs into the Umgeni River. *p,p´*-DDE was found to be the pollutant in highest concentration in water and pore water and endrin the highest in sediment of the Umgeni River. In the future, studies on POPs in the sediment of this river should focus on their distribution according to particle sizes of the sediment and comparison of depth and surface sediment concentrations.

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CHAPTER SIX
MANUSCRIPT THREE

EVALUATION OF CONTAMINATION OF UMGENI RIVER BANK SOIL, IN THE PROVINCE OF KWAZULU-NATAL, SOUTH AFRICA, WITH PERSISTENT ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS

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ABSTRACT

This study investigated the presence and distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in soil collected along the banks of the Umgeni River, which is one of the largest rivers in South Africa, situated in the province of KwaZulu-Natal. The extraction of contaminants was performed using soxhlet extraction with toluene, and subsequent clean-up with florisil. The analysis was performed on gas chromatography-mass spectrometry (GC-MS). The results showed that levels of OCPs in this river bank soil ranged between 3.58 ±0.09 ng/g for HCB and 82.65 ±2.82 ng/g for HCH, with an individual mean concentration of 24.33 ±2.00 ng/g, dw. The levels of PCBs were in the range 10.46 ng/g for PCB105 to 89.46 ng/g for PCB180, with an average value of 25.47 ±1.26 ng/g, dw. The highest levels of OCPs and PCBs were found at Howick Falls (mean OCP: 28.41 ±3.02 ng/g and mean PCB: 34.39 ±1.85 ng/g) and at Northern Wastewater Treatment plant (NWTT) (mean OCP: 32.39 ±3.97 ng/g and PCB: 67.87 ±1.67 ng/g). The two most abundant

contaminants in the river, compared to other investigated pollutants, were found to be endrin and PCB180.

Key words: *Umgeni River bank soil, OCP, PCB, soxhlet extraction, florisil clean-up, gas chromatography-mass spectrometry*

6.1 INTRODUCTION

Many organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are among environmental contaminants that have been included on the list of persistent organic pollutants (POPs) developed at the Stockholm convention and signed in 2001. Most countries have restricted or eliminated their use, storage and manufacture since the 1970s (Voldner and Li, 1995, Zhu et al., 2014). Extensive use of OCPs for pest and disease control and mitigation started in the 1940s which explains their widespread presence in the environment (Woodwell et al., 1971, Barrie et al., 192, Bidleman et al., 1995, Dimond and Owen, 1996, Li et al., 1996, Li, 1999, Li et al., 2006). However, these pollutants are sources of various environmental and human health hazards due to their biomagnification through the food chain (Li and Macdonald, 2005, Jones and de Voogt, 1999).

PCBs were widely used in different applications such as industrial and commercial as dielectric and coolant fluids in transformers and capacitors, or in plasticisers. Even though the termination of their production and usage was implemented since the 1970s (Zhu et al., 2014), research has shown that the primeval dismantling of electronic and electric waste still remains a significant source of PCBs in developing countries of Africa and Asia (Wang et al., 2011, Wong et al., 2007, Breivik et al., 2011).

Although the use and production of many OCPs and PCBs were restricted or banned in many countries, their residues are still being detected in different environmental matrices such as water, soil, air and biota and still are a threat to human health in particular, and the environment in general (Woodwell et al., 1971, Aigner et al., 1998, Li et al., 1996, Falandysz et al., 2001, Nakata et al., 2002a, Ribes and Grimalt, 2002, Miglioranza et al., 2003b, Gong et al., 2004, Barriada-Pereira et al., 2005, Concha-Grana et al., 2006). These POPs are able to partition between different matrices. They can volatilize from soil to the atmosphere and

hence, contaminated soils can be considered as a substantial source of POPs into the atmosphere (Meijer et al., 2002, Wild and Jones, 1995, Harner et al., 2001).

Even though DDT is on the list of priority pollutants, it is still being used today in a restricted form, for malaria control in certain parts of South Africa, due to its effectiveness in vector control. Research showed that during the period of 2000-2004 the indoor results spraying (IRS) with DDT reduced the number of confirmed malaria cases by 83% in South Africa in general and by 90% in KwaZulu-Natal in particular, while the number of confirmed malaria deaths were reduced by 65% in the country as a whole, compared to results obtained during the period of 1996-1999 (WHO, 2010, Naud and Rohwer, 2012, Sadasivaiah et al., 2007). However, studies showed that this powerful pesticide and its metabolites, DDD and DDE, were detected in blood samples taken from individuals exposed to DDT as a result of IRS (Bouwman et al., 1991a). A study by Rollin also revealed the presence of high levels of DDT and its metabolites particularly in the Indian ocean coastal malaria sites and detectable levels of PCBs in the plasma of delivering women in seven geographical regions of South Africa (Rollin et al., 2009).

The Umgeni River is a main source of water supply in the province of KwaZulu-Natal in South Africa which many animals and informal settlements use in its untreated form. Its level of pollution with regard to OCPs and PCBs is presently limited. Furthermore, work has been carried out on the water and sediment of the Umgeni River but there is limited or outdated information on the presence of OCPs and PCBs in the soil along the banks of the river which can leach into the waterways. Vegetable plantations along the banks of the river have been observed and any pesticides applied to those vegetations could remain in the soil for long periods of time as well as make its way into the river due to runoff thus leading to further contamination of the surface water or evaporate into the atmosphere during warmer seasons thus adding to the atmospheric contamination. The aim of this project was therefore to evaluate the status of OCP and PCB contamination of this river by analysing its bank soil. The result of this work adds knowledge to the presence and quantification of OCPs and PCBs in the Umgeni River soil. The structures of all the analytes investigated in this study are given in Figure 6.1 below.
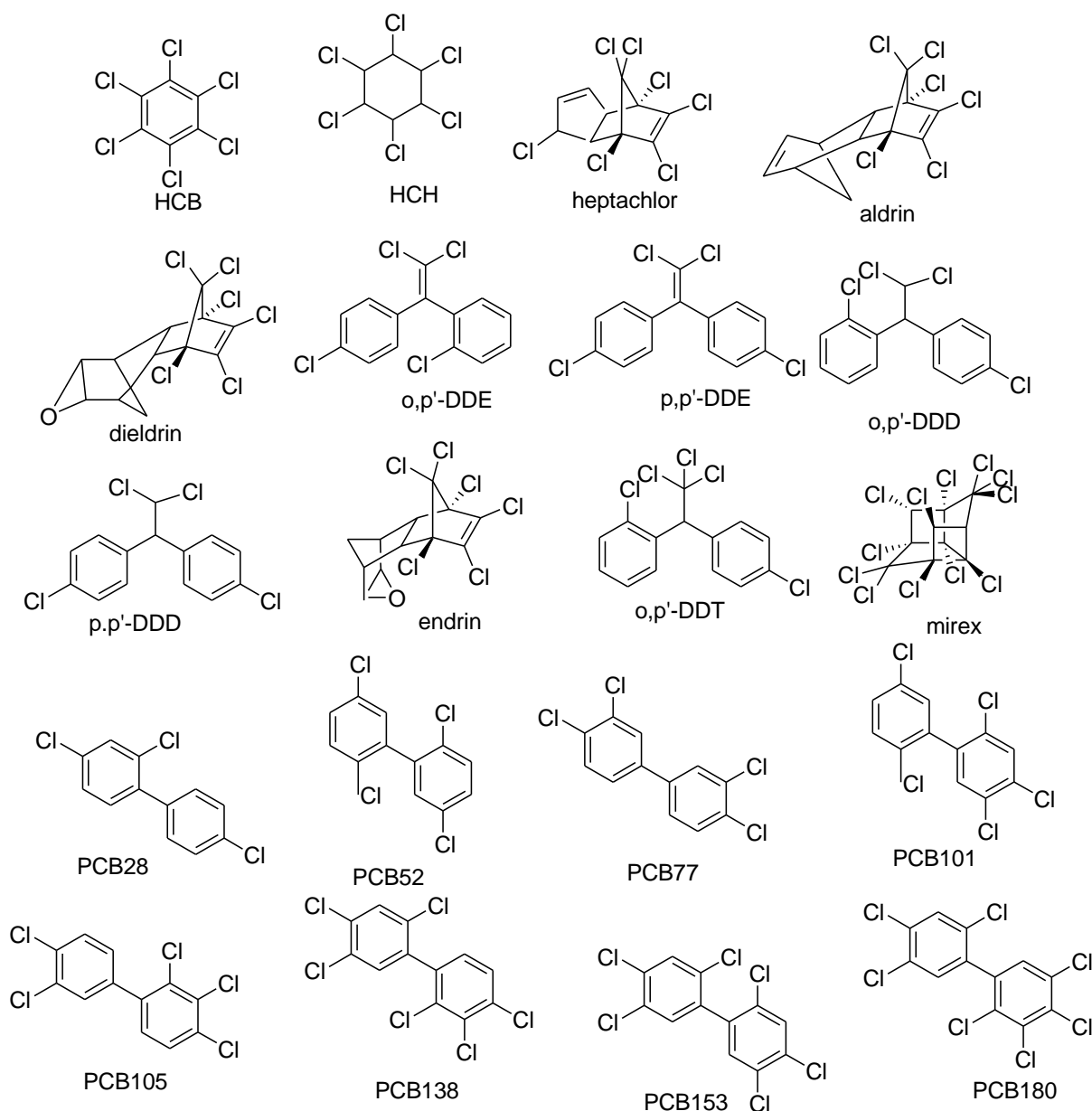
Figure 6.1 Structures of OCPs and PCBs investigated.

6.2 MATERIALS AND METHODS

6.2.1. Chemicals, Standards and Apparatus

HPLC-grade hexane, dichloromethane (DCM) and toluene, florisil (MgO$_3$Si residue analysis grade, mesh 60-100, pore size 60Å) organochlorine pesticides and polychlorinated biphenyl standards, were all purchased from Sigma Aldrich in South Africa. Anhydrous sodium sulfate, (Na$_2$SO$_4$) gold line (CP) and silicon carbide boiling stones (CSi), were obtained from Associated Chemical Enterprises, (ACE, South Africa) and sulfuric acid (98%) was obtained

from Promark Chemicals (UK). The test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm) were obtained from DLD Scientific in South Africa. Also separatory funnel, motor and pestle and column of different sises were used.

6.2.2. Sample Collection

Soil samples were collected on 15 to 17th July 2013 from the banks of the Umgeni River in the province of KwaZulu-Natal in South Africa. The samples were collected from 14 sites; which include 12 sites selected along the river, from the source at Midmar Dam to the mouth at Blue Lagoon, where the Umgeni River empties into the Indian Ocean, (Figure 6.2) and two sites at the Northern Wastewater Treatment Works which treats residential and industrial wastewater from the surrounding Durban city. The sampling site names and geographical coordinates are shown in Table 6.1.

Soil was collected using an auger and stored in 150 mL glass bottles previously washed with hot water and detergent and thereafter rinsed with sulfuric acid, deionized water and river water from the site to be sampled. The bottle caps were lined with aluminium foil. Once the samples were collected, they were kept in a cooler box containing ice and transported to the analytical research laboratory.

Table 6.1 List of sampling sites along the Umgeni River, in the downstream direction.

Sample code	Sample name	Coordinates		Site description
		South	East	
MDI	Midmar Dam inlet	29°29′16.05″	30° 09′ 23.10″	dam for water supply inlet
MDO	Midmar Dam outlet	29°29'34.02″	30° 12′ 09.13″	dam for water supply outlet
HOF	Howick Falls	29°29'18.18″	30° 14′ 19.70″	water falls
AFI	Albert Falls inlet	29°26'31.94″	30° 19 47.10″	dam for water supply inlet
AFO	Albert Falls outlet	29°26'01.81″	30° 25′ 55.76″	dam for water supply outlet
NAD	Nagle Dam	29°35'08.42″	30° 37′ 23.94″	dam water
JUM	Joining point Umgeni/Msunduzi	29°37'16.61″	30° 40′ 46.59″	river banks
IDI	Inanda Dam inlet	29°39'05.20″	30° 48′ 06.24″	dam for water supply inlet
IDO	Inanda Dam outlet	29°42'55.74″	30° 52′ 07.69″	dam for water supply outlet
REH	Reservoir Hills	29°47'08.05″	30° 56′ 25.51″	river banks
UBP	Umgeni business park	29°48'19.05″	30° 58′ 58.08″	river banks
NWTT	Northern Wastewater Treatment after treatment	29°47'47.02″	30° 59′ 50.06″	pond containing treated water
NWTE	Northern Wastewater Treatment effluent	29°48'27.01″	30° 59′ 51.05″	discharge of treated water to the river
BLA	Blue Lagoon	29°48'41.03″	31° 02′ 12.05″	discharge of the river water to the Indian ocean
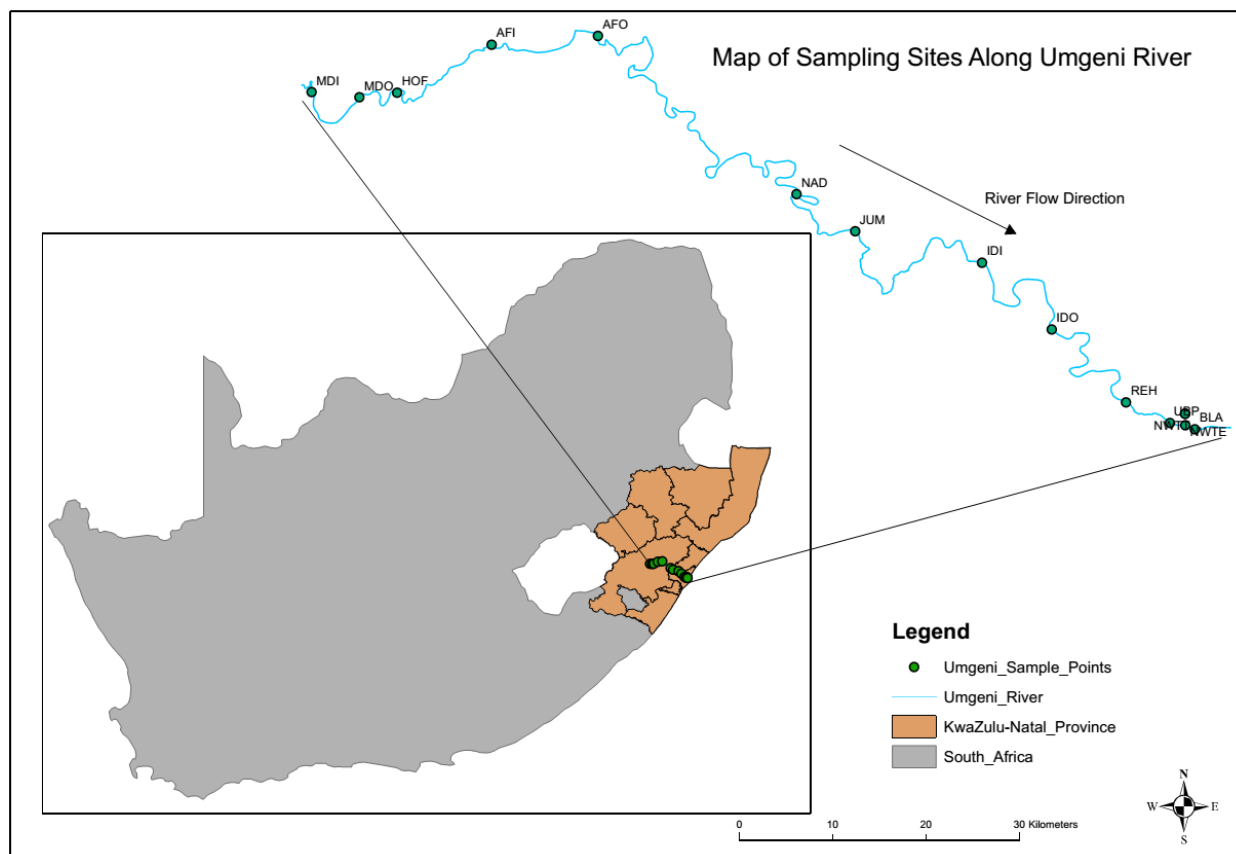
Figure 6.2 Map of sampling sites with the sample collection locations (map was generated from GPS coordinates using ArcGIS 10.2).

6.2.3. Sample Preparation and Treatment

The soil samples were air dried in the laboratory for several days before being ground using a pestle and mortar and thereafter sieved. Portions of soil (60 g) were accurately measured and transferred into a cellulose extraction thimble which was inserted into a soxhlet assembly fitted with a 500 mL round bottom flask. The extraction was carried out with a 300 mL aliquot of HPLC-grade toluene for 24 hours (EPA method 3540c) (EPA, 1996b). Toluene was identified as the most suitable solvent for extraction of aromatic ring bearing compounds such as organochlorine pesticides and PCBs investigated in this study (Oleszek-Kudlak et al., 2007). The obtained extract was concentrated using a rotary evaporator to about 5 mL and subsequently cleaned-up.

The extract was cleaned-up by loading it onto a column packed with florisil (activated at 130 °C for 12 hours) containing a top layer of anhydrous Na_2SO_4 (10 g). Sequential elution was carried out with a solvent system consisting of hexane-DCM (20 mL) (94:6), (85:15),

(50:50) and 100% DCM (modified EPA method 3620-C) (EPA, 2007). The obtained fractions were combined and concentrated with a rotavap to 5 mL, air-dried and reconstituted to 2 mL and analysed using GC-MS. Sample extraction, preparation and clean-up was carried out within 5 days of sampling.

6.2.4. Instrumental Analysis

The sample analyses for OCPs and PCBs were carried out separately to avoid overlapping of peaks. The gas chromatography system (Agilent 6890 series) was attached to a mass spectrometer detector (MSD5973) and equipped with a ZB-5MS (Hewlett Packard; Houston, TX) capillary column (30 m, 0.25 mm, 0.25 μm). Helium was used as the carrier gas, using a constant flow mode (1 mL/min). The oven temperature started at 120 °C and increased to 290 °C at a ramping rate of 14 °C/min and held for 2 min. A 2 μL injection volume was used in splitless mode with a 4 min solvent delay. The MS source and Quad were operated at 250 °C and 200 °C respectively. The electro energy was 70 eV. The MS was operated in selective ion monitoring (SIM) mode and three ions were monitored for each target analyte.

Target analytes were quantified using an external calibration method based on peak areas. The six calibration levels used for both OCPs and PCBs were 0.25; 0.5; 1; 2; 4 and 8 ng/mL. The identification of specific target compounds was achieved by analysis of mass spectra against that found in the NIST library as well as comparison of retention times of sample analytes with those of reference standards.

6.3 QUALITY CONTROL AND ASSURANCE

The procedures used for analysis of selected OCPs and PCBs were monitored with appropriate quality control and assurance measures. Procedural blanks were used in all extraction, clean-up and analysis steps along with sample preparation and analysis to determine if there was any possible input from external sources during analysis. There were no detectable levels of target contaminants in blank samples. Solvent blanks were regularly run after each batch of 10 injections through the GC-MS column. A 0.5 ng/mL reference standard of OCPs and PCBs was run intermittently to ensure that variation from the initial calibration standards were as minimal as possible. Three ions were monitored on GC-MS in order to identify the analytes of interest (Table 6.2). All the data were processed using

Microsoft excel 2010. Target analyte recoveries were performed by spiking real soil subsamples with separate OCP and PCB standards before extraction, as well as leaving one subsample unspiked. The difference between the concentrations of spiked subsamples (X_S) and non-spiked subsamples (X_u) was divided by the known concentration of the spike in the sample (X_k) and multiplied by 100 to obtain the percentage recoveries (%R) (Equation 6.1) (Harry et al., 2008). The recovery and actual sample analyses were carried out in triplicate to ensure the reproducibility and precision of the method used.

Table 6.2 Ions monitored, % recovery, limits of detection (LOD) and quantification (LOQ).

Analytes	Ions monitored	% recovery	LOD (ng/g)	LOQ (ng/g)
OCPs				
HCB	284, 249, 142	68.1 ±0.058	0.50	1.66
HCH	219, 183, 147	108.4 ±3.81	0.50	1.66
heptachlor	374, 272, 237	103.7 ±7.24	0.50	1.62
aldrin	327, 293, 263	53.16 ±10.37	0.78	2.59
o,p-DDE	318, 284, 246	87.66 ±4.77	0.96	3.20
p,p'-DDE	318, 281, 246	51.67 ±1.62[17]	0.62	2.07
o,p'-DDD/dieldrin	320/380, 235/263, 165/147	87.37 ±2.08	1.04	3.45
endrin	317, 263, 207	84.69 ±6.04	1.02	3.41
p,p'-DDD/*o,p*-DDT	320/235, 235/199, 165/165	89.13 ±2.61	1.23	4.11
mirex	402, 272, 237	111.9 ±12.84	0.63	2.07
PCBs				
PCB28	256, 186, 150	60.68 ±0.97	0.76	2.52
PCB52	292, 220, 150	78.73 ±0.58	0.21	0.71
PCB77	292, 255, 220	64.74 ±1.47	0.92	3.06
PCB101	326, 291, 254	72.63 ±0.86	0.30	0.99
PCB105	326, 254, 184	71.88 ±0.74	0.28	1.12
PCB138	360, 290, 145	72.69 ±1.38	0.22	0.75
PCB153	360,290, 145	74.74±1.95	0.31	1.03
PCB180	394, 324, 162	77.80±2.55	0.19	0.66

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[17] The *p,p'*-DDE standard chromatogram showed the presence of DDMU which suggested that some of *p,p'*-DDE may have degraded into this compound which is its break down product (Thomas et al., 2008) and consequently contributed to its low recovery.

The limits of detection (LOD) were calculated as being three times the signal-to-noise ratio using the standard deviation of six calibration intercepts divided by the slope, whereas the limit of quantification (LOQ) was ten times this ratio (refer to Equations 3.2- 3.5 in section 3.1.1.2 and 3.6 in section 3.2.3 of the Chapter three) (Shrivastava and Gupta, 2011).

6.4 RESULTS AND DISCUSSION

Soil samples were analysed for OCPs and PCBs. The sampling points were located along the banks of the Umgeni River except one site (NWTT) located in the area of the Northern Wastewater Treatment Works which empties treated water back into the Umgeni River. The concentrations of various analytes (C_a) were calculated using the following equation 6.5 (USEPA, 2007, USEPA, 2008):

$$C_a = \frac{C_{ex} * V_{ex}}{W_s} \dots\dots\dots\dots\dots\dots\dots\dots\dots (6.5)$$

C_a = concentration of analyte in ng/g

C_{ex} = the concentration of the analyte in the extract in ng/mL

V_{ex} = the extract volume in mL

W_s = the sample weight (dry weight) in g

6.4.1. Organochlorine Pesticides (OCPs) in Soil

Levels of OCPs were determined in the soil collected from the banks of the Umgeni River and the results obtained are shown in Table 6.3. All the OCPs investigated were detected in all sampling sites and their concentrations ranged from 3.58 to 82.65 ng/g. Endrin (37.08–70.18 ng/g) was the most abundant OCP in all sites investigated, except NWTE where the OCP in highest concentration was HCH (Figure 6.3). This was attributed to endrin's low mobility in soil and its long half-life, where once released in soil, it remains for a long period of time up to more than 14 years (USEPA, 2009). Its leaching into ground water and evaporation to air is very limited due to its very strong adsorption to soil particles (Log K_{ow} = 5.6) and low vapour pressure respectively (USEPA, 2009). Other OCPs such as DDDs and DDEs were also detected in substantial amounts. The high concentrations of residues of these break-down products of DDT may be an indication of its extensive use in past years. DDT is still in use in certain areas of South Africa for malaria control, especially in high-risk areas such as northern KwaZulu-Natal, Limpopo and Mpumalanga where its use is monitored

by the government to avoid its widespread and uncontrolled use (Rother and Jacobs, 2008, Naud and Rohwer, 2012, Van Dyk et al., 2010).
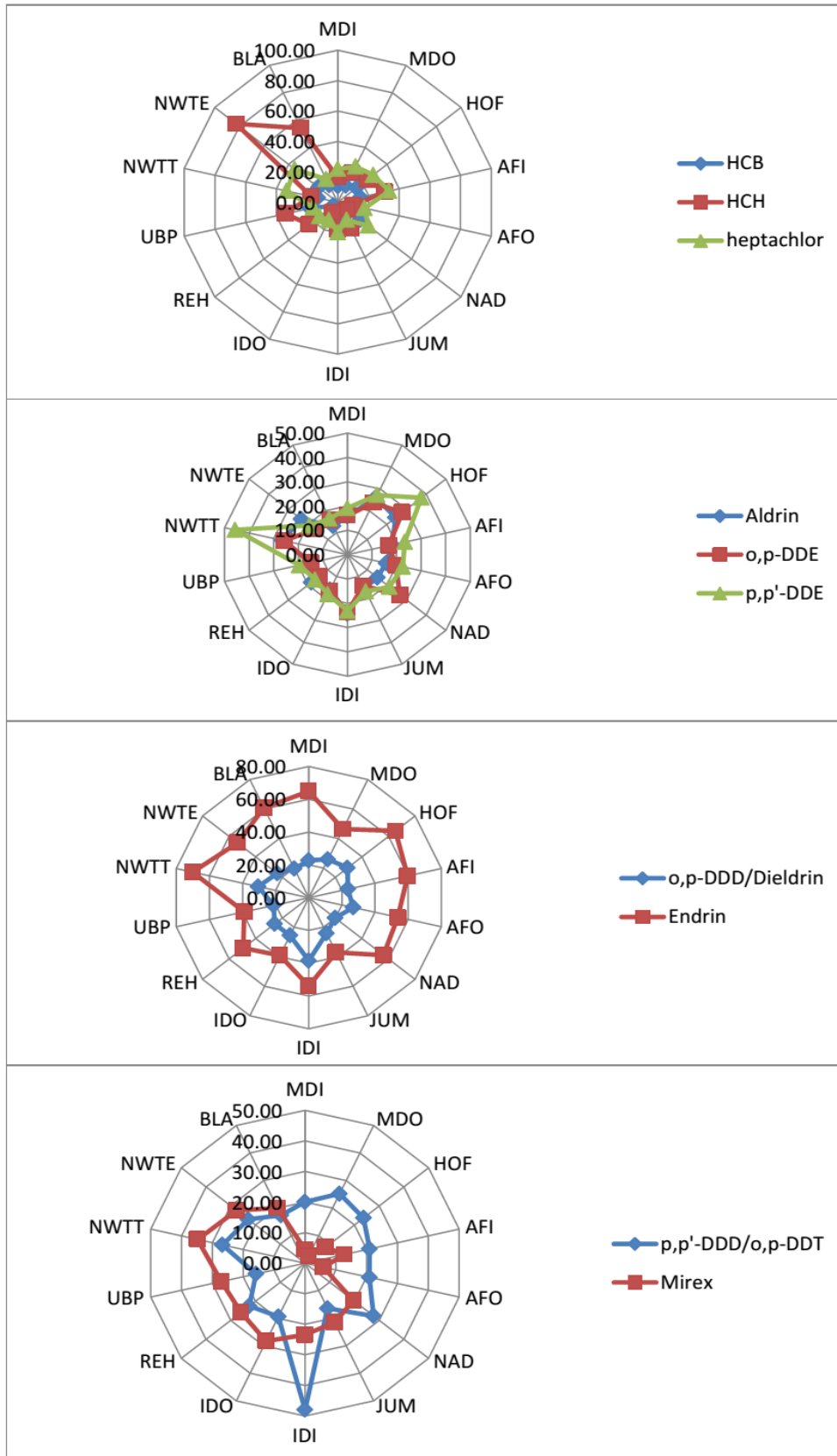
Figure 6.3 Distribution of OCPs in bank soil, throughout the various sampling sites.

Table 6.3 Concentration of OCPs in bank soil of Umgeni River.

Site	HCB	HCH	Heptachlor	Aldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD/Dieldrin	Endrin	*p,p'*-DDD/*o,p'*-DDT	Mirex	∑OCPs
MDI	10.42±0.10	16.35±0.42	21.95±3.06	15.72±1.24	16.15±0.33	19.17±0.10	22.71±0.33	64.90±1.42	20.02±0.30	4.43±2.86	211.82±10.15
MDO	11.97±3.38	21.17±1.20	26.00±1.37	26.02±0.70	23.71±1.28	27.17±0.60	25.90±1.62	46.36±3.52	25.20±1.27	2.52±2.05	236.01±16.97
HOF	15.08±1.10	23.73±4.32	28.75±2.35	24.48±4.62	27.91±1.42	37.57±0.23	29.17±4.95	65.33±3.53	23.70±0.44	8.36±7.20	284.09±30.18
AFI	14.79±0.98	30.69±6.53	33.51±2.11	18.14±1.95	16.84±067	23.33±1.82	23.66±0.97	59.71±3.00	20.91±0.82	12.81±2.77	254.40±21.62
AFO	7.45±1.70	10.07±0.48	17.43±0.10	15.75±2.07	19.75±0.75	22.53±0.86	26.87±0.57	53.77±1.12	20.89±0.75	5.93±3.35	200.44±11.76
NAD	18.63±0.86	7.51±0.33	24.78±1.08	15.20±1.49	26.66±0.63	21.26±0.59	19.83±0.89	56.30±4.99	27.70±0.76	19.61±2.35	237.48±13.97
JUM	5.81±0.50	19.21±0.77	12.90±0.73	15.31±1.56	14.22±0.45	16.77±0.57	24.13±0.72	37.08±7.72	16.41±0.40	21.54±0.37	183.38±13.79
IDI	11.82±0.56	18.18±0.79	19.84±3.07	24.29±1.91	23.75±0.84	23.15±1.24	38.46±0.70	53.87±2.52	48.00±0.75	23.46±2.69	284.82±15.09
IDO	4.24±0.38	7.41±0.61	13.12±0.63	15.99±1.07	16.61±0.85	18.05±0.70	25.56±0.81	39.10±2.37	19.40±0.72	28.29±4.13	187.76±12.27
REH	3.58±0.09	23.27±2.07	14.88±0.85	18.30±2.81	14.43±0.87	16.45±0.80	25.60±1.10	49.41±4.20	22.50±2.00	25.85±3.90	214.27±18.68
UBP	18.19±0.87	34.24±1.24	16.02±1.09	14.96±4.39	14.94±1.24	19.61±0.52	21.29±0.14	38.97±5.98	15.86±0.38	27.12±3.12	221.21±18.97
NWTT	13.00±0.68	17.26±3.14	33.35±2.47	26.48±6.76	25.76±6.23	45.78±3.85	30.53±0.97	70.18±11.54	26.76±1.78	34.82±2.24	323.92±39.66
NWTE	15.55±0.86	82.65±2.82	34.93±7.77	23.52±5.63	16.67±0.72	19.28±1.33	23.72±0.71	53.65±9.12	22.98±1.34	27.65±3.15	320.60±33.45
BLA	12.32±0.63	54.15±0.99	16.87±3.41	13.09±3.11	15.86±0.72	16.44±1.11	19.62±1.45	60.81±8.43	17.37±1.81	20.06±1.98	246.58±23.65
∑OCPs	162.84±12.69	365.91±25.71	314.33±30.08	267.27±39.32	273.25±17.01	326.55±14.32	357.04±15.94	749.42±69.46	327.70±13.50	262.47±3.01	3406.78±28.20
Min	3.58±0.09	7.41±0.61	12.90±0.73	13.09±3.11	14.22±0.45	16.44±1.11	19.62±1.45	37.08±7.72	15.86±0.38	2.52±2.05	183.38±13.79
Mean	11.63±0.91	26.14±1.84	22.45±2.15	19.09±2.81	19.52±1.21	23.33±1.02	25.50±1.14	53.53±4.96	23.41±0.96	18.75±3.01	243.34±20.01
Max	18.63±0.86	82.65±2.82	34.93±7.77	26.48±6.76	27.91±1.42	45.78±3.85	38.46±0.70	70.18±11.54	48.00±0.75	34.82±2.24	323.92±39.66
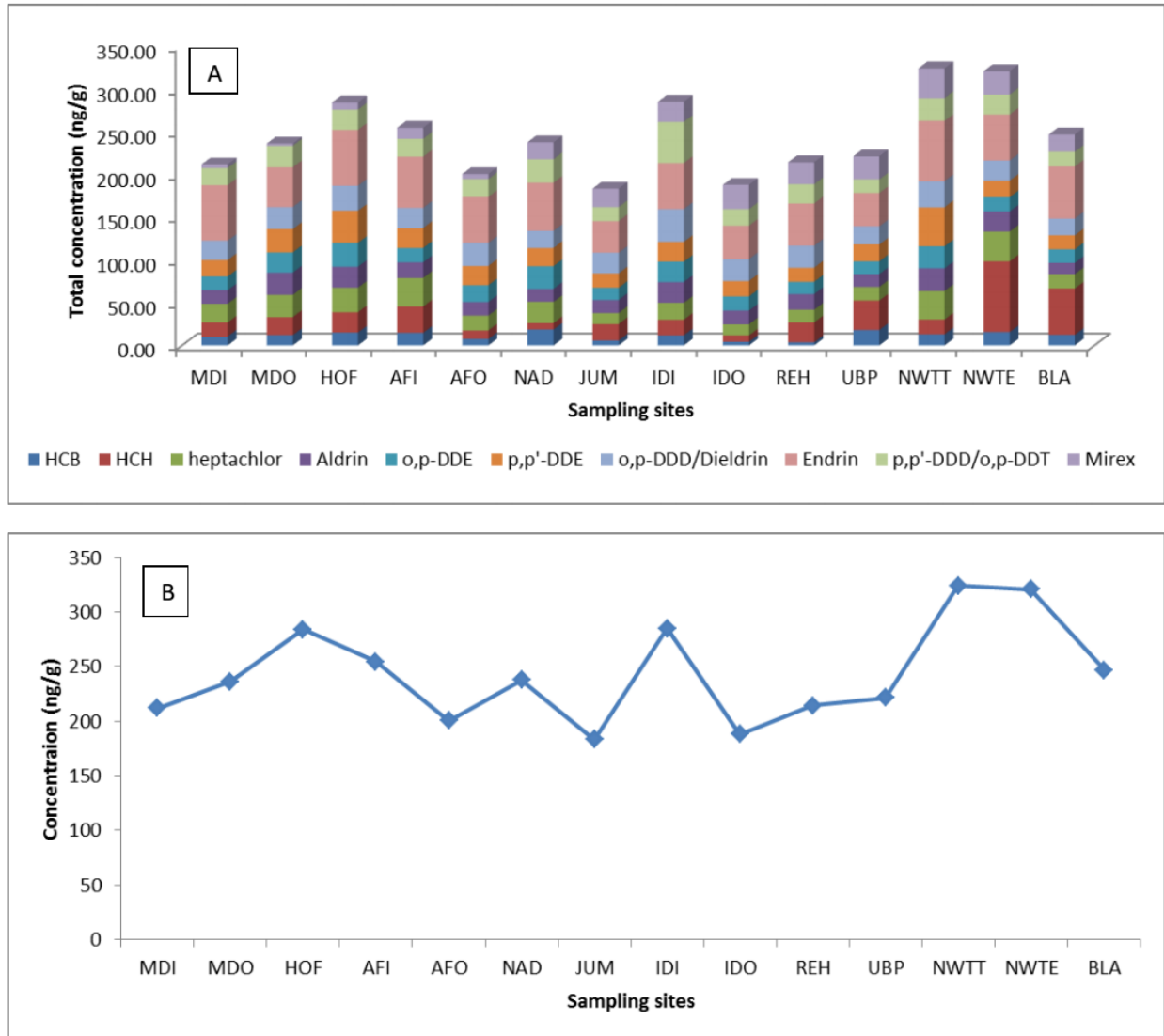
Figure 6.4 A-Total concentration of OCPs and B- Trend of OCP total concentration in bank soil along the Umgeni River.

The total concentrations of OCPs were higher at Howick Falls (HOF) (284.09 ng/g), Inanda Dam inlet (IDI) (284.82 ng/g) and at NWTT (323.92 ng/g) and NWTE (320.60 ng/g) (Figures 6.4 A and B and Table 6.3). The high concentrations at HOF were probably because HOF is in an urban environment and may be influenced by urban activities. There may also be leaching or long range transportation of agricultural pesticides from surrounding farms mainly sugar cane and wood plantations around Howick. In the case of IDI, the high concentration in soil may be due to agricultural runoff and regular spraying of a mixture of herbicides to avoid weed growth around the dam. This spraying was observed during sampling. The high levels of contaminants at NWTT and NWTE were expected since the wastewater treatment works receives residential and industrial waste which may contain

many of these pollutants. The samples collected from these sites were mainly made of bio-solids which may have accumulated more pollutant than soils obtained from the banks of the river.

6.4.2. Polychlorinated Biphenyls (PCBs) in Soil

Selected PCBs were investigated in soil obtained from the banks of the Umgeni River and their concentrations varied from 10.46 to 89.46 ng/g (Table 6.4). Figure 6.5 revealed that HOF had high levels of total concentration of PCBs (275.09 ng/g). This could be attributed to this site being situated in Howick town and pollution by industrial wastes is likely which may contain substantial amounts of contaminants, including PCBs. A high total PCB concentration was also observed in the bio-solids collected from the NWTT (542.95 ng/g) due to industrial and residential waste. The most abundant PCB congener in the river bank soil was found to be PCB180 (17.08-89.46 ng/g) with a mean concentration of 39.17 ng/g (Table 6.4 and Figure 6.5). This is probably due to its strong affinity with organic matter (Log K_{ow} = 6.70 –7.21) in soil to which it strongly adsorbs (Preda et al., 2010). Furthermore, its complexity having 7 chlorine atoms in its structure makes it relatively stable and resistant to degradation and volatilisation from soil to air, compared to other investigated congeners (de Voogt et al., 1990, Vesna et al., 2006). The second most abundant congener was PCB52 (21.64-73.66 ng/g). This PCB is of lower complexity having only four chlorine atoms and together with its relatively lower LogK_{ow} (5.79-6.09) value, it tends to adsorb less strongly to soil and would therefore mean relatively lower concentrations in the soil. Therefore the higher than expected concentrations suggest a possible input of this congener into the river. The other congeners were also present in significant amounts: PCB28 (12.02-64.56 ng/g), PCB77 (12.20-59.36 ng/g), PCB101 (13.64-83.59 ng/g), PCB105 (10.46-36.73 ng/g), PCB153 (12.48-81.11 ng/g) and PCB138 (11.05-54.49 ng/g) (Table 6.4).

Table 6.4 Concentrations of PCBs in Umgeni River bank soil.

Site	PCB28	PCB52	PCB77	PCB101	PCB105	PCB138	PCB153	PCB180	∑PCB
				Concentrations of PCBs in bank soil in ng/g,dw					
MDI	26.13±1.28	39.83±3.14	15.27±0.25	26.96±2.31	22.24±1.96	21.65±1.60	23.68±2.59	35.03±2.01	210.78±15.12
MDO	25.70±1.49	37.55±2.30	15.76±0.20	26.17±1.19	21.69±1.73	19.26±1.38	22.76±1.65	35.25±3.17	204.15±13.83
HOF	36.09±1.61	49.95±2.90	17.52±1.25	37.60±1.87	31.69±1.58	26.49±1.63	30.49±1.71	45.27±1.23	275.09±14.77
AFI	21.98±1.81	33.98±2.40	19.09±1.88	20.00±8.00	18.53±1.79	18.90±0.61	20.87±2.11	29.79±1.33	183.13±19.93
AFO	12.02±1.00	22.50±1.57	13.43±1.28	13.64±1.34	10.60±0.84	11.05±1.84	12.48±1.01	17.08±2.24	112.79±11.12
NAD	18.66±1.20	31.49±1.46	28.61±0.14	20.54±1.28	17.25±1.10	15.35±0.60	18.02±1.12	20.43±0.23	170.35±8.14
JUM	19.09±0.05	31.31±0.32	22.58±0.26	21.05±0.22	16.67±0.24	16.02±0.12	18.45±0.40	30.62±0.07	175.79±1.67
IDI	13.59±0.31	36.59±0.13	12.20±0.42	15.09±0.21	10.79±0.29	11.62±0.34	17.70±0.15	27.15±0.90	144.73±2.76
IDO	13.99±0.97	25.35±1.04	18.56±0.69	15.93±0.58	11.85±0.53	11.85±0.25	14.08±0.41	33.68±0.55	145.29±5.03
REH	13.90±0.72	26.54±0.70	18.38±0.91	15.35±0.51	11.96±0.32	11.68±0.38	14.11±0.39	29.01±0.38	140.93±4.62
UBP	15.70±1.41	25.10±0.89	19.87±0.91	16.95±1.15	12.64±0.60	14.19±0.87	15.22±0.59	26.67±0.85	146.34±6.58
NWTT	64.56±0.72	73.66±2.96	59.36±0.86	83.59±0.82	36.73±1.18	54.49±1.81	81.11±2.52	89.46±1.78	542.95±13.36
NWTE	12.54±1.41	21.64±1.02	41.25±1.63	15.87±1.01	15.23±1.57	12.8±21.27	14.38±0.48	55.19±2.57	188.91±10.03
BLA	12.32±0.46	21.75±2.25	49.31±3.11	17.79±3.28	10.46±1.11	11.41±0.31	14.23±1.16	73.77±2.46	211.03±14.09
∑PCB	306.26±0.42	477.23±23.09	351.19±14.80	346.51±24.50	248.34±14.85	256.76±13.01	317.58±16.27	548.40±20.77	2852.28±141.04
Min	12.02±1.00	21.64±1.02	12.20±0.42	13.64±1.34	10.46±1.11	11.05±1.84	12.48±1.01	17.08±2.24	112.79±11.12
Mean	21.88±0.98	34.09±1.65	25.08±0.06	24.75±1.75	17.74±1.06	18.34±0.93	22.68±1.16	39.17±1.48	203.73±10.07
Max	64.56±0.72	73.66±2.96	59.36±0.86	83.59±0.82	36.73±1.18	54.49±1.81	81.11±2.52	89.46±1.78	542.95±13.36
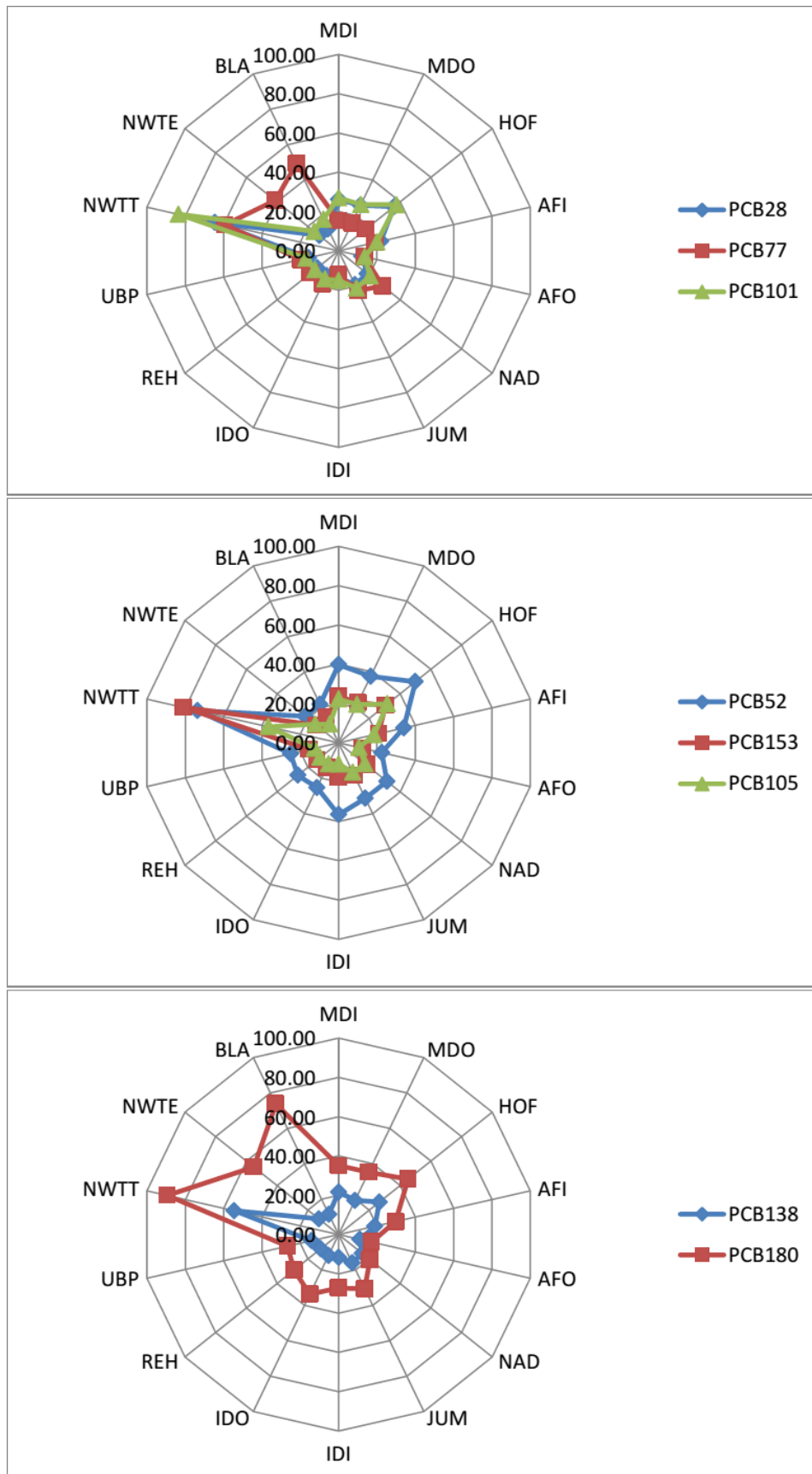
Figure 6.5 Distribution of PCB congeners at different sites.

The most contaminated site was NWTT (Figure 6.5). This was attributed to the accumulation of pollutants from wastewater since this site stores wastewater before being discharged back into the river. Being a store of wastewater and having an excess of plant life as a result of eutrophication, this site (NWTT) may contain more organic carbon than other sites. This may allow for partitioning of more PCBs and may be the reason for the high concentrations found at this site. A study of fate and persistence of PCBs in soil revealed that their persistence was greater in soil with higher organic carbon content (Ayris and Harrad, 1999).

6.4.3. Comparison of Levels of PCBs and OCPs in Soil from Various Locations Globally.

The levels of PCBs obtained in the present study, were compared to levels of PCBs obtained in various locations around the world. The present PCB results (total concentration range :112.79 to 542.95 ng/g, mean: 203.73 ng/g) (Table 6.4) were lower than the results obtained by Yuan and co-workers who found total PCB concentrations in topsoils of Beijing in China in the range 47.04 to 3883.77 ng/g, mean: 679.62 ng/g (Yuan et al., 2014). Levels of PCBs in eastern Romania were determined by Dragan and co-workers who found it to be between 34 and 1132 ng/g, mean: 278 ng/g (Dragan et al., 2006). The total concentrations of OCPs in topsoil of Beijing in China were found to vary from 2.38 to 933.12 ng/g, mean: 68.76 ng/g (Yuan et al., 2014). Table 6.5 summarizes the results obtained from different regions of the globe. The results obtained in this study were far below those reported by Yuan and co-workers in the topsoil of a topical urban area in Beijing, China where the levels of OCPs ranged from 2.4 to 3883.8 ng/g (Yuan et al., 2014); those detected in South East Romanian soil (58–1662 ng/g) (Ene et al., 2012) and those detected at Patagonia in Argentinian soil (38100-46500 ng/g) (Gonzaleza et al., 2010). However, the Umgeni River OCP levels were higher than the levels investigated in the Chao River soil in China (0.8145-16.8524 ng/g) (Yu et al., 2014).

Being ubiquitous, the organochlorine pesticides occur everywhere in any environmental compartment in different parts of the globe. Table 6.6 shows the comparison of the results of the present study with other investigations carried out in the world.

Table 6.5 Comparison of results of this study and PCB concentrations in soil reported in different locations in the world.

Country/location	Site descriptions	No. of congeners	∑PCBs (ng/g)	Sampling date	References
South-Africa	bank of the river, industrial, urban residential, agricultural	8	112.79 -542.95	July-13	This study
China/Beijing	urban	25	47.04 -3883.77	July-11	(Yuan et al., 2014)
United Kingdom	urban	7	1.00-750.00	April-2009	(Vane et al., 2014)
China	contaminated area	32	317.85-927.30	February-2012	(Gao et al., 2015)
Russia/Moscow	background	33	5.50-79.00	1996-2003	(Wilcke et al., 2006)
Russia	Arboretum of botanical garden	-	300.00-24250.0	2012	(Agapkina et al., 2012)
Eastern Romania	vicinity of waste disposal site	21	34.00-1132.00	2002	(Dragan et al., 2006)
Bulgaria	urban	6	7.20-17.20	2013	(Dimitrova et al., 2013)

Table 6.6 Comparison of results of this study and OCP concentrations in soil reported in different locations in the world.

Country/location	Site descriptions	No. of OCPs	∑OCPs (ng/g)	Sampling date	References
South Africa	bank river, urban, residential,	12	183.38-323.92	15-17 July 2013	This study
India	industrial, agricultural, residential	22	129-1001	-	(Manohar et al., 2014)
China/Beijing	urban	23	2.38-933.12	July 2011	(Yuan et al., 2014)
China	paddy soil	14	35–3669	2014	(Wang et al., 2007)
Pakistan	surface soil	-	216-541	September-October 2013	(Sultana et al., 2014a)
China	along the Chao River	24	0.8145-16.8524	2013	(Yu et al., 2014)
South East Romania	Agriculture, industrial	15	58–1662	April 2009	(Ene et al., 2012)
Western China	surface soil	10	0.51–181.63	March-July 2011	(Liu et al., 2013)
North-Eastern Romania	surface soil	-	4.4-95	August-September 2005	(Doina et al., 2013)
Tajikistan	high mountain soil	-	52.83-247.98	2012	(Zhonghua et al., 2013)
Poland	arable, agricultural and industrial	8	0.35-453.20	2005	(Maliszewsk-Kordybach et al., 2014)
Argentina	Agricultural area	15	38100-46500	-	(Gonzaleza et al., 2010)

6.5 CONCLUSION

In this study, the assessment of the levels and distribution of OCPs and PCBs in soil collected from the different sampling sites on the banks of the Umgeni River were carried out. The distribution of OCPs and PCBs in the soil from the banks of the Umgeni River banks was ubiquitous because of different potential sources such as agricultural runoff, industries, wastewater treatment plants and non-point sources. All the contaminants investigated were detected in all sites. Considering the levels of OCPs and PCBs shown in this study, the bank soil from the Umgeni River is contaminated, compared to other places in the world. Therefore, serious measures must be taken by the local government to reduce its contamination effects of the river water and protect the environment. This is the first study on the presence of organic pollutants in the soil of the Umgeni River which has added to the present limited or non-existent knowledge of their environmental distribution in bank river soils from KwaZulu-Natal in South Africa. Our qualitative analysis also found significant amounts of other pollutants and therefore further studies on the levels of other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyls (PBDs) would provide additional knowledge on the levels of contamination of the soil along the banks of the Umgeni River.

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CHAPTER SEVEN
MANUSCRIPT FOUR

SEASONAL VARIATION OF THE DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN THE WATER, SEDIMENT PORE WATER AND SEDIMENT SYSTEMS IN THE UMGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

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ABSTRACT

In this study, the seasonality of polychlorinated biphenyls (PCBs) was investigated in surface water, sediment pore water and surface sediment of the Umgeni River, one of the main rivers in South Africa located in the Province of KwaZulu-Natal, from 2013 to 2014. The samples for all the above matrices were collected concurrently except pore water which was obtained after centrifugation of sediment. The samples were treated using liquid-liquid or soxhlet extraction and cleaned-up using a florisil column. The analysis was done using gas chromatography-mass spectrometry. The mean concentrations of PCBs were 1.36 ±0.39 ng/mL in winter, 0.71 ±0.15 ng/mL in summer, 0.66 ±0.22 ng/mL in autumn and 0.56 ±0.08 ng/mL in spring, for water samples; 14.60 ±7.30 ng/mL in winter, 4.72 ±1.80 ng/mL in summer, 5.53 ±2.25 ng/mL in autumn and 10.73 ±6.00 ng/mL in spring, for pore water samples; 24.31 ±8.92 ng/g in winter, 13.50

±8.07 ng/g in summer, 19.16 ±6.93 ng/g in autumn and 23.67 ±16.39 ng/g in spring for sediment samples. Higher levels of PCBs were found in winter and low levels were generally noted in summer.

Key words: PCBs, seasonal variations, pore-water, sediment, soxhlet extraction, Umgeni River

7.1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are well known and widespread environmental pollutants of global concern and were previously used in several industrial and commercial applications. Research showed that PCBs and their metabolites can cause numerous health risks including carcinogenicity and endocrine, reproductive, immunologic and neurologic disruption (Safe, 1989, Robertson and Ludewig, 2011, Boas et al., 2012, Hallgren et al., 2001). Due to their persistence, biomagnification and toxicity (Diamond et al., 2010, Schecter and Gasiewicz, 2003), they have been analysed in all environmental matrices in order to monitor the level of contamination in water, soil, air and biota. Based on the health risks posed by their production, use and storage, PCBs were included on the list of persistent organic pollutants (POPs) by the Stockholm convention and on the priority pollutant list by the United States Environmental Protection Agency (US EPA) (EPA, 1999, ATSDR, 2005).

Studies have confirmed that the seasonal variations of concentrations of PCBs observed in various environmental compartments are dependent on a number of factors including temperature variation, precipitation, physical and chemical properties of individual congeners, etc. The variations depending on temperature difference were encountered in water (Blemle and Larsson, 1997, Bruhn and McLachlan, 2002), soil (Wilcke and Amelung, 2000) and atmosphere (Manchester-Neesvig and Andren, 1989, Haugen et al., 1999, Kiss et al., 2001). Seasonal precipitations also influence the distribution of concentration of PCBs because it results in transferring airborne PCBs down to surface water which affects the concentrations and normal background levels in river systems (Blemle and Larsson, 1997). The precipitation, either episodic or seasonal, causes intense surface runoff from soil into water bodies and consequently results in diluting the native

bed sediments or burying the native bed sediments with sediment brought in from the surrounding areas containing different contaminants (Barber and Writer, 1998). The factors governing the seasonal variations also depend on location, for instance in tropical areas, temperature is not a dominating factor because temperature difference between seasons is not as significant as in temperate regions; instead runoff may be the influencing factor for variation of pollutant concentrations and distribution during different seasons.

In their PCB seasonal variation study in the East Lake in China, Jong and co-workers found higher concentrations in winter than in summer (Ge et al., 2014) while Fu and Wu, in their study realised the change in PCB distribution from wet peak season to dry valley season for light PCBs in sediment of Er-Jen River estuary in Taiwan was due to precipitations (Fu and Wu, 2006). Other factors such as volatilisation and atmospheric deposition may also have a great influence on the distribution and concentrations of PCBs in the environment. You and his team reported atmospheric deposition impacted the concentrations of PCBs and the dilution of PCB concentration in summer, and increased volatilisation in warmer seasons in water and sediments of Songhua River in China (You et al., 2011).

In South Africa, few studies have reported the occurrence and distribution of PCBs in water bodies and soils. Ryan and co-workers, observed that the concentrations of HCH and DDT were decreasing in South African coastal waters but underlined that it was not clear in the case of PCBs (Ryan et al., 2012). High concentrations of PCBs were reported in urban soils and sediment of KwaZulu-Natal spring and winter (Batterman et al., 2009, Nieuwoudt et al., 2009a, Grobler et al., 1996). Literature also showed the occurrence of PCBs in serum of the Tswana population, in the North West province, who were regularly exposed to combustion of biofuels, and in maternal plasma of delivering women from the seven geographical regions of South Africa (Pieters and Focant, 2014, Röllin et al., 2009, van Dyk et al., 1987).

The Umgeni River is one of the major rivers in KwaZulu-Natal, South Africa. The level of pollution in the Umgeni River with regards to several contaminants is not known. However, some research has revealed the presence of heavy metals with non-point sources (Pegram and Bath, 1995). A recent study by Agunbiade and Moodley also

showed that the Umgeni River is contaminated by emerging organic contaminants such as different classes of pharmaceuticals (Agunbiade and Moodley, 2014); but there is little or lack of information about the levels of contamination of this river with respect to persistent organic pollutants (POPs) such as PCBs, OCPs and PAHs and their seasonal impact on the environment. This study therefore focussed on the chemical analysis of water, sediment pore water and surface sediment with the aim to evaluate the current status of contamination with 8 selected PCBs and also to determine the effects of seasonal variations on the distribution and concentrations of these pollutants.

7.2 EXPERIMENTAL

7.2.1. Study Area and Sampling Sites

This research was carried out on the Umgeni River, one of the main rivers in the province of KwaZulu-Natal, between May 2013 and May 2014. The Umgeni River catchment area is 4,418 km^2 and travels a distance of 257 km from source to the mouth (Van der Zel, 1975). It transverses rural and urban areas such as Howick and Durban towns and comprises four dams including Midmar Dam, Albert Falls Dam, Nagle Dam and Inanda Dam. Different activities observed around the river include agricultural, recreational, commercial, industrial and domestic activities.

A total of 15 sampling sites were selected that cover 12 sites along the river and 3 sites chosen at Northern Wastewater Treatment Works (NWWTW) including the influent, after treatment and effluent (point of discharge of treated water back into the river) sampling sites. The sampling sites and their geographical coordinates are listed in Table 7.1 and Figure 7.1.
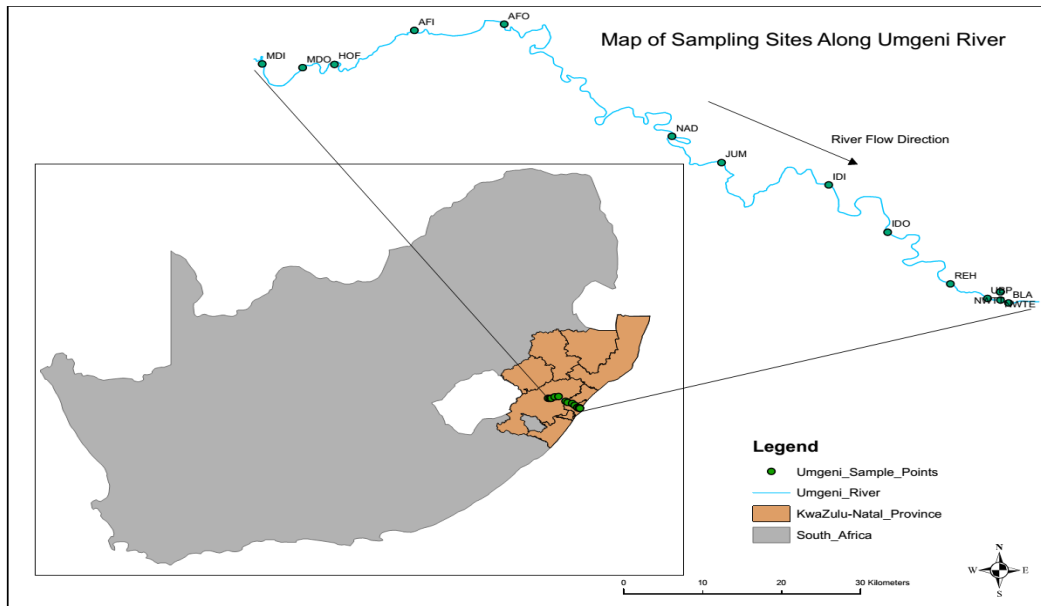
Figure 7.1 Map of sampling sites with the sample collection locations (map was generated from GPS coordinates using ArcGIS 10.2).

Table 7.1 List of sampling sites and geographical coordinates along the Umgeni River

Sampling site (code)	Coordinates		Site description
	South	East	
Midmar Dam inlet (MDI)	29° 29′ 16.05"	30° 09' 23.10"	Dam for water supply (inlet)
Midmar Dam outlet (MDO)	29° 29' 34.02"	30° 12' 09.13"	Dam for water supply (outlet)
Howick Falls (HOF)	29° 29' 18.18"	30° 14' 19.70"	Water falls
Albert Falls inlet (AFI)	29° 26' 31.94"	30° 19 47.10"	Dam for water supply
Albert Falls outlet (AFO)	29° 26' 01.81"	30° 25' 55.76"	Dam for water supply
Nagle Dam (NAD)	29° 35' 08.42"	30° 37' 23.94"	Dam for water supply
Joining point Umgeni-Msunduzi rivers (JUM)	29° 37' 16.61"	30° 40' 46.59"	River surface water
Inanda Dam inlet (IDI	29° 39' 05.20"	30° 48' 06.24"	Dam for water supply (inlet)
Inanda Dam outlet (IDO)	29° 42' 55.74"	30° 52' 07.69"	Dam for water supply (outlet)
Reservoir Hills (REH)	29° 47' 08.05"	30° 56' 25.51"	River surface water
Umgeni business park (UBP)	29° 48' 19.05"	30° 58' 58.08"	River surface water
Northern Wastewater Treatment Works influent (NWTI)	29° 47' 27.08"	30° 59' 50.01"	Domestic and industrial waste water (influent)
Northern Wastewater Treatment Works after treatment (NWTT)	29° 47' 47.02"	30° 59' 50.06"	Treated water from the plant (after water chlorination)
Northern Wastewater Treatment Works effluent (NWTE)	29° 48' 27.01"	30° 59' 51.05"	Discharge of treated water to the river
Blue Lagoon (BLA)	29° 48' 41.03"	31° 02' 12.05"	Discharge of the water into the Indian ocean

7.2.2. Physical Parameters of Sampling Sites

The levels and distribution of contaminants in a given environmental compartment may be influenced by several factors including chemical and physical characteristics of the environment. Physical parameters such as ambient temperature, water temperature and pH were measured at the site for each sampling site and during each season. Some of these parameters are shown in Table 7.2.

Table 7.2 Seasonal physical parameters at sampling sites along the Umgeni River.

site code	winter ambient T° (°C)	winter water T° (°C)	winter water pH	summer ambient T° (°C)	summer water T° (°C)	summer water pH	autumn ambient T° (°C)	autumn water T° (°C)	autumn water pH	spring ambient T° (°C)	spring water T° (°C)	spring water pH
MDI	12.3	11.6	5.54	34.1	24.2	6.39	23.3	23.3	6.39	24.0	19.0	7.80
MDO	12.3	13.2	5.69	34.6	24.1	6.83	25.6	17.8	5.94	23.0	16.0	7.33
HOF	17.8	13.8	5.99	28.8	25.0	6.99	26.1	16.6	6.10	24.0	20.0	7.66
AFI	18.6	13.5	5.78	37.3	24.7	6.60	28.2	14.1	5.94	28.0	22.0	7.65
AFO	19.2	15.4	6.04	38.6	21.8	5.46	25.5	20.4	5.95	29.0	18.0	7.58
NAD	18.4	15.4	5.00	33.6	30.6	6.10	33.3	22.8	6.07	22.0	21.0	8.87
JUM	15.6	15.7	5.56	33.1	30.1	6.36	23.9	19.8	6.70	26.0	25.0	7.60
IDI	17.2	16.6	4.98	32.1	29.4	5.16	18.8	19.2	6.62	23.0	24.0	9.55
IDO	15.1	15.9	4.53	34.6	28.5	5.24	17.9	19.7	6.07	23.0	21.0	8.37
REH	21.4	17.9	5.63	36.4	29.8	5.70	18.8	19.1	5.93	32.8	23.8	9.61
UBP	21.4	17.6	4.90	33.3	29.8	5.11	18.2	19.1	5.46	28.0	23.7	9.63
NWTI	22.8	21.9	4.70	35.6	27.7	5.40	19.2	23.2	5.30	26.4	23.2	7.47
NWTT	19.8	19.9	4.64	34.8	26.0	5.24	18.7	18.5	5.08	26.1	19.6	9.30
NWTE	21.0	19.8	4.94	34.0	29.6	5.23	19.4	19.1	5.47	26.4	22.8	10.2
BLA	21.4	20.0	5.12	29.9	25.6	5.73	22.0	17.2	6.19	22.9	23.0	9.61

7.2.3. Sample Collection

Samples were collected during the four seasons of South Africa. Autumn samples were collected from 08-10th May 2013 and winter samples on 15-17th July 2013. Spring and summer samples were collected on 25-27th September 2013 and 11-13th February 2014 respectively. Water samples were collected in 2.5 L amber glass bottles previously washed with hot water and detergent and rinsed three times with H_2SO_4 and deionized water respectively. At the sampling site, the bottles were again rinsed three times with river water before collecting the sample. The bottles were then filled to the top leaving no head space and closed with caps that were lined with aluminium foil. Bottles were kept in a coolant box containing ice and transported to the analytical research laboratory. The samples were fixed with 50% H_2SO_4 and stored at 4 °C until extraction which was carried out within five days.

Sediment was collected from the bed of the Umgeni River, using a grab sampler and stored in glass bottles washed and rinsed as specified above. The bottles were filled to the top with sediment and sealed with caps lined with aluminium foil. They were also kept in a coolant box containing ice and conveyed to the laboratory where the sediment was centrifuged to separate it from its pore water before being air dried several days before sample pre-treatment. The map of sampling location and sampling points is shown in Figure 7.1

7.2.4. Reagents and Standards

High pressure liquid chromatography (HPLC) grade solvents used wer hexane, dichloromethane (DCM) and toluene, and florisil (MgO_3Si residue analysis grade, mesh 60-100, pore size 60Å), as well as PCB standards (PCB28, PCB52, PCB77, PCB101, PCB105, PCB138, PCB153, and PCB180) were purchased from Sigma Aldrich. Anhydrous sodium sulfate (Na_2SO_4) gold line (CP) and silicon carbide boiling stones (CSi) were obtained from Associated Chemical Enterprises (ACE) and sulfuric acid (98%) was obtained from Promark Chemicals. The test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm) were obtained from DLD Scientific in South Africa.

7.2.5. Sample Treatment and Preparation

7.2.5.1. Water samples

One litre of water sample was transferred to a separating funnel and extracted using 50 mL of DCM (EPA, 1996a). The organic layer was transferred into a beaker. This process was repeated 6 times using fresh aliquots of DCM each time for the same sample of water. The six fractions of organic layers obtained were combined in a 500 mL round bottom flask and concentrated using a rotary evaporator (Heidolph Instruments GmbH & Co.kG) to roughly 5 mL. The concentrated extract was then quantitatively transferred onto a column packed with 5 g of florisil (activated at 130 °C for 12 hours) and comprising 5 g of anhydrous sodium sulfate on top, previously pre-eluted with 10 mL of hexane (EPA, 2007). The column was eluted sequentially with 5 mL aliquots of solvent system made of 94% hexane:6% DCM, 85% hexane:15% DCM, 50% hexane:50% DCM and 100% DCM respectively (EPA method 3620-C) (EPA, 2007). The four fractions obtained were combined and concentrated to about 3 mL with rotary evaporation and quantitatively transferred into a sample vial and air-dried. The cleaned and dry extract was reconstituted with exactly 2 mL of DCM and analysed by GC-MS.

7.2.5.2. Sediment pore water samples

The pore water samples were obtained by centrifugation of fresh sediment samples using a centrifuge (Du Pont instruments [R]SS-automatic centrifuge) at 10 x 1000 rpm for 15 min. The pore water was treated using the same method as that used for water above, using 100 mL of pore water and 10 mL of DCM.

7.2.5.3. Sediment samples

The sediment samples were air-dried, ground with a mortar and pestle and sieved to homogenise and increase the surface area. A 60 g portion of sieved sediment or soil was transferred into an extraction thimble which was subsequently placed into a soxhlet extractor and extracted with 300 mL of toluene for 24 hours (EPA method 3540) (EPA, 1996b). The extract was concentrated using rotary evaporation to almost 5 mL. The concentrated extract was then loaded onto a column packed with 10 g of florisil, previously pre-eluted with 20 mL of hexane. The column was then sequentially eluted with 20 mL aliquots of a solvent system of 94% hexane:6% DCM, 85% hexane:15% DCM, 50% hexane:50% DCM and 100% DCM respectively. The fractions were combined in a 500 mL round bottom flask and concentrated using a rotary evaporator to nearly 3 mL and

quantitatively transferred into a sample vial, air-dried and reconstituted using exactly 2 mL of DCM and analysed with GC-MS.

7.2.6. Instrumental Analysis

The reconstituted samples were analysed using an Agilent 6890 series gas chromatography system attached to a mass spectrometer detector (MSD5973). The GC system was equipped with a ZB-5MS column having the following parameters: 0.25 mm of internal diameter, 0.25 μm of film thickness and 30 m in length (Hewlett Packard; Houston, TX). An injection volume of 2 μL and a flowrate of 1 mL/min were used. The MS was operated using the selective ion monitoring acquisition mode (SIM). The oven temperature was programmed as follows: initial temperature was 120 °C which was increased to 290 °C at a ramping rate of 14 °C/min and held for 2 min. The total run time was 14.14 min. The front inlet temperature was 250 °C and was operated in splitless mode. The pressure was 106 kPa and the carrier gas was ultra-purified helium. The MSD line heater temperature was 280 °C.

The identification of targeted analytes was achieved by analysis of mass spectra and use of the National Institute of Standard (NIST) library together with a comparison of retention times of analytes of interest to those of PCB standards. The quantification of analytes was attained using an external calibration method based on analyte peak area.

7.3 QUALITY ASSURANCE

The recovery of each analyte in water, pore water and sediment, was obtained by target analyte spiking method. For water and pore water samples, tap water was spiked with a PCB and OCP multi-standard solution which was kept overnight before extraction, in order to allow contact and homogenisation of matrix and standards (Agunbiade and Moodley, 2014, Meharg et al., 2003). Tap water being clean do not contain any of analytes of interest and when spiked, it is sure that the obtained recovery is accurate. The spiked tap water was then extracted and the extract obtained was concentrated, cleaned, dried and analysed, using the method described above. The percentage recovery for water and pore water (%R_w) was then calculated using Equation 7.1 below (APHA et al., 1999, USEPA, 2008).

Table 7.3 Ions monitored, limits of detection (LOD) and quantification (LOQ) and percentage recoveries (%R) for the analysis of PCBs in water, pore water, sediment by GC-MS.

Analyte	PC28	PC52	PC77	PCB101	PCB105	PCB138	PCB153	PCB180
	150	150	220	254	184	145	145	162
Ions monitored (m/z)	186	220	255	291	254	290	290	324
	256	292	292	326	326	360	360	394
LOD (ng/mL) in water	0.045	0.015	0.055	0.02	0.015	0.015	0.02	0.01
LOQ (ng/mL) in water	0.15	0.045	0.19	0.06	0.055	0.045	0.06	0.04
LOD (ng/mL) in pore water	0.455	0.13	0.55	0.18	0.17	0.135	0.185	0.115
LOQ (ng/mL) in pore water	1.51	0.43	1.835	0.595	0.56	0.445	0.625	0.39
%Recovery in water and pore water	74.54 ±0.37	76.99 ±0.67	79.27 ±0.83	71.18 ±0.59	73.88 ±0.45	74.67 ±0.40	77.83 ±0.86	82.36 ±0.41
LOD (ng/g in sediment)	0.76	0.21	0.92	0.30	0.28	0.22	0.31	0.19
LOQ (ng/g in sediment)	2.52	0.71	3.06	0.99	1.12	0.75	1.03	0.66
%Recovery in sediment	69.53 ±1.75	80.74 ±2.94	73.67 ±1.22	79.77 ±2.03	78.46 ±1.27	79.39 ±1.05	82.87 ±2.50	84.39 ±1.15

The calibration standards concentrations were 0.25, 0.5, 1, 2, 4 and 8 µg/mL.

For sediment samples, real samples were used where the sample was divided into two subsamples of the same mass (60 g each). The first subsample was spiked and the second left unspiked. The percent recoveries (%R$_s$) of PCBs and OCPs were obtained by calculating the difference between the concentrations of spiked subsample (C$_s$) and unspiked subsample (C$_u$), dividing it by the known spiked concentration (C$_k$) and multiplying by 100 (equation 7.2) (Harry et al., 2008). The limit of detection and limit of quantification were also calculated as three times and ten times, respectively, signal-to-noise ratio divided by the slope, using six calibration intercepts (Shrivastava and Gupta, 2011) (Table 7.3). Procedural blanks were used throughout all steps of sample preparation and showed no detectable levels of OCPs and PCBs. The GC column was cleaned properly before analysis and a regular check for interferences was done by running solvent blanks after every fifteen injections. To monitor the variation from the initial calibration standard and ensure it remained minimal, a 0.5 µg/mL multi-standard was run after each batch of samples. All recovery and actual sample analyses were carried out at least three times in order to check the reproducibility and or precision of the method.

$$\%R_W = \frac{concentration\ found\ (\frac{ng}{mL})}{concentration\ spiked\ (\frac{ng}{mL})} * 100 \ \dots \dots \dots \dots (7.1)$$

$$\%R_s = \frac{C_s - C_u}{C_k} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots . (7.2)$$

Where: R$_w$ = recovery of analyte from water or pore water samples

R$_s$ = recovery of analyte from sediment samples

7.4 RESULTS AND DISCUSSION

Eight selected PCB congeners were analysed in this study. The discussion is focussed on the results obtained in the monitoring of the variation of the levels of these congeners in surface water, sediment pore water and surface sediment of the Umgeni River during the four South African seasons namely, winter, summer, autumn and spring.

7.4.1. Seasonal Variation of PCBs in Water

The concentration ranges and the mean PCB concentrations for each sampling station, in winter, summer, autumn and spring are presented in Table 7.4 and Figure 7.2. The general PCB concentrations in the river water ranged from 0.30–7.34 ng/mL with a mean of 1.36 ±0.39 ng/mL for winter; 0.19–2.44 ng/mL with a mean of 0.71 ±0.15 ng/mL for summer; not detectable–5.50 ng/mL with a mean of 0.66 ±0.22 ng/mL for autumn and 0.29–1.26 ng/mL with a mean of 0.56 ±0.08 ng/mL for spring. The highest mean concentrations were found in winter for all sites (Table 7.4 and Figure 7.2). This was attributed to a number of factors. The ambient and water temperatures (12.3-22.8 °C and 11.6-21.9 °C) were low during winter (Table 7.2) and the level of vaporisation of pollutants from water to air is also expected to be low due to the cooler temperatures. The PCB solubility in water was also very low because, for organic compounds, PCB solubility is directly proportional to the temperature (Delle Site, 2001). Wiegel and Wu showed that the microbial degradation of PCBs is temperature-dependent because there are optimum temperatures that have a significant effect on the growth of microorganisms and catalytic activities of enzymes for microbial reductive dechlorination of PCBs (Wiegel and Wu, 2000). For example, the optimal temperature for complete dechlorination of 2,3,4,6-tetrachlorobiphenyl was 20–27 °C (Wiegel and Wu, 2000). Therefore, the degradation of PCBs was minimal in winter when temperatures were at their lowest values. This together with the low vaporisation contributed to their high concentrations in water. Another factor which would have influenced the concentrations of PCBs in water was precipitation. The South African winter is a dry season with very little precipitation and therefore there was no dilution of the concentration of various pollutants in water; instead the concentration tends to increase as the volume of water decreased. This resulted in the river water being concentrated in contaminants since there was no rain and consequently no runoff to dilute the river water.

PCBs may also be deposited from the atmosphere through diffusive air-water exchange (Meijer et al., 2006). Unlike in winter, the summer ambient and water temperatures were high (28.8-38.6 °C and 21.8-30.6 °C) at all sites (Table 7.2 and Figure 7.1) favouring the evaporation and dissolution processes. Volatilisation was found to be a major phenomenon through which PCBs are lost by the water column in some regions during summer while deposition increased the PCB concentration during cool seasons (Hornbuckle et al., 1994). Furthermore, the volatilisation from contaminated waters during warmer seasons was

confirmed to be an important source of organic pollutants into ambient air (Rowe et al., 2007, Totten et al., 2001). The winter pH values for water were acidic (4.53-6.04). This was due to the high levels of CO_2 dissolved in water which could not easily vaporise due to low water temperatures. It was found that K_{doc}, (association constant DOC (dissolved organic carbon)-organic chemical) for PCBs, decreases with increasing pH of the medium due to increased ionization of humic acid with increased pH (Dell, 2001). Therefore, since winter pH values were lower, this phenomenon could not happen and the binding interaction between PCBs and DOC was strong, resulting in high winter concentrations. The South African summer is a wet season and high precipitation leads to diluted concentrations in the water. All these weather conditions may be possible causes of lower PCB concentrations in summer than in winter (Figure 7.2). Note that the individual PCB concentrations for all seasons (winter, summer, autumn and spring) were given in appendix D.

Table 7.4 Concentration ranges and mean of PCBs in water at each selected site along the Umgeni River.

Site code	Winter (ng/mL)			Summer (ng/mL)			Autumn (ng/mL)			Spring (ng/mL)		
	range	mean	∑PCBs	range	mean	∑PCBs	range	mean	∑PCBs	range	mean	∑PCBs
MDI	0.73-2.19	1.23	9.81	0.19-0.83	0.42	3.34	nd-1.82	0.75	5.98	0.46-0.81	0.61	11.09
MDO	0.74-2.21	1.24	9.92	0.57-1.36	0.85	6.80	0.13-3.20	0.79	6.35	0.41-0.68	0.54	15.33
HOF	0.42-2.26	0.96	7.67	0.26-2.44	0.77	6.16	nd-1.56	0.64	5.11	0.39-0.67	0.52	13.20
AFI	0.85-2.37	1.34	10.70	0.53-1.18	0.78	6.26	nd-1.32	0.45	3.58	0.37-0.61	0.49	11.57
AFO	0.71-2.53	1.24	9.96	0.33-0.84	0.55	4.38	nd-0.76	0.33	2.64	0.37-0.63	0.50	8.39
NAD	0.83-2.53	1.37	10.95	0.41-1.03	0.69	5.52	nd-1.16	0.51	4.07	0.62-0.87	0.75	11.54
JUM	1.02-2.08	1.51	12.12	0.64-1.11	0.85	6.84	nd-2.65	0.69	5.52	0.48-0.69	0.60	14.50
IDI	0.84-1.54	1.24	9.89	0.56-1.12	0.81	6.50	nd-1.57	0.48	3.82	0.45-0.66	0.57	12.18
IDO	0.98-1.77	1.39	11.15	0.63-1.25	0.90	7.18	nd-1.12	0.30	2.43	0.48-0.71	0.61	11.42
REH	0.94-2.74	1.45	11.59	0.33-1.12	0.68	5.45	nd-3.02	0.84	6.68	0.43-0.84	0.59	14.23
UBP	0.81-2.48	1.31	10.47	0.32-0.84	0.55	4.38	nd-1.65	0.62	4.94	0.37-0.64	0.51	11.00
NWTI	1.09-7.34	2.68	21.43	0.39-1.03	0.59	4.71	0.52-2.46	1.09	8.73	0.38-1.26	0.63	15.75
NWTT	0.66-1.74	1.17	9.39	0.44-0.66	0.55	4.42	0.08-5.50	0.92	7.35	0.34-0.67	0.48	13.72
NWTE	0.72-1.51	1.15	9.21	0.61-1.08	0.76	6.06	0.15-1.98	0.67	5.36	0.38-0.76	0.52	13.37
BLA	0.30-2.30	1.15	9.16	0.67-1.15	0.90	7.18	0.08-2.80	0.90	7.21	0.29-0.59	0.42	16.60
Range	0.30-7.34	0.96-2.68	7.67-21.43	0.19-2.44	0.42-0.90	3.34-7.18	nd-5.50	0.33-1.09	2.43-7.35	0.29-1.26	0.42-0.75	8.39-16.60
mean		1.36	10.90		0.71	5.68		0.66	5.32		0.56	12.93
SD		0.39	3.11		0.15	1.19		0.22	1.80		0.08	2.00

nd = not detected

The mean concentrations of PCBs at each site in winter were statistically different from mean concentrations in summer. The calculated p-value was less than 0.0001 ($p < 0.0001$). The confidence interval was 95%. According to conventional criteria, such a p-value indicates that the difference is statistically significant (GraphPad, 2014). The mean concentrations of PCBs in autumn and spring were below the mean winter concentrations. The t-test showed that the calculated p-values between mean concentrations in winter and autumn and winter and spring were less than 0.0001 ($p < 0.0001$) which confirmed that the difference was statistically significant between winter PCB levels and autumn or spring levels. The autumn and spring seasons have generally mild weather conditions. The mean concentrations in autumn were slightly higher than in spring (Table 7.4 and Figure 7.2). However, although at many sites, the autumn concentrations were slightly higher than the mean concentrations in spring, statistical results showed that the difference between the two seasons was not statistically significant ($p = 0.0867$). The concentrations of some congeners were below the limit of detection at some sampling stations. These were PCB52 at IDO, PCB105 at JUM and IDO and PCB138 at AFI, NAD, IDI and IDO. Figure 7.2 shows the trends of mean concentrations across sites in winter, summer, autumn and spring. The trends were quite similar. The concentrations at NWTI were higher especially in winter. This was expected because the industrial and residential wastewater which arrives at the inlet of the treatment plant, is still concentrated since it has not yet undergone any kind of treatment, be it physical or chemical.
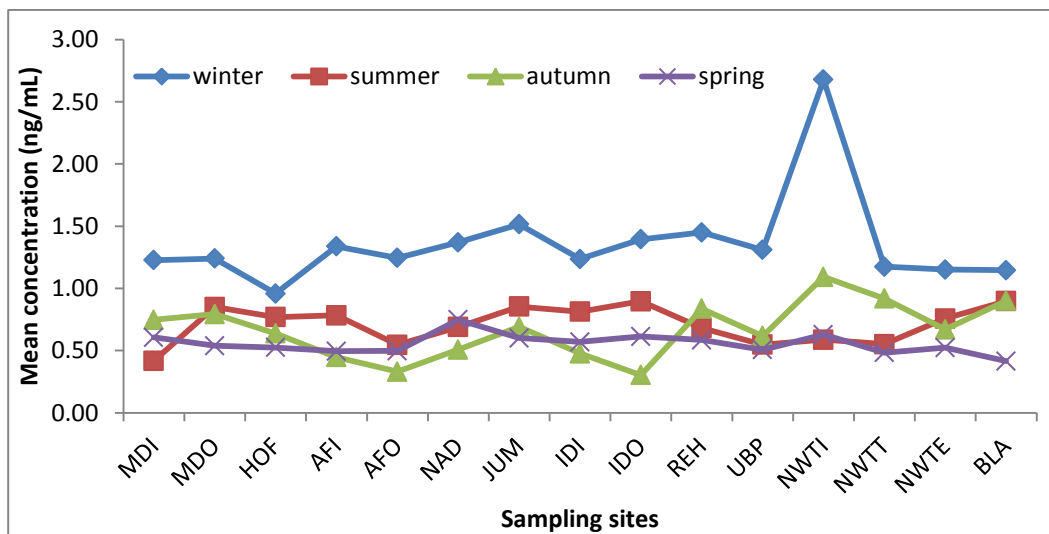
Figure 7.2 Trend of mean concentrations of PCBS in water across the sites in each season.

7.4.2. Seasonal Variations of PCBs in Sediment Pore Water and Sediment

Table 7.5 and Figure 7.3A display the ranges and averages of concentrations of different congeners of PCBs in sediment pore water at each site during winter, summer, autumn and spring. The general concentration ranges and mean concentrations in the pore water were nd-52.30 ng/mL with a mean concentration of 14.60 ±7.30 ng/mL in winter, 0.11-15.70 ng/mL with a mean of 4.72 ±1.80 ng/mL in summer, 0.03-19.52 ng/mL, with a mean of 5.53 ±2.25 ng/mL in autumn and 2.29-62.24 ng/mL with a mean of 10.73 ± 6.00 ng/mL in spring. Note that the individual PCB concentrations for all seasons (winter, summer, autumn and spring) were given in appendix D.

Table 7.5 Concentration of PCB congeners in the Umgeni River pore water in winter, summer, autumn and spring.

	Winter (ng/mL)			Summer (ng/mL)			Autumn (ng/mL)			Spring (ng/mL)		
Site code	range	mean	∑PCBs	range	mean	∑PCBs	range	mean	∑PCBs	range	mean	∑PCBs
MDI	3.42-23.17	8.50	68.02	2.84-7.04	3.98	31.85	0.03-12.83	4.44	35.51	4.34-7.19	5.58	44.64
MDO	2.44-22.47	7.09	56.73	1.32-8.06	2.46	19.65	0.35-10.88	3.50	27.99	5.07-8.70	6.50	52.02
HOF	4.71-21.91	8.05	64.43	nd-9.78	2.50	19.99	0.50-6.71	2.92	23.32	2.29-7.07	3.51	28.04
AFI	5.20-11.10	7.57	60.60	2.09-9.64	4.08	32.65	0.20-6.78	3.19	25.51	7.37-9.76	8.68	69.41
AFO	2.90-8.86	4.46	35.65	0.86-3.87	1.78	14.23	0.28-7.09	2.93	23.45	5.59-12.02	7.74	61.95
NAD	8.21-15.33	12.32	98.52	3.24-6.94	4.83	38.67	0.66-14.32	5.24	41.95	5.23-8.28	6.57	52.57
JUM	6.71-22.22	13.11	104.86	4.57-12.66	6.87	54.92	0.09-14.53	3.13	25.03	6.60-10.94	8.14	65.08
IDI	9.30-18.98	14.47	115.75	2.74-15.70	6.43	51.41	1.27-16.10	7.33	58.67	8.79-12.72	10.78	86.25
IDO	15.44-33.79	23.89	191.15	1.78-13.36	6.30	50.43	0.43-19.52	9.58	76.65	5.67-9.98	7.66	61.25
REH	8.48-48.72	19.06	152.47	3.82-12.87	7.52	60.14	0.96-16.31	7.36	58.89	6.01-16.54	9.05	72.37
UBP	10.82-52.30	23.46	187.72	2.20-11.45	5.75	46.04	1.33-17.90	7.54	60.31	5.26-44.13	15.17	121.37
NWTT	14.38-45.26	24.71	197.69	2.10-13.46	5.56	44.51	3.14-13.38	7.86	62.91	8.40-62.24	22.63	181.06
NWTE	17.73-32.10	25.47	203.78	0.93-14.93	5.00	39.97	1.88-11.92	7.31	58.45	9.50-58.87	22.31	178.46
BLA	7.36-14.35	11.07	88.57	1.48-7.11	3.06	24.51	2.10-12.44	5.12	40.96	2.83-45.93	15.92	127.39
Range	2.44-52.30	4.46-25.47	35.65-203.78	0.11-15.70	1.78-7.52	14.23-60.14	0.03-19.52	2.92-9.58	23.32-76.65	2.29-62.24	3.51-22.63	28.04-181.06
mean		14.52	116.14		4.72	37.78		5.53	44.26		10.73	85.85
SD[18]		7.41	59.28		1.80	14.40		2.25	18.03		6.00	48.02

nd = not detected

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[18] This is the standard deviation of total concentrations of analytes in pore water across different sampling sites and is high because some sites were much more polluted while others were only slightly polluted.

The highest concentration of PCBs in pore water was recorded in winter. This may be assigned to contaminant sorption on suspended solids which is then transferred to the sediment layer by settling (Bao-Feng et al., 2004); and the fact that in general the sorption coefficients of organic pollutants on natural sorbent (soil and sediment) in water systems, increases with decreases in temperature (Delle Site, 2001). These phenomena were favoured during winter due to low water temperature. Furthermore, the winter season had very little to no precipitation together with low temperature. This further added to an environment which discouraged the dissolution of the hydrophobic contaminants and as a result they preferred to settle down towards the sediment and were extracted with winter sediment pore water.

The mean concentrations of PCB congeners in sediment showed the same pattern as in pore water. Table 7.6 and Figure 7.3B present the mean concentrations in winter, summer, autumn and spring in sediment for each investigated site. The seasonal general ranges and mean concentrations were 10.16-93.74 ng/g with a mean of 24.31 ±8.92 ng/g in winter, nd-73.58 ng/g with an average of 13.50 ±8.07 ng/g in summer, nd-97.40 ng/g with an average of 19.16 ±6.93 ng/g in autumn and 4.26–89.26 ng/g with an average of 23.67 ±16.39 ng/g in spring. Again high concentrations were observed in winter. This can be explained by the low winter temperatures that encourage pollutants to accumulate in the sediment instead of dissolving in the water or volatilisation (Table 7.2). In other words, the high levels of PCBs in winter were due to fast dynamics of water-to-sediment transport (Meijer et al., 2009). The second highest levels of PCBs were recorded in spring which is characterised by mild weather conditions. The temperatures and pH values were medium. Under these mild conditions for a short period of time (September & October), we assume that the high concentrations that were observed in winter did not have an opportunity to change significantly and therefore resulted in the second highest concentrations observed. The bio-solid collected at the Northern Wastewater Treatment Works sites (NWTI, NWTT) and the sediment at NWTE in spring, showed even higher concentrations than in winter. This may be because the bio-solid at NWTI was collected, into a large skip, from water before treatment, and therefore was not exposed to weather conditions as sediment in the river. At the NWTT, macrophytic growth was observed and acted as a blanket between air and water disturbing the partitioning of pollutants between air and water to achieve equilibrium and therefore pollutants were less exposed to air and their concentrations were not much

influenced by climatic factors. At the NWTE, the treated water carrying pollutants from the wastewater treatment plant arrives at this point through an underground pipeline and was not really influenced by weather conditions and as a result, concentrations of pollutants did not depend on climatic factors but on the concentrations in wastewater received at the inlet.

The t-test results showed p-values that indicated there was no statistical significant difference between mean PCB concentrations in winter and spring sediment concentrations ($p = 0.8872$) and no significant change between PCB levels in winter and spring pore water ($p = 0.1000$) (GraphPad, 2014).

Table 7.6 Concentration of PCB congeners in the Umgeni River sediment for winter, summer, autumn and spring.

Site code	Winter (ng/g) range	mean	∑PCBs	Summer (ng/g) range	mean	∑PCBs	Autumn (ng/g) range	mean	∑PCBs	Spring (ng/g) range	mean	∑PCBs
MDI	15.04-36.69	19.60	156.83	6.57-29.41	13.05	104.44	4.64-52.44	18.72	149.77	10.67-33.46	20.48	163.83
MDO	15.73-35.64	23.08	184.66	5.42-30.53	11.07	88.60	7.51-55.33	19.05	152.41	13.84-39.56	18.79	150.34
HOF	1875-55.78	28.88	231.07	3.16-37.92	11.27	90.13	7.31-50.77	17.26	138.06	15.50-45.07	21.94	175.55
AFI	13.46-30.75	19.13	153.05	6.72-59.21	18.14	145.14	6.07-72.62	24.68	197.46	7.24-42.09	17.16	137.32
AFO	14.38-43.73	22.83	182.64	4.99-26.56	15.37	122.98	nd-42.18	13.26	106.09	8.09-43.23	15.09	120.70
NAD	13.70-34.66	19.28	154.20	2.07-13.96	5.85	46.83	2.78-42.79	12.91	103.27	8.87-24.99	11.83	94.61
JUM	15.63-43.15	26.43	211.42	1.30-13.24	5.60	44.79	2.25-45.95	15.02	120.17	8.71-16.50	12.17	97.33
IDI	22.12-25.97	24.01	192.09	0.74-13.68	5.04	40.32	1.53-44.13	13.56	108.45	12.57-21.79	15.86	126.91
IDO	10.16-19.46	12.96	103.65	3.45-19.34	8.44	67.52	1.92-41.05	14.80	118.40	5.12-13.59	7.71	61.72
REH	16.11-21.48	19.40	155.17	2.42-15.69	7.35	58.83	2.01-42.88	13.03	104.28	13.03-23.13	18.19	145.54
UBP	22.21-28.48	25.54	204.28	1.28-18.00	8.03	64.27	nd-49.17	16.35	130.79	9.55-45.17	18.06	144.49
NWTI	18.48-31.86	24.42	195.35	nd-73.58	26.64	213.10	9.72-72.07	23.82	190.54	18.03-65.32	33.92	271.40
NWTT	26.67-93.74	53.48	427.83	13.73-71.95	32.28	258.22	3.34-90.25	25.34	202.74	49.08-84.46	65.91	527.29
NWTE	18.05-29.35	22.70	181.61	11.68-48.58	21.50	172.03	1.19-63.04	20.72	165.79	36.80-89.26	56.29	450.35
BLA	14.25-36.17	22.95	183.58	2.89-35.62	12.84	102.70	7.23-97.40	38.86	310.89	4.26-77.03	21.67	173.38
Range	10.16-93.74	12.69-53.48	103.65-427.83	nd-73.58	5.04-32.28	40.32-258.22	nd-97.40	12.91-38.86	103.27-310.89	4.26-89.26	7.71-65.91	61.72-527.29
Mean		24.31	194.50		13.50	107.99		19.16	153.27		23.67	189.38
SD[19]		8.92	71.34		8.07	64.55		6.93	55.41		16.39	131.11

nd = not detected

[19] This is the standard deviation of total concentrations of analytes in sediment at different sampling sites and is high because some sites are much more polluted while others are only slightly polluted.

The lowest concentrations in sediment pore water and sediment were detected in summer. This was attributed to the climatic factors in summer that were opposite to those in winter.

The water and ambient temperatures were high (Table 7.2 and Figure 7.1) which resulted in maximum dissolution and vaporisation. A study by Meijer and co-workers found that there is strong temperature dependence for less volatile PCBs in sediment (Meijer et al., 2009).

For the more volatile PCBs, their fluxes between water and air was due to diffusive air-water exchange (Meijer et al., 2006). The movement effected by contaminants in summer, was in the opposite direction compared to that of winter. Instead of settling down from water into the sediment, they tend to dissolve in water from the sediment and continue to make their way into the atmosphere by evaporation.

The t-test results gave a p-value confirming that the difference between the PCB winter and summer levels was statistically significant ($p = 0.0016$) in sediment, while for pore water, the difference between PCB levels of the two seasons was very significant ($p < 0.0001$) (GraphPad, 2014). The levels of PCBs in autumn were the third highest after winter and spring levels. The South African autumn is a short season that starts in mid-March to May. It is characterised by average rainfall, warm but not hot and gets cooler as time progresses. Since the temperatures were not high, the water-air pollutant fluxes were minimal and were dominated by the accumulation of pollutants in the river due to runoff from industrial areas.
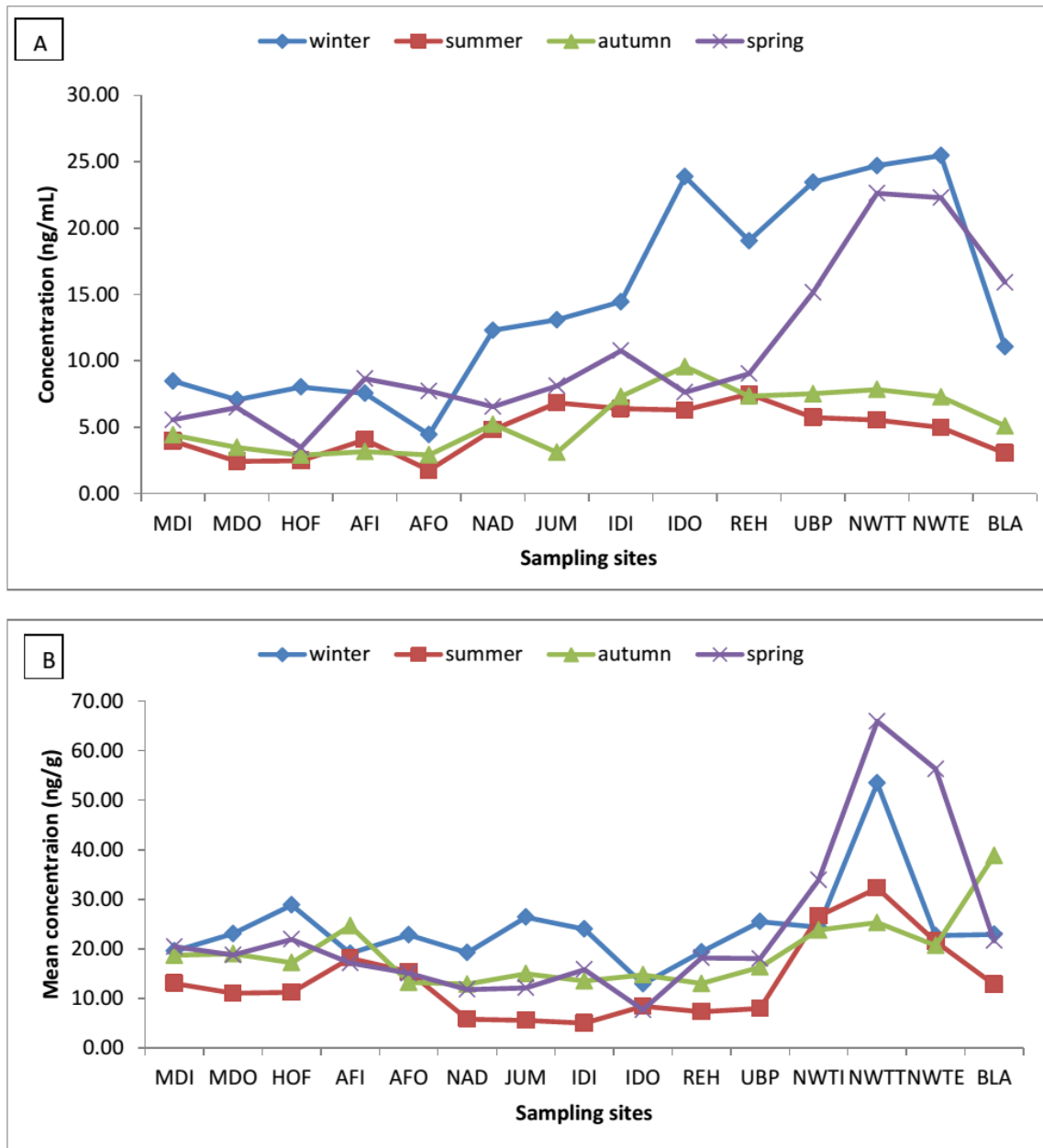
Figure 7.3 Seasonal trend of PCB levels across sites A: in pore water B: in sediment.

The t-test p-value showed a significant difference between the concentrations of PCBs in autumn and spring for pore water (p = 0.0054) but for sediment samples the difference was not statistically significant (p = 0.3343). The trend of seasonal mean concentrations of PCBs in water and pore water from the source to the mouth of the river is similar (Figure 7.3). This suggests that the effects of the climatic factors and environmental physical chemical parameters on the PCBs in sediment pore water and surface sediment may be considered as the same. In other words the the above-mentionned factors have similar influence on water and pore water pollutants in terms of increase or decreases of their levels. At IDO, the

concentrations are higher in pore water than sediment, especially in winter which is attributed to a low flow rate at this dam outlet. It was observed in the dry winter season, the water level was low and there was less water exiting the dam to carry the PCBs away thus resulting in them accumulating. Any organic matter from upstream ends up in the dam and this site consequently contain much of organic carbon. (DOC) which establishes a strong pollutant (PCB)-DOC association (high K_{doc}) that enhances PCB solubility in pore water. This has been confirmed by research that has shown pollutant solubility increases linearly with DOC concentration (Dell, 2001).

7.5 CONCLUSION

An investigation of seasonal variations of polychlorinated biphenyls in water, pore water and sediment of Umgeni River was undertaken. The results showed significant variation between seasons. The seasonal variation of PCB levels have been discussed taking into account the physical-chemical parameters observed during seasonal sampling such as temperature, precipitation, pH and organic matter which induced phenomena such as volatilisation, atmospheric deposition, vaporisation, run-off and partitioning, The highest levels were recorded in winter due to the low water temperature which discourages solubility, the low ambient temperature which reduces vaporisation and the low precipitation which reduces runoff and the dilution effect. The lowest concentrations were generally observed in summer due to the high water temperatures which encouraged solubility, the high ambient temperatures which increased volatilisation and increased precipitation which led to dilution of the pollutants in the river systems. Further studies are needed in order to analyse the occurrence and seasonal variation of these contaminants in aquatic life in the Umgeni River catchment. These are the first results reported on the seasonal variation of PCBs in the Umgeni River and provide much needed knowledge on the levels of PCBs that animals and people, who consume its untreated water, are exposed to during the year.

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CHAPTER EIGHT
MANUSCRIPT FIVE

SEASONAL VARIATIONS OF CHLORINATED PESTICIDES IN SURFACE WATER, SEDIMENT PORE WATER AND SURFACE SEDIMENT OF UMGENI RIVER, KWAZULU-NATAL, SOUTH AFRICA

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ABSTRACT

This study focussed on monitoring and assessment of seasonal distribution and variations of twelve organochlorine pesticides (OCPs) for a period of one year. Liquid-liquid extraction was used for liquid samples and soxhlet for sediment samples. Analysis was performed on gas chromatography-mass spectrometry. The results obtained from unfiltered water analysis showed higher concentrations in winter (not detectable (nd) levels-3.48 ng/mL, mean: 1.19 ±0.25 ng/mL) than in summer (nd-3.02 ng/mL, mean: 0.90 ±0.36 ng/mL), autumn (nd-4.76 ng/mL, mean: 0.76 ±0.32 ng/mL) and the lowest levels in spring (nd-4.86 ng/mL, mean: 0.67 ±0.16 ng/mL). The same trend was also observed in unfiltered pore water where winter concentrations were the highest (0.76-34.92 ng/mL, mean: 11.01 ±5.04 ng/g) compared to the lowest levels in summer (nd-22.42 ng/mL, mean: 5.16 ±1.38 ng/mL), autumn (nd-48.27 ng/mL, mean: 9.68 ±5.34 ng/g) and spring (nd-26.59 ng/mL, mean 6.39 ±3.20 ng/mL). For

sediment samples winter also showed higher concentrations (2.29-93.02 ng/g, mean: 30.87 ±7.38 ng/g, dry weight) as compared to the lower concentrations in summer (nd-146.82 ng/g, mean: 18.41 ±11.20 ng/g). There was no substantial difference between autumn (nd-186.55 ng/g, mean: 31.78 ±8.85 ng/g) and spring (nd-276.39 ng/g, mean: 31.50 ±14.83 ng/g) concentrations. However there was a statistically significant difference between summer levels and other seasons ($p < 0.05$) for all matrices and all seasons.

Key words: Umgeni River, OCPs, seasonal variation, surface water, pore water, sediment

8.1 INTRODUCTION

Organochlorine pesticides (OCPs) are a group of ubiquitous persistent organic pollutants (POPs) that are well-known as environmental (Assem et al., 2013, Cafer et al., 2012, Miglioranza et al., 2003a). They were extensively used worldwide in agriculture and public health sectors before the 1970s (Wong et al., 2005, Bolognesi and Merlo, 2013, Thomas et al., 2008). The total pesticide global market is estimated to be 31 billion US dollars of which Africa accounts only 2-4% (Agrow, 2006) without including donations from developed countries, which is a substantial source of pesticides for agriculture in Africa (Fleischer and Waibel, 2003, Tobin, 1996). In sub-Saharan Africa, South Africa is the leading user of pesticides (Dalvie et al., 2009). Indoor spraying, runoff and leaching allows pesticides to reach non-target areas (Dalvie et al., 2003) and consequently numerous studies reported the occurrence of these pesticides in various water ways (Dabrowski et al., 2002a, London et al., 2000b, Villaverdea et al., 2008). The exposure to pesticides such as OCPs causes numerous health effects such as carcinogenesis, genotoxicity, immune impacts, chronic neurotoxicity, disruption of endocrine system and mutagenicity (Bolognesi and Merlo, 2013, Hallenbeck and Cunningham-Burns, 2011).

There are many poor and rural South Africans who make direct use of surface water from rivers and lakes or ground water, due to lack of treated water (STATSSA, 2012). As a result these individuals may have direct exposure to these pesticides and long term use of contaminated water may result in health disorders. The OCPs investigated in this project were banned in most countries due to their toxicity (Mrema et al., 2013, Appenzeller and Tsatsakis, 2012, Rhouma et al., 2001, Bornman et al., 2010, Campbell et al., 1983, Gourounti et al.,

2008), but due to their persistence their residues are still detected in all environmental compartments such as air (Cindoruk, 2011, Sultana et al., 2014b), water (Lin et al., 2012, Yuan et al., 2013), soil (Gai et al., 2014, Xing et al., 2010) and biota (Zhou et al., 2008, Santhi et al., 2012) many years after their banning. In addition, some pesticides, such as DDT, are currently still used in South Africa today for malaria control (Bouwman et al., 1991b, Eskenazi et al., 2014, Dalvie et al., 2004d, Channa et al., 2012, Dalvie et al., 2004a, Naudé and Rohwer, 2012b).

The seasonal variations of POPs depend largely on the type of climate of a region. Most studies on POP temporal trends have been conducted in Northern hemisphere countries which are characterised by moderate climatic conditions unlike South Africa which experiences high temperatures, little precipitation during winter and long summers (Quinn et al., 2009). Therefore, the comparison and use of Northern hemisphere seasonal data is not suitable for explaining seasonal data from Southern hemisphere countries such as South Africa. However, the fate of toxic pollutants, such as organochlorine pesticides, in the environment is governed by various chemical, physical and biological processes (Callahan et al., 1979, Plimmer and Klingebiel, 1976). Limited studies on seasonal distribution of POPs in the South African environment, such as in water of the Hartbeespoort Dam, has found that generally the concentrations of OCPs were higher in winter than in other seasons and suggested it was due to seasonality of their atmospheric deposition (Amdany et al., 2014).

The occurrence of OCPs and especially their variations due to seasonal climatic factors in KwaZulu-Natal water ways in particular, and in South Africa in general, is not well known. Therefore, the present study is aimed at investigating the occurrence and evaluation of seasonal distribution of 12 organochlorine pesticides in the water, sediment pore water and sediment in the Umgeni River in KwaZulu-Natal, South Africa. The Umgeni River water (unfiltered) is used directly by people for several activities and is the reason unfiltered surface and sediment pore water were analysed in order to evaluate the total concentration of pollutants (freely dissolved + dissolved organic carbon + suspended matter) to which they are exposed.

8.2 MATERIALS AND METHODS

8.2.1. Study Area and Physical Chemical Parameters

This study was conducted between February 2013 and February 2014 and focused on the analysis of OCPs in different matrices in the Umgeni River which is one of the major rivers in the province of KwaZulu-Natal in South Africa. The Umgeni River catchment (area of 4387 km^2) is home to 3.5 million people and is one of the most developed catchments producing nearly 20% of South Africa's gross national product (Shand, 1996). It is a source of potable water to more than two million people (Howard et al., 1995). The river houses four dams namely Midmar Dam, Albert Falls Dam, Nagle Dam, and Inanda Dam, all used for water supplies. It empties into the Indian Ocean in Durban. A brief description of the sampling sites investigated and the geographical coordinates are tabulated in Table 8.1. Figure 8.1 shows the different locations for the sampling sites.

The physical and chemical parameters of a particular area influence the occurrence and distribution of environmental pollutants. These were recorded at the site at each sampling station during sampling trips and included ambient temperature, water temperature and water pH. Table 8.2 shows the values of the environmental physical and chemical parameters recorded at each sampling station of the Umgeni River.

8.2.2. Sample Collection

Four sampling campaigns corresponding to the four South African seasons were organised for sample collection. Autumn samples were collected from 08-10th May 2013 and winter samples from 15-17th July 2013. Spring and summer samples were collected on 25-27th September 2013 and 11-13th February 2014 respectively.

Figure 8.1 Map of sampling sites with the sample collection locations identified as red dots (maps were generated from GPS coordinates using an online tool—GPS visualizer).

Table 8.1 List of Umgeni River sampling sites and GPS coordinates in the downstream direction.

Sampling site (code)	Coordinates		Description of site
	South	East	
Midmar Dam inlet (MDI)	29° 29′16.05″	30° 09′23.10″	Dam for water supply (inlet)
Midmar Dam outlet (MDO)	29° 29'34.02″	30° 12'09.13″	Dam for water supply (outlet)
Howick Falls (HOF)	29° 29'18.18″	30° 14'19.70″	Water fall
Albert Falls inlet (AFI)	29° 26'31.94″	30° 19 47.10″	Dam for water supply
Albert Falls outlet (AFO)	29° 26'01.81″	30° 25'55.76″	Dam for water supply
Nagle Dam (NAD)	29° 35'08.42″	30° 37'23.94″	Dam for water supply
Joining point Umgeni-Msunduzi rivers (JUM)	29° 37'16.61″	30° 40'46.59″	River surface water
Inanda Dam inlet (IDI	29° 39'05.20″	30° 48'06.24″	Dam for water supply (inlet)
Inanda Dam outlet (IDO)	29° 42'55.74″	30° 52'07.69″	Dam for water supply (outlet)
Reservoir Hills (REH)	29° 47'08.05″	30° 56'25.51″	River surface water
Umgeni Business park (UBP)	29° 48'19.05″	30° 58'58.08″	River surface water
Northern wastewater treatment works influent (NWTI)	29° 47'47.08″	30° 59′50.01″	Domestic and industrial waste water
Northern wastewater treatment works after treatment	29° 47'47.02″	30° 59′50.06″	Treated water from the plant
Northern wastewater treatment works effluent (NWTE)	29° 48′27.01″	30° 59′51.05″	Discharge of treated water to the river
Blue Lagoon (BLA)	29° 48'41.03″	31° 02'12.05″	Discharge of the water into the Indian

Table 8.2 Seasonal physical and chemical parameters of the Umgeni River.

site code	winter			summer			autumn			spring		
	ambient T° (°C)	water T° (°C)	water pH	ambient T° (°C)	water T° (°C)	water pH	ambient T° (°C)	water T°(°C)	water pH	ambient T° (°C)	water T°(°C)	water pH
MDI	12.3	11.6	5.54	34.1	24.2	6.39	23.3	23.3	6.39	24.0	19.0	7.80
MDO	12.3	13.2	5.69	34.6	24.1	6.83	25.6	17.8	5.94	23.0	16.0	7.33
HOF	17.8	13.8	5.99	28.8	25.0	6.99	26.1	16.6	6.1	24.0	20.0	7.66
AFI	18.6	13.5	5.78	37.3	24.7	6.6	28.2	14.1	5.94	28.0	22.0	7.65
AFO	19.2	15.4	6.04	38.6	21.8	5.46	25.5	20.4	5.95	29.0	18.0	7.58
NAD	18.4	15.4	5.00	33.6	30.60	6.10	33.3	22.8	6.07	22.0	21.0	8.87
JUM	15.6	15.7	5.56	33.1	30.13	6.36	23.9	19.8	6.7	26.0	25.0	7.60
IDI	17.2	16.6	4.98	32.1	29.4	5.16	18.8	19.2	6.62	23.0	24.0	9.55
IDO	15.1	15.9	4.53	34.6	28.5	5.24	17.9	19.7	6.07	23.0	21.0	8.37
REH	21.4	17.9	5.63	36.4	29.8	5.70	18.8	19.1	5.93	32.8	23.8	9.61
UBP	21.4	17.6	4.90	33.3	29.8	5.11	18.2	19.1	5.46	28.0	23.7	9.63
NWTI	22.8	21.9	4.70	35.6	27.7	5.4	19.2	23.2	5.3	26.4	23.2	7.47
NWTT	19.8	19.9	4.64	34.8	26.0	5.24	18.7	18.5	5.08	26.1	19.6	9.30
NWTE	21.0	19.8	4.94	34.0	29.6	5.23	19.4	19.1	5.47	26.4	22.8	10.21
BLA	21.4	20.0	5.12	29.9	25.6	5.73	22.0	17.2	6.19	22.9	23.0	9.61

Water samples were collected in 2.5 L amber Winchester glass bottles previously washed with hot water and detergent and rinsed three times with H_2SO_4 and deionized water respectively. The bottles were again rinsed three times with river water to be sampled, before water collection at each sampling site. The bottles were then filled to the top leaving no head space and closed with caps lined with aluminium foil. The bottles were kept in a coolant box containing ice and transported to the analytical research laboratory. They were fixed with 50% H_2SO_4 and stored at 4 °C until extraction, which followed within five days. Surface sediment was collected from the river bed of the Umgeni River, using a grab sampler and stainless steel spade respectively. The sediment samples were stored in glass bottles washed and rinsed as specified above. The bottles were filled to the top with sediment and closed with caps lined with aluminium foil. They were also kept in a coolant box containing ice and conveyed to the laboratory. Soil samples were immediately transferred onto aluminium foil and air-dried for several days before treatment. The sediment samples were centrifuged to separate pore water, before being dried and treated.

8.2.3. Reagent, Standards and Apparatus

High pressure liquid chromatography (HPLC) grade solvents such as hexane, dichloromethane (DCM) and toluene, and florisil (MgO_3Si residue analysis grade, mesh 60-100, pore size 60Å), as well as OCP standards (HCB, HCH, heptachlor, aldrin, *o,p*-DDE, *p,p'*-DDE, *o,p'*-DDD, dieldrin, endrin, *p,p'*-DDD, *o,p'*-DDT and mirex) were purchased from Sigma Aldrich, South Africa. Anhydrous sodium sulfate (Na_2SO_4) gold line (CP) and silicon carbide boiling stones (CSi) were obtained from Associated Chemical Enterprises (ACE, South Africa) and sulfuric acid (98%) was obtained from Promark Chemicals. The test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm) were obtained from DLD Scientific, South Africa. A mortar and pestle and separatory funnel were also used.

8.2.4. Sample Treatment

A 1 L portion of water sample was accurately transferred to a separatory funnel and extracted using 50 mL of DCM. The mixture was left to stand for 5 min to allow the two phases to separate. The organic phase was then separated from the aqueous phase and transferred to a round bottomed flask. This process was repeated six times using fresh aliquots of DCM each

time for the same water sample, to increase recovery of pollutants (EPA, 1996a). The six fractions obtained were combined and the extract concentrated using a rotavap (Heidolph Instruments GmbH & Co.kG) at 45 °C to approximately 5 mL. The concentrated extract was quantitatively transferred onto a hexane conditioned florisil column (activated at 130 °C for 12 hours) containing anhydrous Na_2SO_4 (5 g) on top for clean-up. It was eluted with an increasing polarity solvent system of hexane:DCM (5 mL) (94:6), (85:15), (50:50) and 100% DCM (modified EPA method 3620-C) (EPA, 2007) in order to allow elution of different OCPs with various polarity indexes.

The four fractions obtained were combined and concentrated with a rotary evaporator to about 5 mL and transferred to a vial. The extract was air evaporated to dryness and was reconstituted using exactly 2.00 mL of DCM and analysed using GC-MS. The pore water obtained after centrifugation of sediment using 10 x 1000 rpm (Du Pont instruments[R] SS-automatic centrifuge) (Ankley and Schubauer-Berigan, 1994, Zhang et al., 2003) was treated as per surface water using 100 mL sample aliquots.

The remaining sediment as well as soil samples were transferred onto aluminium foil and air-dried. The dried sediment and soil samples were ground using a mortar and pestle and sieved using test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm). A portion of 60 g of dried sediment was transferred into an extraction thimble and placed in a soxhlet extractor and extracted for 24 hours using 300 mL of toluene (modified EPA method) (EPA, 1996b). The extract was concentrated with a rotavap to about 5 mL. It was loaded onto a florisil column and cleaned-up following the same procedure as the water extract mentioned above using 20 mL of a solvent system of hexane and DCM (EPA, 2007). The sediment and soil extracts were concentrated to about 5 mL which were subsequently evaporated to dryness and reconstituted in exactly 2.00 mL of DCM and analysed with GC-MS.

8.2.5. Instrumental Analysis

Samples from all matrices were analysed in triplicate using an Agilent 6890 series gas chromatography system attached to a mass spectrometer detector (MSD5973). The GC system was equipped with a ZB-5MS capillary column, 0.25 mm internal diameter, 0.25 μm film thickness and 30 m length (Hewlett Packard; Houston, TX). The MS was operated using

the selective ion monitoring (SIM) acquisition mode. The carrier gas was ultrapure helium. A 2 μL sample was injected in splitless mode onto the GC-MS column with injector and detector temperatures set at 250 and 280 ^{o}C respectively. The oven temperature for analysis of OCPs was programmed as follows: the initial temperature was 120 ^{o}C increased to 290 ^{o}C with a ramping rate of 14 ^{o}C/min and held for 2 min. The MS source was operated at 250 ^{o}C and Quad at 200 ^{o}C. The electro energy was 70 eV.

Targeted OCPs were quantified based on peak areas and by using an external calibration technique with the following six calibration standards: 0.25; 0.5; 1; 2; 4 and 8 μg/mL. The identification of OCPs of interest was achieved by analysis of mass spectra, comparison of the analyte mass spectrum to that obtained in the National Institute of Standard and Technology (NIST) library and comparison of retention times of analytes with those of reference OCP standards.

8.3 QUALITY CONTROL

Quality assurance and control parameters were measured. The extraction recovery as well as limits of detection (LOD) and limits of quantification (LOQ) were calculated (Table 8.3). The recoveries of OCPs in water and pore water were obtained by spiking tap water with standards (Agunbiade and Moodley, 2014, Meharg et al., 2003) and extraction using the method described in section 8.2.4. The recoveries were calculated using Equation 8.1 below (APHA et al., 1999). For sediment and soil samples, real samples were used where one portion (60 g) of the sample was spiked and the other subsample of the same sample left unspiked and both extracted, cleaned and analysed using the methods described in sections 8.2.4 and 8.2.5. The recoveries were obtained using Equation 8.2 below (Harry et al., 2008). Procedural blanks were included in all phases from extraction to analysis and no OCPs of interest were detected in the blank samples. The solvent blanks were periodically run through the column of the GC-MS to determine the presence of interferences that may be in the GC system. The variation of initial calibration must be kept to a minimum and this was confirmed by running a calibration standard of 0.5 μg/mL after each batch of samples. The identification of OCPs of interest was performed by analysis of MS spectra, comparison of retention times with those of reference standards and the NIST library within the instrument. In addition, the

base peak and two other confirming ions were used in selected ion monitoring (SIM) mode. All data were processed using Microsoft excel 2010.

$$\text{Recovery } (\%) = \frac{\text{Concentration found (ng/mL)}}{\text{Concentration spiked (ng/mL)}} * 100 \dots\dots\dots\dots\dots (8.1)$$

$$\text{Recovery } (\%) = \frac{(\text{conc. for spiked sample} - \text{conc. for unspiked sample})(\text{ng/mL})}{\text{known value for the spike in the sample (ng/mL)}} * 100 \dots (8.2)$$

8.4 RESULTS AND DISCUSSION

Twelve selected OCPs were analysed in this study. This discussion focusses on the results obtained in the monitoring of the variations and distribution of these pesticides in surface water, sediment pore water and surface sediment from the Umgeni River during the four South African seasons namely, winter, summer, autumn and spring.

8.4.1. Seasonal Variations of OCPs in Surface Water

The concentrations of OCPs in extracts obtained from sixty water samples collected during the four seasons (15 samples each season) were calculated using the concentration of the analyte in the extract and the volume of water extracted (USEPA, 2008). The individual concentrations of OCPs in each season were mentioned in appendix E)

Table 8.3 Ions monitored, LOD, LOQ and percent recoveries (%R) in the analysis of OCPs in water, pore water and sediment of Umgeni River.

Analyte	HCB	HCH	heptachlor	aldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p*-DDD/ dieldrin[20]	endrin	*p,p'*-DDD/ o,p-DDT[21]	mirex
	284	219	374	327	318	318	320/380	317	320/235	402
Ions monitored (*m/z*)	249	183	272	293	284	281	235/263	263	235/199	272
	142	147	237	263	246	246	165/147	207	165/165	237
LOD (ng/mL) in water	0.025	0.06	0.03	0.045	0.06	0.07	0.035	0.06	0.075	0.07
LOQ (ng/mL) in water	0.58	0.10	0.10	0.155	0.19	0.125	0.205	0.205	0.245	0.23
LOD (ng/mL) in pore water	0.24	0.295	0.295	0.465	0.06	0.37	0.06	0.615	0.74	0.69
LOQ (ng/mL) in pore water	0.795	0.35	0.975	1.55	0.19	1.24	0.205	2.05	2.47	0.235
%R in water and pore water	51.90±0.47[22]	64.38±0.28	32.66±0.67[23]	69.66±0.36	84.36±1.39	87.42±0.68	103.43±0.97	61.08±0.87	75.27±0.19	65.31±0.33
LOD (ng/g) in sediment	0.50	0.50	0.50	0.78	0.96	0.62	1.04	1.02	1.23	1.15
LOQ (ng/g) in sediment	1.66	1.66	1.62	2.59	3.20	2.07	3.45	3.41	4.11	3.83
%R in sediment	79.14±3.64	98.22±3.81	99.15±10.0.3	116.97±5.36	95.60±12.15	52.73±1.35[24]	90.02±3.59	94.19±14.81	96.68±2.71	109.28±6.19

[20] *o,p*-DDD and dieldrin could not be separated on the GC and were reported as a single peak. The exact EPA method and changes like temperature program, injection volume did not separate them in the GC column

[21] *p,p*-DDD and *o,p*-DDT could not be separated on the GC and were reported as a single peak . Also the above mentioned changes did not separate the in the GC column

[22]HCB stock solution was prepared in hexane and it was found that in hexane, it easily undergoes reductive dechlorination with light of wavelength more than 260 nm and forms pentachlorobenzene and tetrachlorobenzene (Plimmer and Klingebiel, 1976). These compounds were observed in the gas chromatograms and may be the reason for its low recovery.

[23]Heptachlor was in contact with tap water for some days to allow it to partition with the matrix before extraction. It may have degraded into heptachlor epoxide by oxidation, photolysis and can also volatilise in air (Callahan et al, 1979) which was observed in some of the chromatograms, and consequently this may have led to its low recovery during extraction.

[24]The *p,p'*-DDE standard chromatogram showed the presence of DDMU which suggested that some of *p,p'*-DDE may have degraded into this compound which is its break down product (Thomas et al., 2008) and consequently contributed to its low recovery.

The concentration ranges, the mean and total concentrations for each sampling site in winter, summer, autumn and spring seasons were tabulated in Table 8.4 and shown in Figure 8.2 A. The concentrations ranged from non-detectable (nd) level-3.48 ng/mL with a mean of 1.19 ±0.25 ng/mL in winter, nd-3.02 ng/mL with a mean of 0.90 ±0.36 ng/mL in summer, nd-4.76 ng/mL with a mean of 0.76 ±0.32 ng/mL in autumn, nd-4.86 ng/mL with a mean of 0.67 ±0.16 ng/mL in spring. The highest mean concentration (1.19 ±0.25 ng/mL) and mean total concentration (19.92 ±2.50 ng/mL) (Table 8.4) were found in winter. This could be a result of several climatic factors. Using the Clausius–Clapeyron equation to examine gas-phase partial pressure and temperature, Gioia and his team found that all OCPs were dependent on temperature and concluded that the gas-phase of OCPs increased with an increase in temperature, which has an effect on environmental processes such as air-water exchange and volatilisation (Gioia et al., 2005). The ambient and water temperature values in winter were the lowest (12.3–22.8 °C and 11.6-21.9 °C respectively) (Table 8.2) which may result in cold-trapping and therefore atmospheric deposition of OCPs in the water column (Odabasi et al., 2008, Lin et al., 2012, Siddik and Yucel, 2014b, Lam et al., 2004). Note, that the pesticides investigated in this study were also found in Durban ambient air (Batterman, 2008). On the contrary in summer, which showed a lower mean concentration (0.90 ±0.36 ng/mL) and mean total concentration (9.01 ±3.65 ng/mL), the ambient and water temperatures were high (28.8-38.6 °C and 24.2–30.6 °C) (Table 8.2) which may suggest volatilisation of OCPs from the water column to air (Xinghua et al., 2008, Mohammed et al., 2014, Nelson et al., 1998). The calculated t-test results showed a p-value of 0.0163 (p = 0.0163). By conventional criteria, this value shows a statistically significant difference between winter and summer mean concentrations (GraphPad, 2014). The concentrations at all sites were the highest in winter except at MDO and JUM (Figures 8.2 A and B) where the summer concentrations were slightly higher but the difference was not significant and cannot be considered as seasonal. Another factor was precipitation. The South African summer is a rainy season and much water from runoff makes its way into the river, and hence, the pollutant concentrations were reduced by dilution. On the contrary during winter, a cold a dry season, the volume of water diminished which led to an increase in the concentrations of pollutants. The spring season showed the lowest concentration.

Table 8.4 Seasonal concentrations of OCPs (ng/mL) in Umgeni River surface water.

Site code	winter (ng/mL) range	mean	∑OCPs	summer (ng/mL) range	mean	∑OCPs	autumn (ng/mL) range	mean	∑OCPs	spring (ng/mL) range	mean	∑OCPs
MDI	0.41-1.64	1.10	10.99	nd-0.99	0.41	4.10	nd-2.22	0.54	5.42	nd-1.40	0.68	6.76
MDO	0.47-1.61	1.08	10.80	nd-2.22	1.28	12.81	nd-2.08	0.62	6.15	nd-1.29	0.54	5.38
HOF	0.36-1.42	1.00	9.97	nd-2.07	0.56	5.58	nd-1.81	0.56	5.55	nd-1.44	0.63	6.26
AFI	0.43-1.64	1.09	10.87	nd-0.73	0.64	6.42	nd-2.78	0.58	5.79	nd-1.38	0.55	5.53
AFO	0.34-1.43	0.95	9.47	nd-1.53	0.54	5.44	nd-1.90	0.48	4.75	nd-1.34	0.55	5.47
NAD	0.35-1.47	0.97	9.73	nd-1.75	0.77	7.70	nd-2.45	0.53	5.27	nd-1.39	0.55	5.47
JUM	0.53-1.84	1.27	12.69	0.70-2.27	1.38	13.77	nd-2.38	0.53	5.35	nd-1.59	0.65	6.53
IDI	0.40-1.55	1.03	10.31	nd-2.62	0.66	6.61	nd-2.75	0.63	6.34	nd-1.47	0.57	5.69
IDO	0.41-1.65	1.11	11.12	nd-1.46	0.50	5.04	nd-2.52	0.67	6.70	nd-1.37	0.60	6.04
REH	nd-1.87	1.17	11.69	nd-2.08	0.98	9.79	nd-2.35	0.67	6.70	nd-1.69	0.75	7.53
UBP	0.67-1.99	1.38	13.76	nd-2.65	1.18	11.76	nd-3.37	0.77	7.73	nd-1.52	0.67	6.72
NWTI	1.02-3.48	1.94	19.41	nd-3.02	1.63	16.26	nd-4.70	1.53	15.28	nd-1.50	0.68	6.84
NWTT	0.49-2.07	1.44	14.36	nd-2.75	1.18	11.80	nd-4.76	1.15	11.50	nd-2.63	0.78	7.82
NWTE	0.32-1.90	1.23	12.26	nd-2.45	1.00	9.98	nd-2.80	0.80	7.99	nd-4.86	1.19	11.92
BLA	0.35-1.78	1.14	11.38	nd-1.88	0.80	8.05	nd-4.05	1.37	13.68	nd-1.35	0.65	6.47
Range	nd-3.48	0.95-1.94	9.47-19.41	nd-3.02	0.41-1.63	4.10-16.26	nd-4.76	0.48-1.53	4.75-15.28	nd-4.86	0.54-1.19	5.38-11.92
Mean		1.19	11.92		0.90	9.01		0.76	7.61		0.67	6.70
SD		0.25	2.50		0.36	3.65		0.32	3.25		0.16	1.63
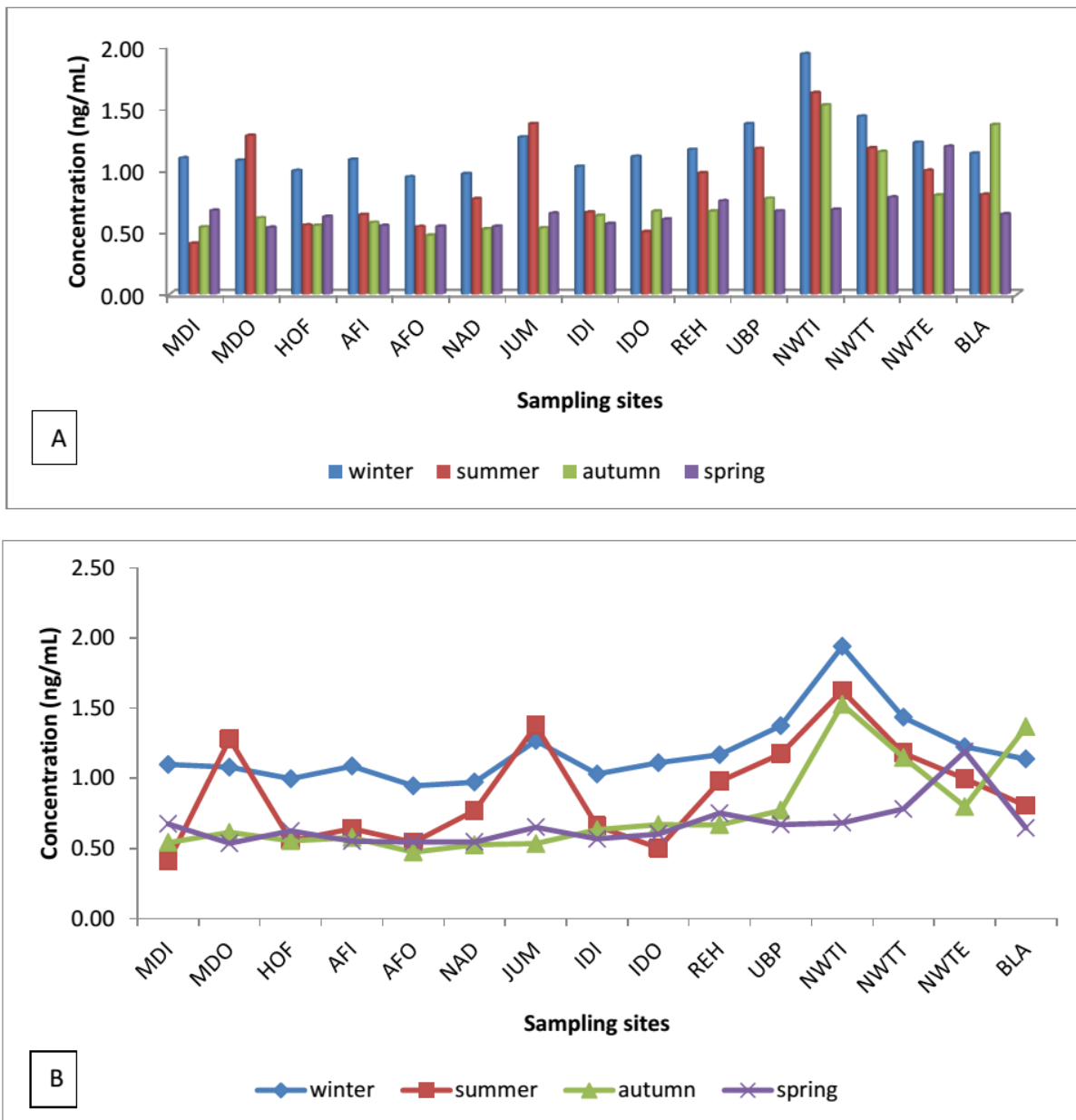
Figure 8.2 A: Seasonal concentrations of OCPs in water, B: seasonal trend of OCPs across sites (n = 3).

The differences between winter mean concentrations and autumn and spring mean concentrations were statistically very significant with p-values less than 0.0001 (p < 0.0001). The autumn mean concentration 0.76 ±0.32 ng/mL and mean total concentration (7.61 ±3.25 ng/mL) were slightly different from the spring mean concentration (0.67 ±1.16 ng/mL) and mean total concentration (6.70 ±1.63 ng/mL). The climatic factors for the two short seasons were not significantly different and therefore, the seasonal variation in pollutant distribution

was not so pronounced. The calculated t-test between mean concentrations of these two short seasons gave a p-value of 0.3554 (p = 0.3554). Such a value shows that the mean concentrations of the two seasons were not statistically different (GraphPad, 2014).

8.4.2. Seasonal Variation of OCPs in Sediment Pore Water and Sediment

The concentrations of analytes in pore water were calculated as per in surface water, and for sediment were calculated using the concentration of the compound in the extract and the weight of the dry sediment (USEPA, 2007).

The levels of OCPs were obtained from 52 surface sediment and 8 bio-solids samples (13 surface sediment and 2 bio-solid samples each season). The seasonal variations in sediment pore water and in surface sediment followed the same pattern. Table 8.5 and Figure 8.3 A show results obtained from pore water samples. The pore water concentrations ranged from 0.76–34.92 ng/mL with a mean concentration of 11.01 ±5.04 ng/mL in winter, nd–22.44 ng/g with a mean of 5.16 ±1.48 ng/mL in summer, nd–48.27 ng/mL with a mean of 9.68 ±5.34 ng/mL in autumn and nd–26.59 ng/mL with a mean concentration of 6.39 ±3.20 ng/mL in spring. The concentrations obtained in analysis of sediment are summarised in Table 8.6 and Figure 8.3 B. The levels of OCPs in sediment fluctuated from 2.29–93.02 ng/g with a mean concentration of 30.87±7.38 ng/g in winter, nd–146.82 ng/g with a mean of 18.41 ±11.20 ng/mL in summer, nd– 186.52 ng/g with a mean of 31.78 ±8.85 ng/g in autumn and nd–276.39 ng/g with mean concentration of 31.50 ±14.83 ng/g in spring. The above-mentioned results are mean concentrations calculated based on the concentrations obtained from all sampling sites and all analytes. The high standard deviations from the mean concentrations and from the total mean concentrations indicate high variations of concentrations between sites and high variations of concentrations between analytes and sampling sites respectively. The individual concentrations of OCPs in each season were mentioned in appendix E)

Table 8.5 Seasonal concentrations of OCPs in the Umgeni River sediment pore water.

Site code	winter (ng/mL) range	mean	∑OCPs	summer (ng/mL) range	mean	∑OCPs	autumn (ng/mL) range	mean	∑OCPs	spring (ng/mL) range	mean	∑OCPs
MDI	1.90-9.98	5.96	55.63	nd-9.00	3.41	34.14	nd-16.58	5.89	58.91	nd-8.96	3.16	31.56
MDO	0.76-7.15	3.68	34.32	nd-10.26	4.48	44.83	nd-14.18	4.45	44.54	nd-5.44	1.61	16.12
HOF	1.62-11.87	6.80	61.28	nd-6.01	2.75	27.50	nd-7.55	3.25	32.49	nd-7.43	4.61	46.12
AFI	1.69-11.42	6.49	61.35	nd-9.66	3.61	36.14	nd-12.71	3.90	38.97	nd-8.91	3.59	35.89
AFO	1.06-9.30	4.80	45.29	nd-13.96	4.78	47.76	nd-15.40	4.69	46.88	nd-7.03	2.06	20.60
NAD	2.94-19.64	10.07	94.40	nd-13.70	4.91	49.09	nd-15.43	4.71	47.09	nd-15.14	5.71	57.08
JUM	2.97-20.69	11.06	103.61	nd-17.25	6.19	61.85	nd-48.27	10.62	106.25	nd-15.43	6.25	62.46
IDI	1.27-26.53	13.75	128.30	nd-19.03	6.69	66.94	nd-30.44	11.93	119.33	nd-20.65	8.62	86.23
IDO	4.31-34.92	17.35	162.88	nd-22.42	7.59	75.86	nd-42.07	15.66	156.59	nd-26.59	9.76	97.60
REH	4.24-29.27	15.02	140.18	nd-16.61	5.91	59.10	nd-41.96	13.86	138.64	nd-22.49	8.78	87.81
UBP	3.84-27.96	15.15	141.22	nd-14.50	5.19	51.89	nd-39.35	19.33	193.26	nd-21.71	9.42	94.16
NWTT	6.08-32.54	17.51	162.88	nd-17.91	6.14	61.43	nd-33.37	14.64	146.40	nd-25.40	10.98	109.77
NWTE	5.20-33.38	17.73	166.23	nd-16.83	6.28	62.78	nd-33.39	14.68	146.79	nd-25.22	10.24	102.35
BLA	2.91-16.70	8.75	81.69	nd-12.28	4.35	43.46	nd-17.59	7.97	79.70	nd-12.85	4.71	47.09
Range	0.76-34.92	3.68-17.73	34.32-166.23	nd-22.42	2.75-7.59	27.50-75.86	nd-48.27	3.25-19.33	32.49-193.26	nd-26.59	1.61-10.98	16.12-109.77
Mean		11.01	102.80		5.16	51.63		9.68	96.85		6.39	63.92
SD		5.04	47.19		1.38	13.77		5.34	53.41		3.20	32.03

nd = not detected
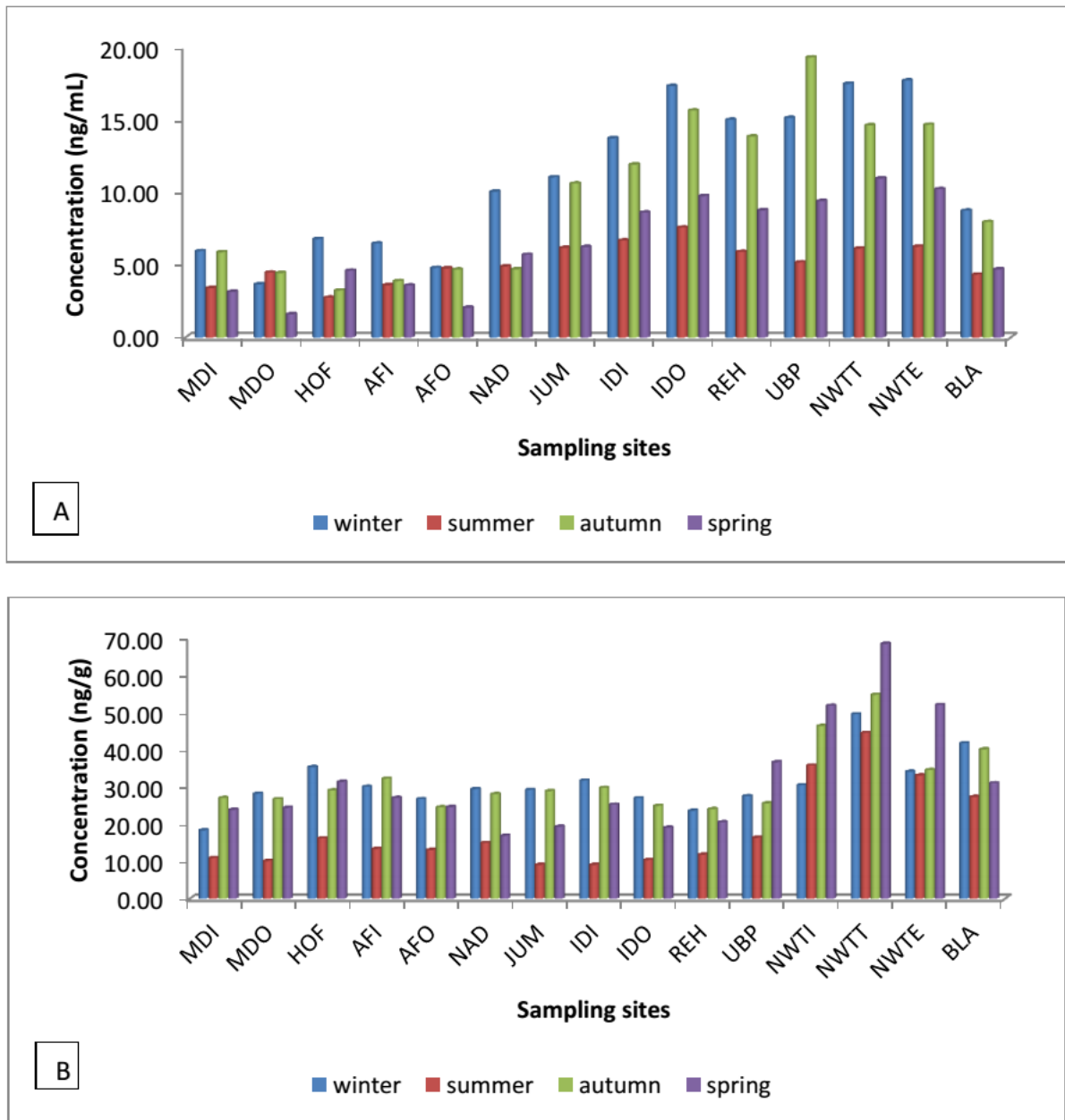
Figure 8.3 Seasonal concentrations of OCPs at each site: (A) in pore water, (B) in sediment (n=3).

The highest mean concentration (11.01 ±5.04 ng/mL) and mean total concentration (102.80 ±47.19 ng/mL) in sediment pore water were recorded in winter. This may be due to the partitioning of hydrophobic OCPs from water to solid particles and to sediment by settling (Bao-Feng et al., 2004), as well as the sorption of OCPs on sediment since research has found that the sorptive capacities of organic pollutants on sediment and soil, increases with a decrease in temperature (Delle Site, 2001).

The high winter concentrations may also be explained by low photochemical degradation due to less winter sunlight which in turn may cause accumulation of pollutants on the organic particulate matter in the aquatic environment (Brunciak et al., 2001).

The lowest mean concentration (5.16 ±1.38 ng/mL) and mean total concentration (51.63 ±13.77 ng/mL) were obtained in summer. This could be explained by two main environmental factors which are vaporisation and runoff. During summer the ambient and water temperatures were high (Table 8.2) and hence the pollutants tended to leave the bed sediment, re-dissolve in water and volatilise to the atmosphere and hence their concentration was lowered in pore water and sediment (Meijer et al., 2006). Research has also found that OCPs can be transported from pore water to surface water by diffusion which is enhanced in summer due to high temperatures (Zhang, 2003). The sediment thus may became a source of OCPs for water and indirectly for the atmosphere (Hui et al., 2007). In addition, the South African summer is a rainy season with high levels of precipitation. This caused much runoff in the Umgeni River catchment area. Due to excess rain water, the pollutants were diluted and their concentrations reduced.

The second highest mean concentration (9.68 ±5.34 ng/mL) and mean total concentration (96.85 ±53.41 ng/mL) (Table 8.5) was obtained in autumn followed by spring with a mean concentration of 6.39 ±3.20 ng/mL and mean total concentration of 63.92 ±32.03 ng/mL. The environmental conditions for the two short seasons were not very different. These two seasons had warmer temperatures and mild precipitation. The t-test showed a p-value of 0.0587, indicating that the difference between the concentrations obtained in autumn and spring pore water was not statistically significant (GraphPad, 2014). Considering the four seasons, the lowest concentration in pore water was obtained at MDO in spring (nd–5.44 ng/mL) with a mean concentration of 1.61 ng/mL and the highest was found at UBP in autumn (nd–39.35 ng/mL) with a mean concentration of 19.33 ng/mL (Table 8.5 and Figure 3 A).

The analysis of sediment samples revealed lower concentrations in summer (Figure 8.3 B) with a mean concentration (18.41 ±11.41 ng/g) and mean total concentration (184.12 ±112.03 ng/g) lower than those in winter (30.87 ±7.38 ng/g and 308.70 ±73.78 ng/g), in autumn (31.78 ±8.85 ng/g and 317.84 ±88.45 ng/g) and in spring (31.50 ±14.83 ng/g and 314.99

±148.29 ng/g) (Table 8.6). This was probably due to re-suspension of sediment OCPs into the water column (Chau, 2006, Elena et al., 2011) due to higher water temperatures of summer (Table 8.2) and then vaporisation to air. The lowest concentration in sediment was found at IDI in summer (nd–18.10 ng/g) with a mean concentration of 9.09 ng/g and the highest concentration was obtained at NWTT in spring (24.25–276.39 ng/g) and mean of 68.47 ng/g (Table 8.6 and Figure 8.3B).

In general for both pore water and sediment and in all seasons, the sites NWTT and NWTE showed high concentrations. These were bio-solids, and sediment and their pore water samples, collected at Northern Wastewater Treatment after treatment and at the effluent (point of discharge to the river) respectively. In both cases the trends of concentrations throughout the river are similar except for the spring season (Figures 8.4 A and B).

Table 8.6 Seasonal concentrations of OCPs in the Umgeni River sediment.

Site code	winter (ng/g)			summer (ng/g)			autumn (ng/g)			spring (ng/g)		
	range	mean	∑OCPs	range	mean	∑OCPs	range	mean	∑OCPs	range	mean	∑OCPs
MDI	4.34-36.86	18.36	183.63	nd-20.87	10.93	109.27	nd-72.47	27.06	270.58	nd-37.20	23.88	238.78
MDO	4.51-48.56	28.19	281.93	nd-16.18	10.13	101.35	nd-73.41	26.74	267.39	2.38-56.57	24.41	244.14
HOF	10.75-73.84	35.34	353.39	nd-32.05	16.21	162.05	nd-95.67	29.07	290.66	4.40-87.31	31.39	313.89
AFI	6.81-63.70	30.05	300.53	4.40-21.90	13.39	133.88	nd-96.61	32.21	322.11	8.83-63.53	27.07	270.66
AFO	7.41-60.50	26.76	267.58	nd-31.55	13.08	130.79	nd-62.69	24.56	245.58	15.60-52.92	24.62	246.17
NAD	8.68-70.50	29.45	294.45	2.15-29.55	14.96	149.56	nd-88.54	28.09	280.92	3.72-27.29	16.89	168.92
JUM	4.40-59.25	29.20	292.04	2.26-17.97	9.10	90.96	nd-90.11	28.89	288.94	6.60-31.67	19.34	193.45
IDI	7.30-78.51	31.71	317.06	nd-18.10	9.09	90.93	nd-84.06	29.77	297.67	nd-99.90	25.25	252.49
IDO	2.29-67.20	26.99	269.91	nd-19.92	10.41	104.05	nd-75.32	24.93	249.26	7.68-31.14	19.08	190.83
REH	5.49-56.36	23.63	236.28	3.82-23.90	11.83	118.26	nd-66.17	24.06	240.61	13.85-34.36	20.54	205.38
UBP	11.35-50.32	27.53	275.30	6.62-33.61	16.39	163.90	4.88-69.45	25.60	256.02	25.52-66.78	36.66	366.62
NWTI	7.07-87.87	30.47	304.74	9.53-130.19	35.77	357.67	2.20-176.34	46.36	463.59	19.77-159.02	51.84	518.35
NWTT	26.40-82.96	49.52	495.21	15.09-146.82	44.50	444.99	6.97-186.55	54.74	547.42	24.25-276.39	68.47	684.68
NWTE	10.57-93.02	34.10	341.01	12.61-98.36	33.10	330.98	3.09-95.92	34.56	345.63	19.29-176.79	52.03	520.32
BLA	11.27-87.72	41.75	417.49	6.14-52.71	27.32	273.22	6.30-108.38	40.12	401.23	13.11-59.82	31.01	310.12
Range	2.29-93.02	18.36-49.52	183.63-495.21	nd-146.82	9.09-44.50	90.93-444.99	nd-186.55	24.06-54.74	240.61-547.42	nd-276.39	16.86-68.47	168.92-684.68
Mean		30.87	308.70		18.41	184.12		31.78	317.84		31.50	314.99
SD		7.38	73.78		11.20	112.03		8.85	88.45		14.83	148.29

nd = not detected
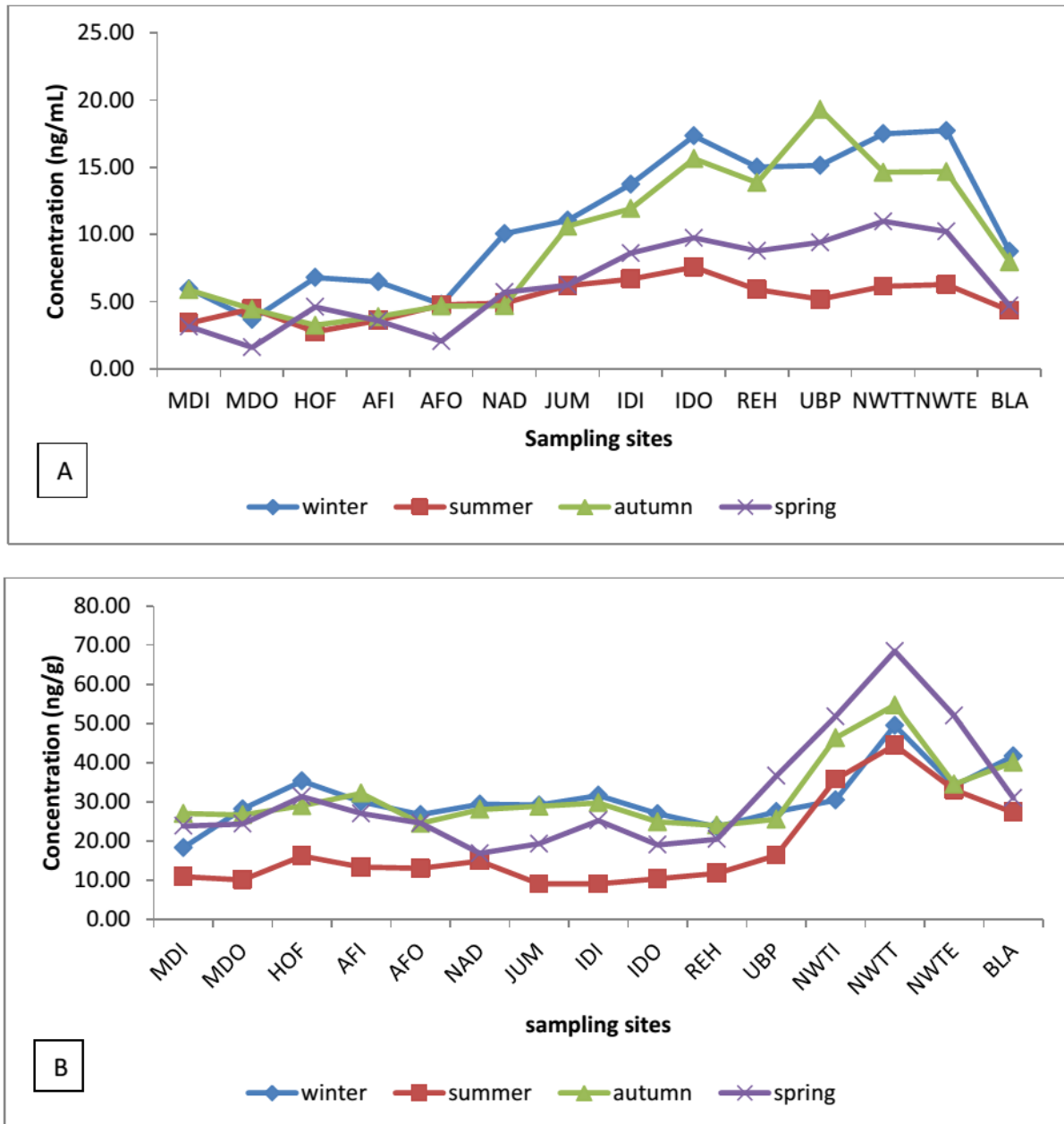
Figure 8.4 A: Seasonal trend of OCPs in pore water, B: seasonal trend of OCPs in sediment (n=3).

8.4.3. Seasonal Mean Levels of OCPs in Water, Pore Water and Sediment

The general seasonal average levels of OCPs were lower in water than in pore water and sediment. The sediment averages for all seasons were higher than in water and pore water. This was not unexpected because sediment are known to be both a pollutant sink and carrier and source of contaminants in the aquatic environment (Chee et al., 1996, Chau, 2006, Usha, 2013, Hongwen and Wen, 2011).
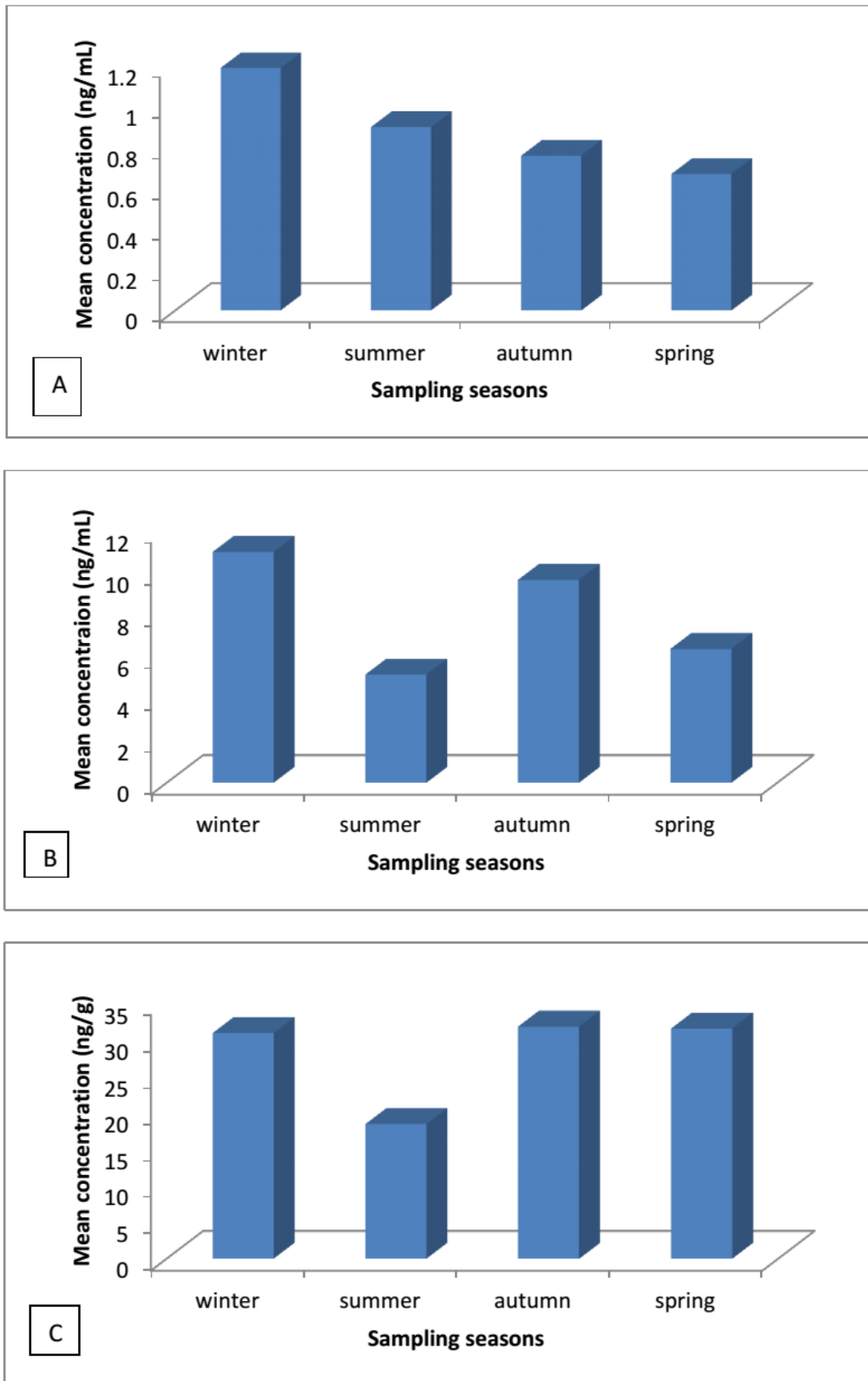
Figure 8.5 Mean seasonal concentrations: A- in water, B- in pore water, C- in sediment.

The highest mean concentration was generally found in winter for all matrices. The winter, autumn and spring mean concentrations did not differ significantly for sediment because, being less mobile, its concentration in OCPs will take a relatively longer time to change significantly, except in the presence of extreme conditions like those in summer. The seasonal climatic mild conditions like those in autumn and spring may not change the sediment concentrations immediately. A monitoring study which covers more than one year is needed to know their temporal change in sediment. The lowest mean concentration was obtained in spring for water samples and in summer for pore water and sediment samples (Figure 8.5). The mean concentrations of water in summer were a bit high due to increase in concentration at wastewater treatment sites (NWTI, NWTO and NWTE) during that period probably due to continued release of household wastewater which was not much influenced by climatic conditions.

8.5 CONCLUSION

Based on a year monitoring, we present the first comprehensive assessment and seasonal variations of levels of OCPs in the Umgeni River. The concentrations of selected OCPs were generally higher in the following order of increasing concentrations: unfiltered water, unfiltered pore water and sediment during the winter sampling season. However, for sediment, the autumn and spring seasons also presented higher concentrations as in winter. In all matrices, the difference between winter and summer concentrations was statistically significant. In most cases the difference of concentrations between autumn and spring was not statistically significant. Seasonal variation of OCPs in the river may be governed by certain phenomena such as precipitation, volatilisation, atmospheric deposition and biogeochemical degradation among others. Our investigation focussed on surface water and surface sediment and further investigations are needed to understand seasonal distributions in deep water and sediment depth.

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CHAPTER NINE
MANUSCRIPT SIX

ASSESSMENT AND SEASONAL VARIATION OF POLYCHLORINATED BIPHENYLS AND ORGANOCHLORINE PESTICIDE RESIDUES IN THE UMGENI RIVER BANK SOIL SYSTEM, KWAZULU-NATAL, SOUTH AFRICA

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ABSTRACT

The assessment and seasonal variation of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the Umgeni River bank soil was investigated. Soxhlet extraction and gas chromatography-mass spectrometry were used for sample treatment and analysis respectively. The seasonal OCP total levels ranged between 2.52-82.65 ng/g,dw) with a mean of 24.33 ±4.55 ng/g, dw in winter, not detected (nd)-76.54 ng/g with a mean of 13.50 ±5.33 ng/g, dw in summer, nd-158.51 ng/g with a mean of 42.62 ±10.41 ng/g, dw in autumn and nd-91.96 ng/g with a mean concentration of 21.38 ±6.42 ng/g, dw in spring. The PCB total concentrations varied between 10.46-89.46 ng/g with a mean of 25.47 ±13.21 ng/g, dw in winter, nd-77.32 ng/g with a mean of 11.79 ±7.15 ng/g, dw in summer, nd-80.40 ng/g with a mean of 26.79 ±6.98 ng/g, dw in autumn and 4.64-85.35 ng/g with a mean of 19.61 ±8.11ng/g, dw in spring. The highest mean concentrations were observed in autumn and the

lowest in summer for both OCPs and PCBs. The difference between these two seasons' concentrations was statistically significant. The second highest mean concentrations were recorded in winter. The winter and spring mean concentrations were not statistically significant.

Keywords: Umgeni River, OCPs, PCBs, seasonal variation, river bank soil

9.1 INTRODUCTION

The occurrence and seasonal distribution of persistent organic pollutants (POPs) in the environment is not static but highly dynamic. The temporal and seasonal trends of concentrations of organic pollutants in various environmental matrices have been extensively documented (Hornbuckle et al., 1994, Yenisoy-Karakasx et al., 2012, Di Leo et al., 2014, You et al., 2011, Salihoglu et al., 2013, Kaya et al., 2012). The changes of concentrations of POPs such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in time and space are dependent on seasonality or seasonal variations which determine their fate and behaviour in all biotic and abiotic environments (Noegrohati et al., 2008). The seasonal variation of patterns of both OCPs and PCBs in soil is governed by their physical-chemical properties on one hand and mostly by regional geographic conditions on the other hand. The leading factors in seasonal variation include temperature differences, precipitation, specificity of congener properties, physiological behaviour of biota, etc. which induce the six major ways of dissipation including volatilization, photo-oxidation, chemical oxidation, sorption, leaching and biodegradation (Quantin et al., 2005). These phenomena occur more speedily in tropical conditions than in temperate conditions or arctic/sub-arctic regions (Hassan, 1994, Larsson et al., 1995). Both OCPs and PCBs have a tendency to volatilise from soil, water and vegetation to air due to high summer temperatures (Halsall et al., 1999). The water solubility and the vapour pressure of individual OCPs and PCBs play an important role in its volatilization (Walker et al., 1996).

Both soil and air temperatures have a fundamental effect on partitioning of OCPs and PCBs and therefore on their deposition (Jury et al., 1987). Lower temperatures increase deposition rates and decrease re-volatilization processes. Temperature-dependent seasonal variations have been observed in soil and research has shown that in some regions, the concentrations of

PCBs decreased in soil with an increase in annual temperatures (Wilcke and Amelung, 2000). Ma and his team reported lower concentrations of PCBs in soil during summer than in winter which they attributed to temperature increase (Ma et al., 2007). Seasonal precipitations also play a role in OCP and PCB seasonal distribution. It not only transfers the airborne OCPs and PCBs to water bodies but also induces surface runoff to the aquatic environment thus leading to higher concentrations in the water matrix (Blemle and Larsson, 1997, Barber and Writer, 1998).

Extensive research has been carried out to study the occurrence of OCPs and PCBs in different environmental matrices in South Africa such as freshwater dwelling animals (Barnhoorn et al., 2015a), in birds (van Wyk et al., 2001, Bouwman et al., 2008), in human milk (van Dyk et al., 1987), in air (Batterman, 2008), in lakes (Greichus et al., 1977) and rivers (Sibali et al., 2008) but none of these studies have considered the seasonality of these contaminants in these matrices. Seasonality studies are important as they allow researchers to determine the movement and partitioning of pollutants between different matrices based on climate conditions.

To our knowledge, there is no study of the status of seasonal variation of persistent organic pollutants (POPs) such as organochlorine pesticides and polychlorinated biphenyls in this river or its bank soil. Therefore, the aim of this study was to assess and evaluate the seasonal fluctuations of the levels of OCPs and PCBs in the bank soil system of the Umgeni River catchment in KwaZulu-Natal Province of South Africa. This river water is consumed by people and livestock and in addition the river banks, in some locations, are used to grow crops such as, vegetables which are known to take up these pollutants thus resulting in human exposure based on consumption of these contaminated vegetables. It is the first seasonal study on the river bank soil which will provide much needed information to other researchers in this field and in the South African context. The structures of all monitored analytes were given in figure 9.1.
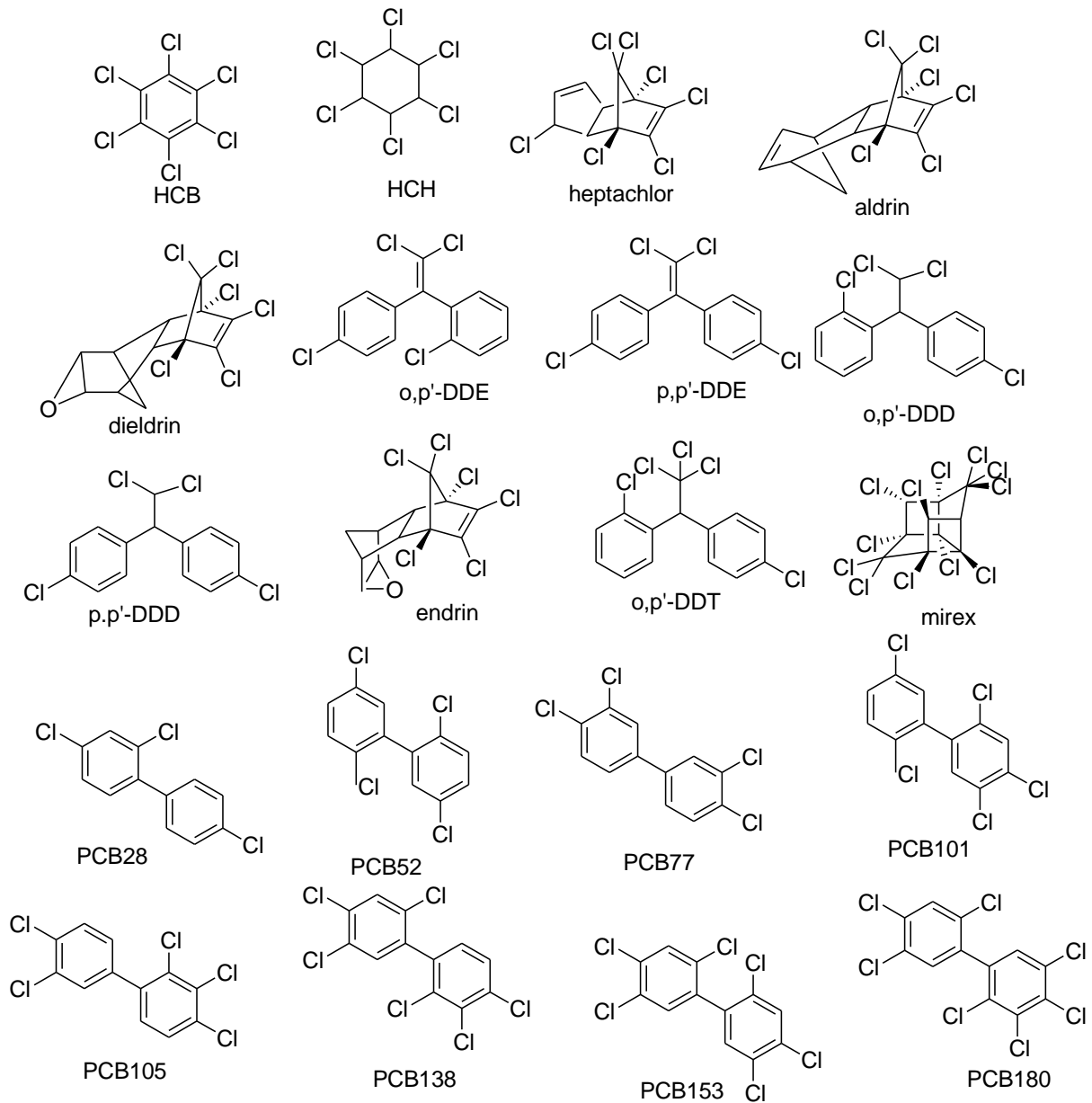
Figure 9.1 Structures of OCPs and PCBs monitored.

9.2 MATERIALS AND METHODS

9.2.1. Reagents, Standards and Apparatus

Solvents used for extraction were high pressure liquid chromatography (HPLC) grade. Dichloromethane (DCM), hexane and toluene were obtained from Sigma Aldrich, South Africa. The florisil (MgO$_3$Si residue analysis grade, mesh 60-100, pore size 60Å) used for

clean-up and OCP and PCB standards were also purchased from Sigma Aldrich. Anhydrous sodium sulfate (Na_2SO_4) gold line (CP) used as a drying agent and silicon carbide boiling stones (CSi) were bought from Associated Chemical Enterprises (ACE, South Africa) and sulfuric acid (98%) was obtained from Promark Chemicals (USA). The test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm) used for sieving, were obtained from DLD Scientific, South Africa.

9.2.2. Sample Collection

The sampling activities were organised in four periods for four South African seasons. The autumn samples were collected from 08-10th May 2013; the winter samples were collected from 15-17th July 2013, the spring samples from 25-27th September 2013 and summer from 11-13th February 2014. Fifty six samples (fourteen samples each season) were collected from 14 sampling sites, including 52 river bank soil samples and 4 bio-solid samples, using an auger. The samples were stored in 150 mL glass bottles previously washed with hot water and detergent and rinsed with sulfuric acid and deionised water respectively. Before sampling the sample bottles were rinsed three times with river water at the site. The bottles filled with river bank soil were capped with caps lined with aluminium foil and kept in an ice chest at 4 °C and transported to the laboratory. Sites were selected in agricultural, industrial and residential areas to show the effects of the various activities along the river on the soil. The sampling sites and their geographical coordinates are shown in Table 9.1 and Figure 9.2.
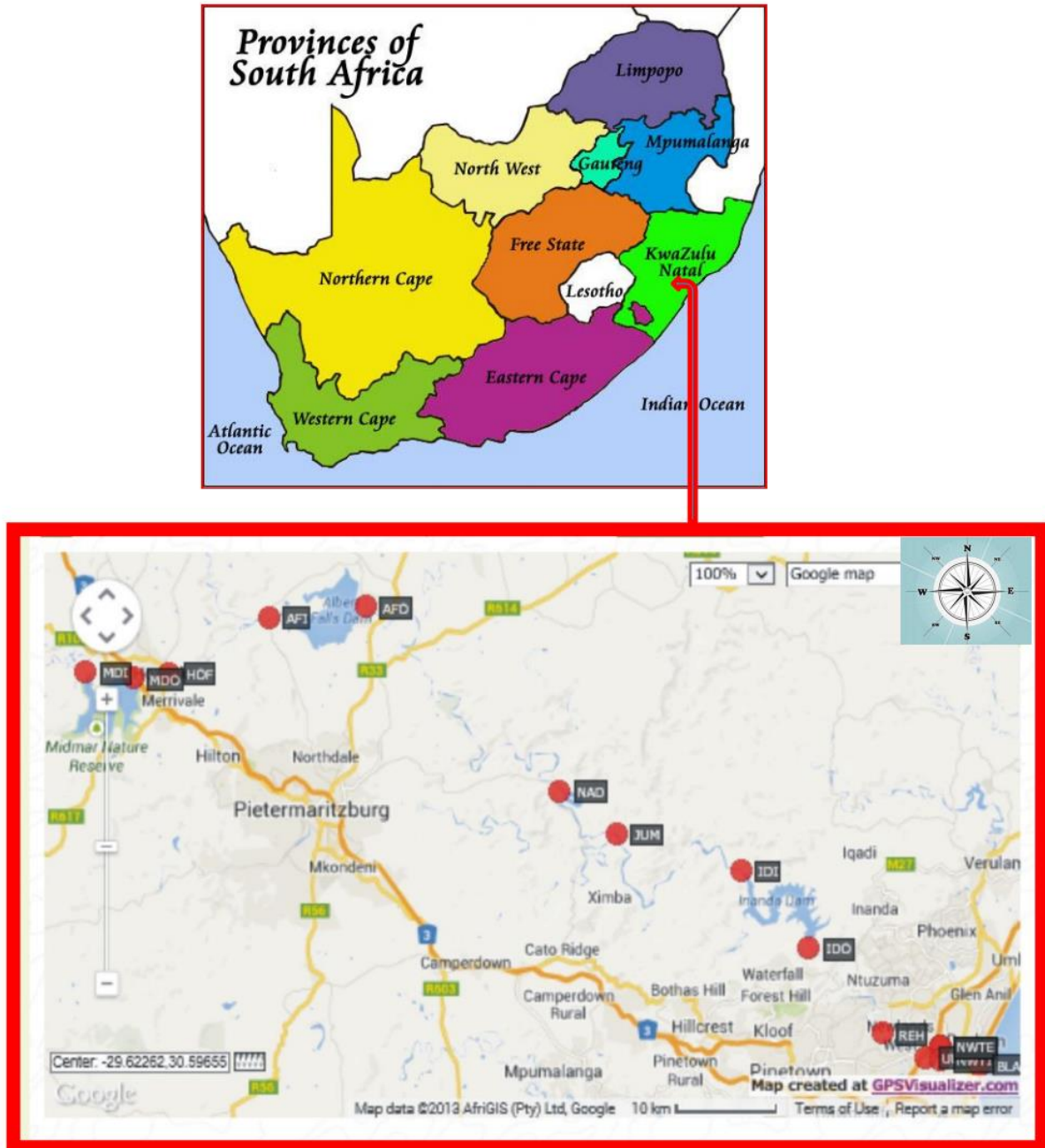
Figure 9.2 Map of sampling sites with the sample collection locations identified in red dots (maps were generated from GPS coordinates using an online tool—GPS visualizer).

Table 9.1 List of Umgeni River sampling sites and GPS coordinates in the downstream direction.

sample code	sample name	coordinates		site description
		South	East	
MDI	Midmar Dam inlet	29° 29′ 16.05"	30° 09' 23.10"	Dam for water supply inlet
MDO	Midmar Dam outlet	29° 29' 34.02"	30° 12' 09.13"	Dam for water supply outlet
HOF	Howick Falls	29° 29' 18.18"	30° 14' 19.70"	Water falls
AFI	Albert Falls inlet	29° 26' 31.94"	30° 19' 47.10"	Dam for water supply inlet
AFO	Albert Falls outlet	29° 26' 01.81"	30° 25' 55.76"	Dam for water supply outlet
NAD	Nagle Dam	29° 35' 08.42"	30° 37' 23.94"	Dam water
JUM	Joining point Umgeni/Msunduzi	29° 37' 16.61"	30° 40' 46.59"	River bank surface soil
IDI	Inanda Dam inlet	29° 39' 05.20"	30° 48' 06.24"	Dam for water supply inlet
IDO	Inanda Dam outlet	29° 42' 55.74"	30° 52' 07.69"	Dam for water supply outlet
REH	Reservoir Hills	29° 47' 08.05"	30° 56' 25.51"	River bank surface soil
UBP	Umgeni Business park	29° 48' 19.05"	30° 58' 58.08"	River bank surface soil
NWTT	Northern wastewater treatment after treatment	29° 47' 47.02"	30° 59' 50.06"	Pond containing treated water from the treatment plant
NWTE	Northern wastewater treatment effluent	29° 47' 47.08"	30° 59' 51.05"	Discharge point of treated water to the river
BLA	Blue Lagoon	29° 48' 41.03"	31° 02' 12.05"	Discharge point of the river water to the Indian ocean

9.2.3. Sample Treatment

9.2.3.1. Drying and extraction

On arrival at the laboratory, the samples were transferred onto aluminium foil and air dried for 5 days in an isolated drying room. After drying, the stones and other objects such as plastics, glass and wood, were hand-picked. The dried soil was ground using a mortar and pestle and sieved using test sieves (ss 200 mm ϕ x 100 μm to ss 200 mm ϕ x 600 μm). A sample of dried and sieved soil (60 g) was transferred into a cellulose extraction thimble and placed in the soxhlet extractor fitted with a 500 mL round bottom flask seated in a heating mantle. The samples (EPA, 1996b) were extracted with 300 mL of toluene for 24 hours (modified EPA method 3540C). Toluene was found to be the best solvent to extract compounds having aromatic rings in their chemical structure (Oleszek-Kudlak et al., 2007).

9.2.3.2. Concentration and clean-up

The extract obtained from soxhlet extraction was concentrated using a rotary evaporator (Heidolph Instruments GmbH & Co.kG) to about 5 mL. The concentrated extract was loaded onto a hexane pre-eluted florisil column containing 10 g of anhydrous sodium sulfate on top and cleaned-up. The column was eluted using increasing polarity fractions of hexane:DCM solvent system composed of 94% hexane: 6% DCM, 85% hexane: 15% DCM, 50% hexane:50% DCM and 100% DCM respectively. The four fractions obtained were combined in a round bottom flask and concentrated using a rotary evaporator to about 5 mL. The extract was then quantitatively transferred to a poly top vial and air dried. The dried extract was reconstituted with DCM to exactly 2.00 mL and analyzed for OCPs and PCBs using gas chromatography-mass spectrometry (GC-MS).

9.2.4. Instrumental analysis

The samples were analysed using an Agilent 6890 series gas chromatography with mass spectrometer (MSD5973). The GC was equipped with a ZB-5MS capillary column, 0.25 mm internal diameter, 0.25 μm film thickness and 30 m length (Hewlett Packard; Houston, TX). Aliquots of 2 μL were injected onto the GC column using a splitless mode and the MS was operated using the selective ion monitoring (SIM) acquisition mode. The carrier gas was ultra-purified helium gas. The injector and detector were set at 250 and 280 ^{o}C respectively.

The MS source was operated at 250 °C. The analysis of OCPs and PCBs were done separately in order to avoid co-elution of analytes and overlapping of peaks. The oven programme was initially set at 120 °C and increased to 290 °C with a ramping rate of 14 °C/min and held for 2 min. The scan mode of the mass spectrometer was used to identify the target OCPs and PCBs, together with the National Institute of Standards (NIST) library and a comparison of the retention times of reference standards with the retention times of the analyte peaks. The analyte quantification was carried out using peak areas of the compound of interest and by the use of external calibration standards at the following calibration levels: 0.25, 0.5, 1, 2, 4 and 8 µg/mL. All samples were analysed in triplicate and the mean was calculated.

9.3 QUALITY ASSURANCE

All the experimental steps were subjected to quality control and assurance measures. The percent recoveries of targeted OCPs and PCBs were obtained using real soil samples. Two subsamples of the same mass and from the same sample were chosen. The first subsample was spiked and the second left unspiked, and both were extracted and analysed. The percent recoveries ($\%R$) were obtained by calculating the ratio of the difference obtained by subtracting the concentration of unspiked subsample (X_u) from that of spiked subsample (X_s) and known spiked concentration of standard (K), multiplied by 100 (Equation 9.1) (Harry et al., 2008). Recoveries varied from 51.67 to 116.97% (Table 9.2). The limits of detection (LOD) and quantification (LOQ) were determined as three and ten times respectively of the standard deviation of three calibration intercepts (s) divided by the average slope (m) (Equations 9.2 and 9.3) (Shrivastava and Gupta, 2011). Solvent blanks were run regularly through the GC system to determine the presence of interferences. In order to determine the variation of the initial calibration curve and ensure it was minimal, the 0.5 µg/mL multi-element standard for OCPs and PCBs were run after each batch of samples. Procedural blanks were used through all stages of sample treatment and analysis and no OCPs and PCBs were detected in the blank samples. The analysis of mass spectra, the comparison of retention times with those of reference standards and National Institute of Standards (NIST) library were used for identification of analytes. In addition, the base peaks together with other two confirming ions for each compound of interest (Table 9.2) were used in selective ion monitoring (SIM) mode.

$$\%R = \frac{X_s - X_u}{K} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.1)$$

$$\text{LOD} = \frac{3s}{m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.2)$$

$$\text{LOQ} = \frac{10s}{m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.3)$$

Table 9.2 Ions monitored, % recoveries, limits of detection (LOD) and quantification (LOQ).

analytes	ions monitored	% recovery	LOD (ng/g)	LOQ (ng/g)
OCPs				
HCB	284, 249, 142	68.1±0.058	0.50	1.66
HCH	219, 183, 147	108.4±3.81	0.50	1.66
heptachlor	374, 272, 237	103.7±7.24	0.50	1.62
aldrin	327, 293, 263	53.16±10.37[25]	0.78	2.59
o,p-DDE	318, 284, 246	87.66±4.77	0.96	3.20
p,p'-DDE	318, 281, 246	51.67±1.62[26]	0.62	2.07
o,p'-DDD/dieldrin[27]	320/380, 235/263, 165/147	87.37±2.08	1.04	3.45
endrin	317, 263, 207	84.69±6.04	1.02	3.41
p,p'-DDD/*o,p*-DDT[28]	320/235, 235/199, 165/165	89.13±2.61	1.23	4.11
mirex	402, 272, 237	103.22±5.84	1.15	3.83
PCBs				
PCB28	256, 186, 150	60.68±0.97	0.76	2.52
PCB52	292, 220, 150	78.73±0.58	0.21	0.71
PCB77	292, 255, 220	64.74±1.47	0.92	3.06
PCB101	326, 291, 254	72.63±0.86	0.30	0.99
PCB105	326, 254, 184	71.88±0.74	0.28	1.12
PCB138	360, 290, 145	72.69±1.38	0.22	0.75
PCB153	360,290, 145	74.74±1.95	0.31	1.03
PCB180	394, 324, 162	77.8±2.55	0.19	0.66

[25] When scanned, the mixture of OCPs investigated showed the presence of chlordene. This compound may have been produced by photocatalytic degradation of aldrin (Bandala., et al. 2002). This may have resulted in aldrin's low recovery.

[26] The *p,p'*-DDE standard chromatogram showed the presence of DDMU which suggests that some of the *p,p'*-DDE may have been degraded into this compound which is its breakdown product (Thomas et al., 2008) and consequently contributed to its low recovery.

[27] *o,p'*-DDD and dieldrin could not be resolved on the GC and were reported as a single peak.

[28] *p,p'*-DDD and *o,p*-DDT could not be resolved on the GC and were reported as a single peak.

9.4 RESULTS AND DISCUSSION

The 12 selected OCPs and 8 selected PCBs were investigated in this study. The discussion focuses on the monitoring of the seasonal variations of the 20 analytes above-mentioned by analysing their distribution in Umgeni River bank soil during the South African winter, summer, autumn and spring seasons.

9.4.1. Seasonal Variation of OCPs in River Bank Soil

In total, 52 river bank soil samples (13 each season) and 4 bio-solid samples (1 each season) from the wastewater treatment outlet were analysed. The concentrations (C) in the soil and bio-solid samples were calculated using Equation 9.4 below (USEPA, 2008, USEPA, 2007).

$$C = \frac{C_{ex} * V_{ex}}{W_s} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (9.4)$$

Where: C_{ex} = the concentration of the compound in the extract in ng/mL

V_{ex} = the extract volume in mL

W_s = sample weight (dw) in g

The concentrations of different OCPs at various sampling sites for all seasons are presented in Table 9.3. The OCP levels varied from 2.52–82.65 ng/g with a mean of 24.33 ±4.55 ng/g in winter, non-detected (nd)–76.54 ng/g with a mean of 13.50 ±5.33 ng/g in summer, nd-158.51 ng/g with a mean of 42.62 ±10.41 ng/g in autumn and nd–91.96 ng/g with a mean of 21.38 ±6.42 ng/g in spring. The highest mean concentration (42.62 ±10.41 ng/g) and mean total levels ($\sum^{12}$ OCPs = 426.16 ±104.10 ng/g) were obtained in autumn. This was because the weather conditions in this season were mild. Autumn is known to have mild precipitations (autumn average monthly rainfall in KwaZulu-Natal: 40.4-96.7 mm) (DWO, 2011) and the runoff would have favoured the accumulation of the OCPs from the surrounding environment into the river bank soil. Research by Qi and his team found that during the wet season, the runoff contributes much to the accumulation of contaminants in bank soil (Qi et al., 2014, Fu and Wu, 2006). In addition, the lower temperatures also may have contributed much to the atmospheric deposition of the OCPs into the river bank soil all contributing to the accumulation of OCPs in the soil during this season (Siddik and Yucel, 2014b). The combined contribution of both phenomena mentioned-above increased autumn concentrations more than in winter season which has only atmospheric deposition as the contributing factor.

On the contrary the lowest mean concentration and mean total levels were recorded in summer. Among others, there are actually two factors that may have contributed significantly to the distribution of the OCPs in soil, namely runoff and vaporisation. Since the precipitations were actually high in summer (average monthly rainfall in KwaZulu-Natal: 96.7-126.6 mm), there should have been an increase in concentration of the pollutants in bank soil due to runoff from soil that is higher up. However, this was not the case, probably because the runoff effect of gathering OCPs in bank soil was dominated by vaporization of the pollutants to the atmosphere since the summer ambient temperatures were high (28.8–38.6 °C). Huang and co-workers found that evaporation of pollutants from soil is the major source of the phasing out of OCP pollutants from soil to the air (Huang et al., 2014). As the temperature rises, vaporisation of pollutants occurs which results in a decrease in its concentration in soil and an increase in their levels in air (Sofuoglu et al., 2004, Hillery et al., 1997). The p-value ($p < 0.0001$) obtained by the t-test method indicated a statistically significant difference between OCP mean levels in the river bank soil in autumn and in summer.

The second highest levels were obtained in winter (Table 9.3). This is a dry and cold season. The precipitation was little to none (winter average monthly rainfall in KwaZulu-Natal: 28.6-37.4 mm) (DWO, 2011) which meant there was no runoff. The ambient temperatures were very low (12.3-19.2 °C) which would have resulted in little to no evaporation of pollutants to the air. However, due to low air temperatures, there may have been OCP deposition from atmosphere to soil. The persistent organic pollutants are known to re-condense in the atmospheric air and deposit to land and therefore increase their normal level in soil (Siddik and Yucel, 2014a, Huang et al., 2014).

Table 9.3 Seasonal concentrations of OCPs in Umgeni River bank soil.

Site code	winter (ng/g)			summer(ng/g)			autumn(ng/g)			spring (ng/g)		
	range	mean	∑OCPs	range	mean	∑OCPs	range	mean	∑OCPs	range	mean	∑OCPs
MDI	4.43-64.90	21.18	211.82	nd-21.53	11.35	113.54	nd-88.74	30.76	307.61	5.68-31.26	18.70	186.96
MDO	2.52-43.36	23.60	236.01	nd-18.64	10.08	100.82	1.41-79.78	30.79	307.89	2.88-50.41	18.60	185.96
HOF	8.36-65.33	28.41	284.09	nd-24.00	12.28	122.84	5.07-99.01	39.69	396.94	3.43-91.96	30.65	306.47
AFI	12.81-59.71	25.44	254.40	nd-38.96	14.18	141.82	8.62-104.22	46.42	464.22	nd-62.33	24.72	247.25
AFO	5.93-53.77	20.04	200.44	nd-29.96	10.81	108.11	3.87-102.61	42.42	424.23	nd-39.59	16.57	165.72
NAD	7.51-56.30	23.75	237.48	nd-27.79	12.56	125.59	4.06-100.98	38.68	386.83	4.21-48.82	22.67	226.70
JUM	5.81-37.08	18.34	183.38	nd-25.81	9.19	91.94	nd-123.64	37.87	378.70	3.57-31.10	14.39	143.94
IDI	11.82-53.87	28.48	284.82	nd-27.15	9.64	96.38	nd-142.83	35.78	357.79	nd-32.41	13.07	130.67
IDO	4.24-39.10	18.78	187.76	nd-27.71	9.23	92.29	11.61-151.40	47.93	479.27	nd-27.92	13.64	136.43
REH	3.58-49.41	21.43	214.27	nd-21.36	10.33	103.32	nd-122.26	41.80	418.02	nd-24.97	17.04	170.39
UBP	14.94-38.97	22.12	221.21	nd-43.10	15.87	158.72	11.24-158.51	60.78	607.80	5.58-32.71	20.97	209.67
NWTT	13.00-70.18	32.39	323.92	nd-76.54	27.44	274.38	16.07-147.35	67.14	671.45	14.61-91.04	31.67	316.65
NWTE	15.55-82.65	32.06	320.60	nd-62.19	22.55	225.50	11.94-80.44	34.93	349.27	8.95-84.31	28.64	286.43
BLA	12.32-60.81	24.66	246.58	nd-27.49	13.44	134.41	14.60-84.59	41.62	416.17	10.56-47.27	27.95	279.51
Range	2.52-82.65	18.34-32.39	183.38	nd-76.54	9.19-27.44	91.94-274.38	nd-158.51	30.76-67.14	307.61-671.45	nd-91.96	130.67-316.65	13.07-31.67
Mean		24.33	243.34		13.50	134.98		42.62	426.16		21.38	213.77
SD		4.55	45.50		5.33	53.34		10.41	104.10		6.42	64.17

nd = not detected
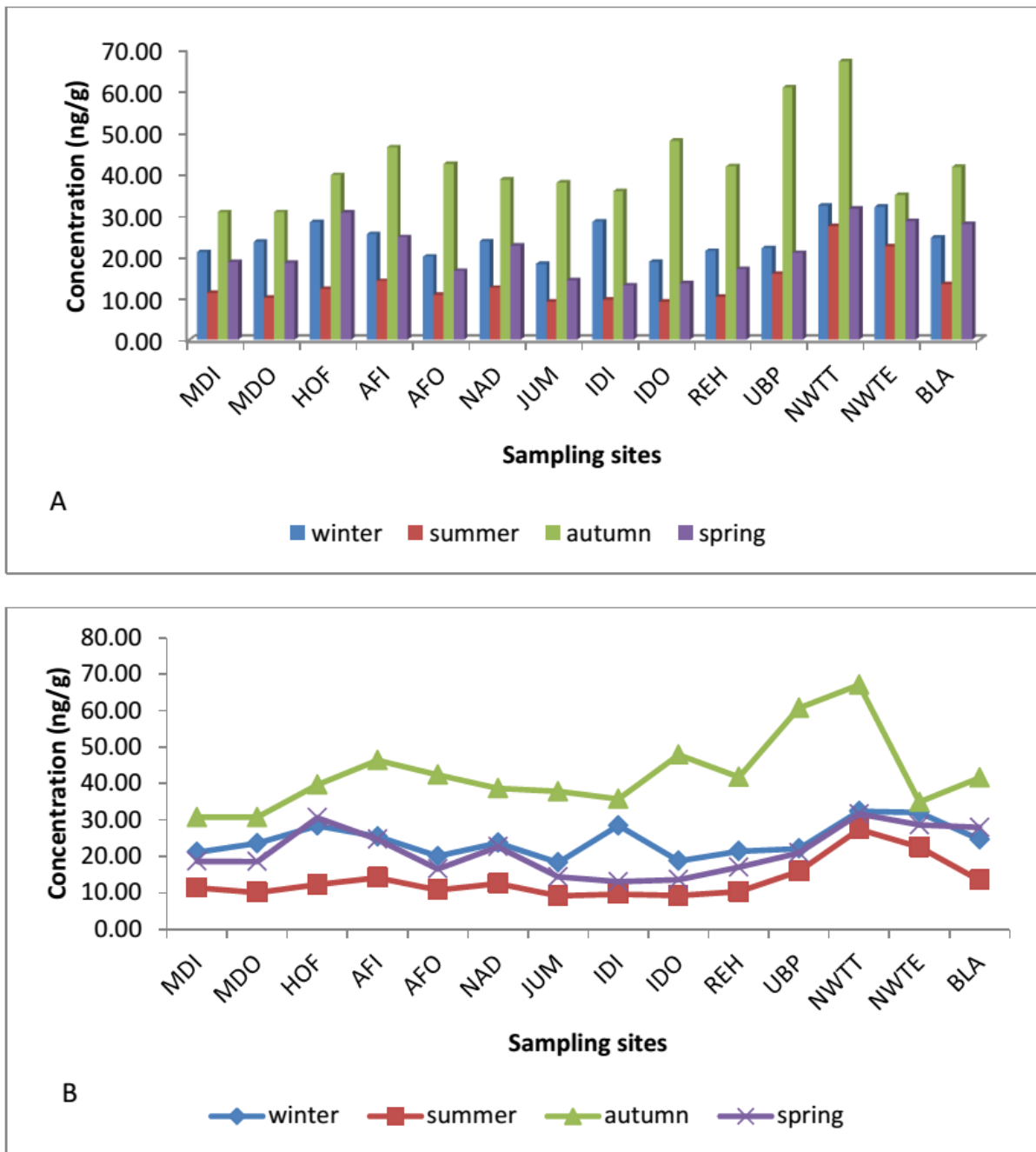
Figure 9.3 A-Seasonal mean OCP concentrations at each site, B- Trend of seasonal mean concentrations.

The mixture of bio-solid and soil collected from NWTT was the most concentrated in OCPs in all seasons compared to river bank soil samples (Table 9.3 and Figure 9.3). This was expected since wastewater treatment plants were found to be sources of organic contaminants (Samara et al., 2006). The p-value indicated a pronounced statistically significant difference between winter and summer concentrations ($p < 0.0001$) and winter and autumn

concentrations (p < 0.0001). There was no statistically significant difference between winter and spring OCP levels (p = 0.1714) although winter seemed to show higher concentrations. The following figure shows the levels of OCPs in Umgeni River bank soil which varied in the order: autumn > winter > spring > summer (Figure 9.4).
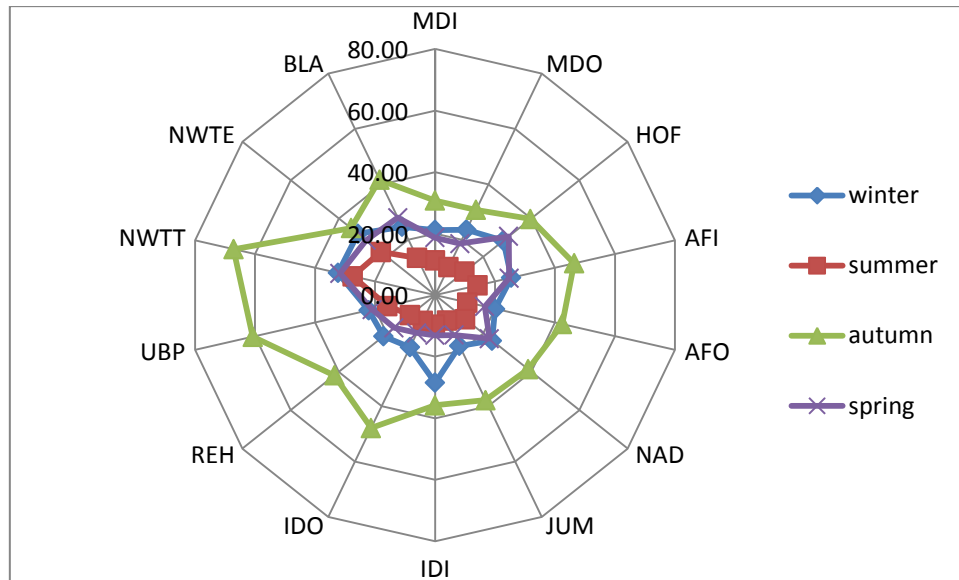

Figure 9.4 Radar chart showing OCP seasonal spatial distribution in the Umgeni river bank soil.

9.4.2. Seasonal Variation of PCBs in River Bank Soil

The bank soil from the Umgeni River was investigated for the PCB congeners. The results obtained are tabulated in Table 9.4 and Figure 9.5. The seasonal overall ranges and means of concentrations of congeners, were 10.46-89.46 ng/g with a mean of 25.47 ±13.21 ng/g in winter, nd-77.32 with a mean of 11.79 ±7.15 ng/g in summer, nd-80.40 ng/g with a mean of 26.79 ±6.98 ng/g in autumn and 4.64–85.35 ng/g with a mean of 19.61 ±8.11 ng/g in spring. The lowest mean concentrations were found in summer. This may be explained by instantaneous air-soil exchange. During summer the ambient temperature was high (29.9-38.6 °C) (Table 9.2) which encouraged volatilisation of the PCBs from soil into air. This was confirmed by Tasdemir and co-workers and Cabrerizo and his team from experiments on air-soil exchange of PCBs where flux levels were positive and indicated volatility of PCBs from soil to air (Tasdemir et al., 2012, Cabrerizo et al., 2011). During the hot summer months, the soil raises its strength as a source of PCBs to the atmosphere (Cabrerizo et al., 2011, Elife et al., 2012, Salihoglu et al., 2013). The highest concentrations were noted in winter and

autumn. Studies found that the exchange of PCBs between soil and atmosphere tends to attain equilibrium but there is net deposition during winter combined with a decrease in fugacity[29] during the colder seasons (Ckover et al., 2008). This resulted in increased concentrations in the soil during winter. The high levels in autumn may be assigned to the deposition of PCBs onto the Umgeni River catchment area that occurs during autumn due to the low ambient temperatures together with runoff from surrounding industrial activities due to some low rainfall. The calculated probability using the t-test showed a statistically very significant difference between winter and summer levels ($p = 0.0020$) and extremely significant difference between summer and autumn levels ($p < 0.0001$). However, the differences between winter and spring ($p = 0.1691$) and winter and autumn ($p = 0.7425$) concentrations were not statistically significant (GraphPad, 2014).

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[29] Fugacity can be defined as the escaping tendency or propensity to migrate. According to Harner et al. (2001), fugacities of a compound in soil (f_s) and air (f_a) can be calculated as follows: $f_s = C_sRT/0.41\Phi_{OM}K_{OA}$, where C: the concentration of the compound in the medium (mol m^{-3}); R: gas constant (8.314 J mol^{-1} K^{-1}); T: absolute temperature(K) , Φ_{OM}: the fraction of the organic matter in the soil and K_{OA}: the octanol-air partitioning coefficient of the compound.

Table 9.4. Seasonal concentrations of PCBs in Umgeni River bank soil.

| Site code	winter (ng/g)			summer (ng/g)			autumn (ng/g)			spring (ng/g)		
	range	mean	$\sum$PCBs	range	mean	$\sum$PCBs	range	mean	$\sum$PCBs	range	mean	$\sum$PCBs
MDI	15.27-39.83	26.35	210.78	0.81-15.16	7.43	59.45	0.75-46.51	16.00	127.97	14.26-29.48	21.16	169.26
MDO	15.76-37.55	25.52	204.15	2.41-18.04	8.85	70.77	2.55-58.16	23.72	189.76	8.28-24.80	14.69	117.50
HOF	17.52-49.95	34.39	275.09	3.86-19.90	10.78	86.20	12.53-59.55	27.69	221.54	14.87-83.48	28.93	231.42
AFI	18.53-33.98	22.89	183.13	nd-13.04	5.62	44.95	11.03-66.96	30.32	242.56	10.40-63.36	27.11	216.90
AFO	10.60-22.50	14.10	112.79	3.41-16.93	9.07	72.58	5.58-69.87	29.23	233.85	8.71-51.07	18.60	148.83
NAD	15.35-31.49	21.29	170.35	3.34-16.52	9.22	73.77	nd-67.45	21.81	174.47	13.25-29.38	18.79	150.31
JUM	16.02-31.31	21.97	175.79	2.47-19.16	9.08	72.63	7.80-51.57	22.57	180.52	6.10-18.65	10.78	86.21
IDI	10.79-36.59	18.09	144.73	1.80-18.85	7.94	63.54	5.39-67.07	25.63	205.03	6.23-20.46	11.40	91.23
IDO	11.85-33.68	18.16	145.29	5.97-25.25	12.92	103.36	0.77-67.10	19.89	159.09	4.64-17.71	9.87	79.00
REH	11.68-29.01	17.62	140.93	nd-26.53	7.32	58.53	4.01-65.08	24.46	195.72	9.51-77.78	19.66	157.26
UBP	12.64-26.67	18.29	146.34	5.15-29.16	13.86	110.85	14.88-79.37	38.98	311.83	5.63-44.61	15.71	125.65
NWTT	36.73-89.46	67.87	542.95	7.03-77.32	34.47	275.74	5.49-58.26	25.56	204.47	21.61-85.35	40.17	321.33
NWTE	12.54-55.19	23.61	188.91	nd-74.66	16.43	131.47	7.29-77.08	26.91	215.30	6.81-73.31	20.44	163.51
BLA	10.46-73.77	26.38	211.03	nd-56.18	12.06	96.50	7.20-80.40	42.33	338.61	5.45-59.21	17.17	137.40
Range	10.46-89.46	14.10-67.87	112.79-542.95	nd-77.32	5.62-34.47	44.95-275.74	nd-80.40	16.00-38.98	127.97-338.61	4.64-85.35	9.87-40.17	79.00-321.33
Mean		25.47	203.73		11.79	94.31		26.79	214.34		19.61	156.84
SD		13.21	105.69		7.15	57.19		6.98	55.86		8.11	64.92
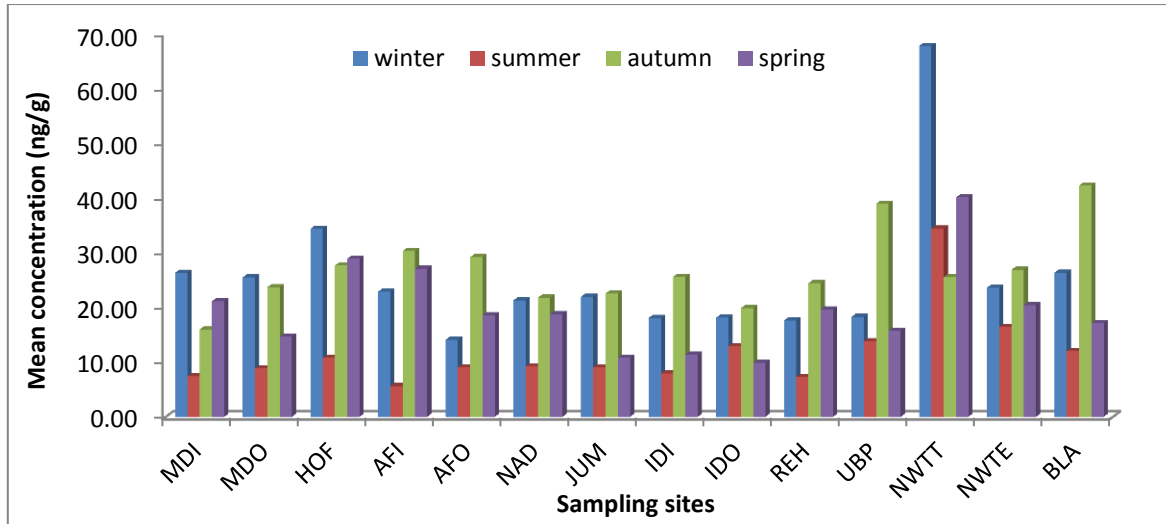
Figure 9.5 Mean concentrations of PCBs in river bank soil at each site (n =3).

Figures 9.6 and 9.7 show the trends of levels of PCBs across the Umgeni River from the source to the mouth. The general trend for all four seasons is that the concentrations of pollutants increased from the source at Midmar Dam inlet (MDI) to Howick Falls (HOF). The increase in concentrations at HOF could be due to industrial activities taking place at Howick town (an industrial plant is situated close to the Howick Falls sampling site). From Howick, the concentrations decreased up to Albert Falls outlet (AFO) and then did not vary much downstream until Reservoir Hills (REH). From REH, the concentration increased to a maximum at NWTT. Note that the NWTT is a wastewater treatment site where the bio-solid constituted of mainly decomposed plant material (as a result of eutrophication) which was removed from treated water and thrown aside. The increase of concentration in autumn at UBP was mainly due to the heavy machinery and other equipments that were used for road construction at that site, which may be the source of PCBs. (The road construction activities were high in autumn during sampling time).
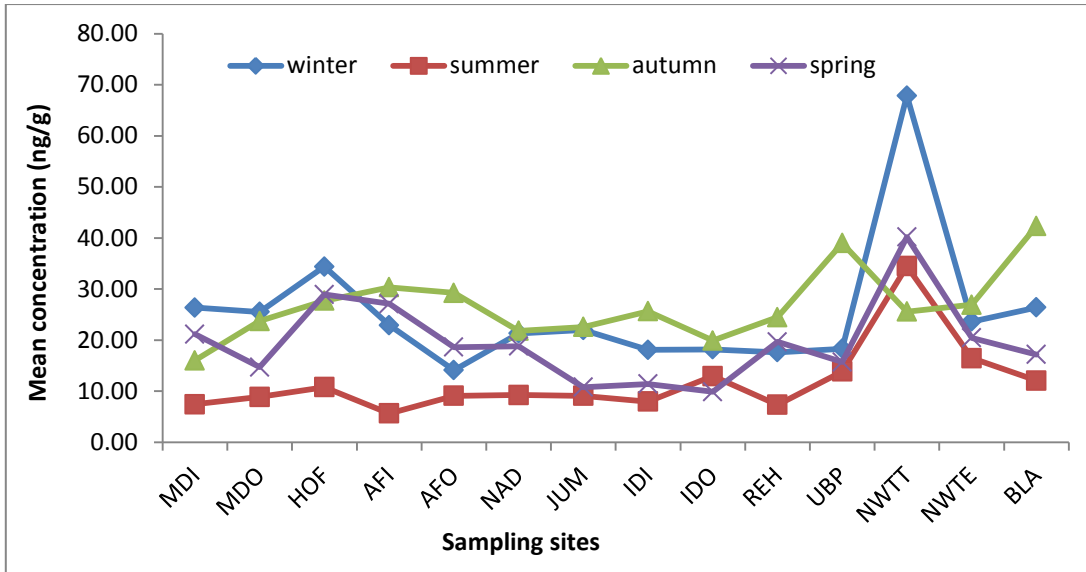
Figure 9.6 Trend of seasonal PCB mean concentrations across sites (n = 3).

The dried bio-solid was treated as soil samples. There is a need for further research to investigate which and how much pollutants are up-taken by which species of plants growing at that site of treated water before discharge into the river. After NWTT, the concentrations revert to levels as before.

Figure 9.7 Radar chart showing PCB seasonal spatial distribution in the Umgeni river bank soil.

9.5 CONCLUSIONS

In this study, soil samples were collected from the banks of the Umgeni River, in KwaZulu-Natal in four South African seasons during 2013-2014 and were analysed for OCPs and PCBs. The highest mean concentrations were observed in autumn and w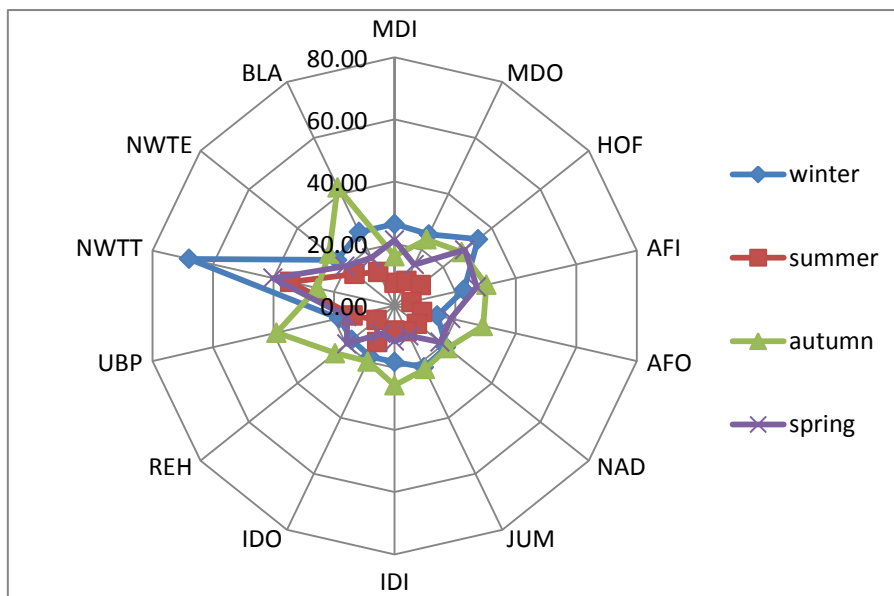inter for both OCPs and PCBs. This increase in concentration may be mainly due to runoff from neighbouring environments and atmospheric deposition which allows accumulation of pollutants at the bank of the river. The lowest mean levels were observed in summer where the runoff effect may have been dominated by the vaporisation of contaminants from soil to air due to high temperatures. Although the winter concentrations seem to be higher than spring concentrations for both OCPs and PCBs in bank soil samples, the difference of levels between the two seasons was not statistically significant. The calculated probability showed a statistically significant difference between summer and autumn and summer and winter levels for both OCPs and PCBs.

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CHAPTER TEN

GENERAL CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

The analysis and monitoring of persistent organic pollutants in the Umgeni River revealed that this river is polluted by OCPs and PCBs in substantial amount. The EPA method of extraction and analysis was modified and developed to fit the analysis of our various matrices. The different matrices investigated accumulate the organic pollutants in the following increasing order: surface water, sediment pore water, river bank soil and surface sediment. Generally, the levels of contaminants were found to be higher in winter that in other seasons. The lowest concentration was found in the summer season for all investigated matrices. Note that the t-test showed that there was always a statistically significant difference between summer and other seasons with respect to pollutant concentrations for all environmental matrices studied. Generally the Northern wastewater treatment works may be considered as the source of these pollutants at the point of discharge back into the river close to its mouth situated at the Indian Ocean in Durban. However, some levels of the studied OCPs and PCBs were reduced as shown in chapters 4 to 9.

The sediment had the highest levels of OCPs and PCBs confirming it as a sink for these pollutants. A relatively high portion of these organic pollutants was also found to be present in sediment pore water.

Compared to some of the international standards such as Canadian Quality Guidelines, the results of this study were generally higher than the interim freshwater sediment quality guidelines (ISQG) but when compared to Ontario Sediment Quality Guidelines, the level of some investigated pollutants were lower than their Lowest Effect levels (LEL). All the pollutant concentrations were far below their severe effect levels (SEL). The Umgeni River water PCB and OCPs levels were higher than the EPA maximum recommended levels in fresh water.

10.2 RECOMMENDATIONS FOR FUTURE WORK

The following are recommended for future studies on OCPs and PCBs in the Umgeni River environment:

- The surface water was analysed in combined form (freely dissolved + dissolved organic carbon + total suspended solids) because this is the form of the water that humans and animals are exposed to. For future research, separation of different phases should be carried out and, compared. In the case of soil and sediment, the organic matter content may be determined for each sampling station in order to compare organic matter contents *versus* concentrations of pollutants.

- The screening of extracts obtained from the studied matrices from the Umgeni River showed the presence of other various micro-pollutants in the river such as polycyclic aromatic hydrocarbons, steroids, polycyclic musks, long chain hydrocarbons, polyphenols, phthalates, pharmaceuticals, chlorinated pesticides such as chlorothalonil and chloroxylenol etc. Future research should focus on the analysis and monitoring of the above-mentioned micro-contaminants in the Umgeni River as well to provide knowledge on other organic pollutants in this river.

- Particle size of sediment and soil is an important phenomenon that affects POP partitioning between sediment and water. Future research on the effect of particle size on partitioning would provide important information in understanding why some organic pollutants partition more to some types of soils and would help to explain the possible high levels in some matrices.

- Some other environmental compartments in the river were not investigated. In the future a research project on analysis of POPs in aquatic life such as fish or plant life along the Umgeni River would provide information on how these pollutatns in the Umgeni River affect the aquatic life.

- Results obtained from this study allow us to confirm that the Umgeni River is chemically polluted; therefore, we recommend the local government of the province of KwaZulu-Natal, in collaboration with the water research commission (WRC) of South Africa, to put in place an adequate mechanism to regularly monitor organic pollutants in the Umgeni River. This will allow the stakeholders to take action and develop methods to reduce pollution in this river.
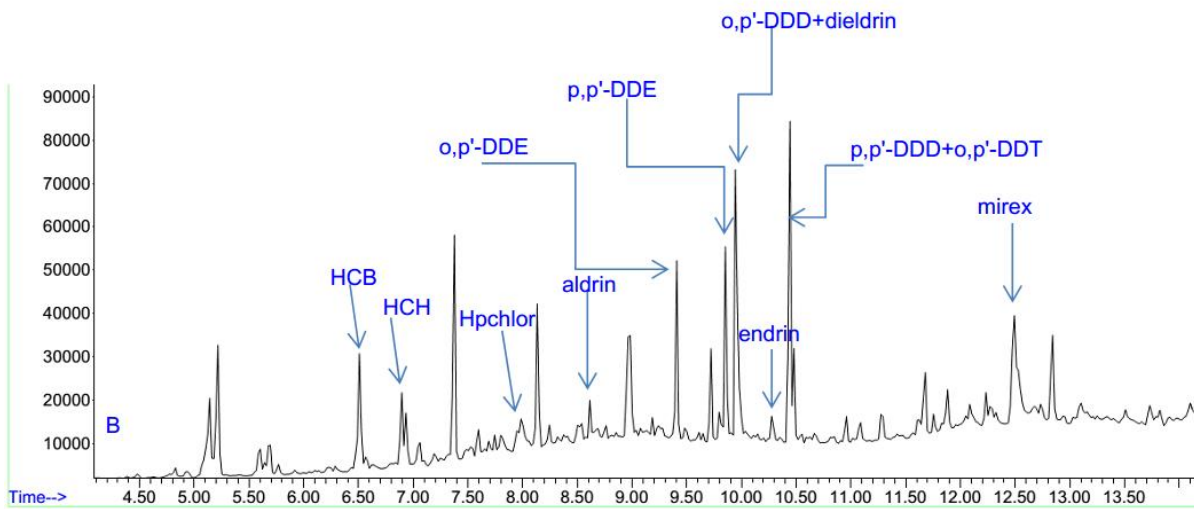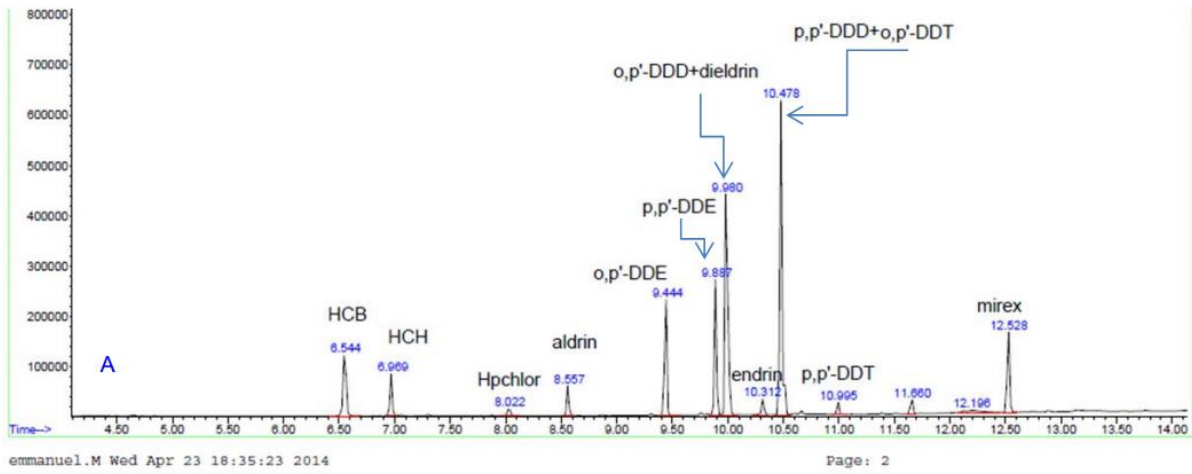
APPENDICES

APPENDIX A: CHROMATOGRAMS

A.1 PCB Chromatograms: A- mixture of 8 PCB standards, B-clean sediment extract fortified with 0.125 ppm of PCB standard mixture
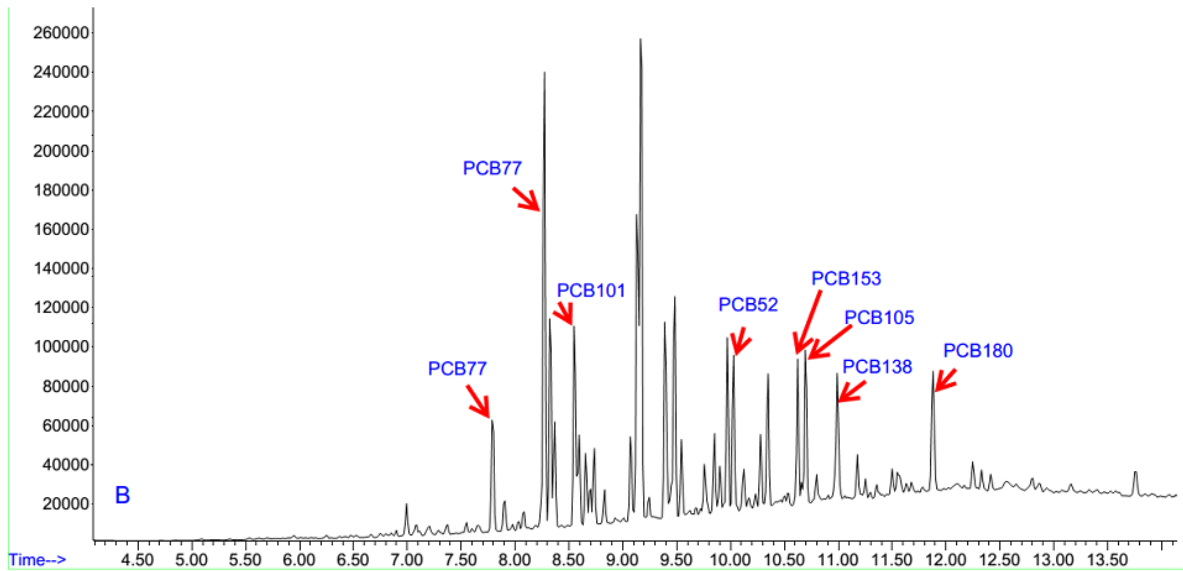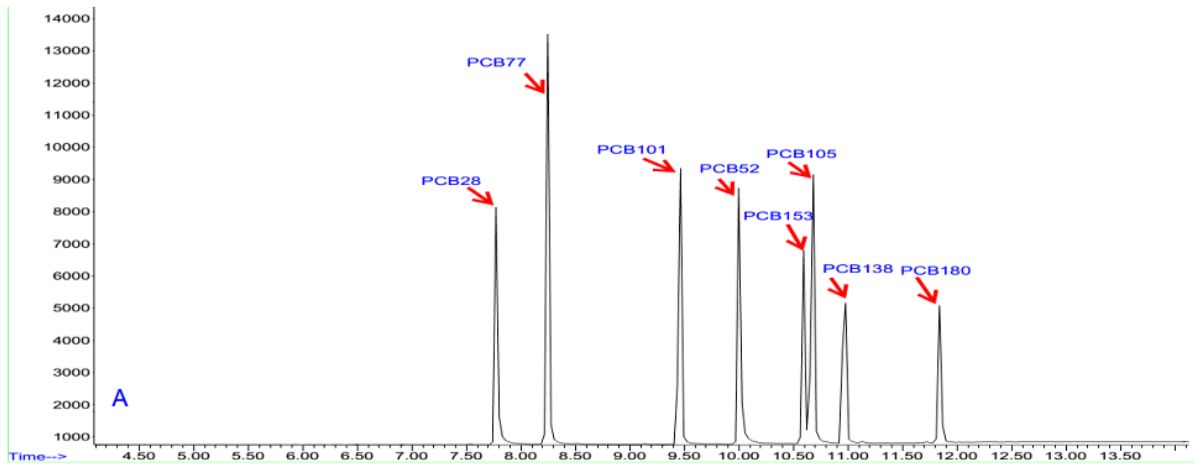
A.2 OCP chromatograms: A-mixture of 12 OCP standards, B- clean water extract fortified with 0.125 ppm of OCP standard mixture

APPENDIX B: EXAMPLES OF CALIBRATION CURVES AND CALCULATIONS

B.1 Example of PCB calibration curves: PCB180 and calculation of its concentration in water/pore water samples.

conc.(µg/mL)	peak area
0.25	9022
0.5	25496
1	50956
2	111010
4	251902
8	547255

PCB180 calibration curve 1

$y = 69596x - 16751$
$R^2 = 0.9981$
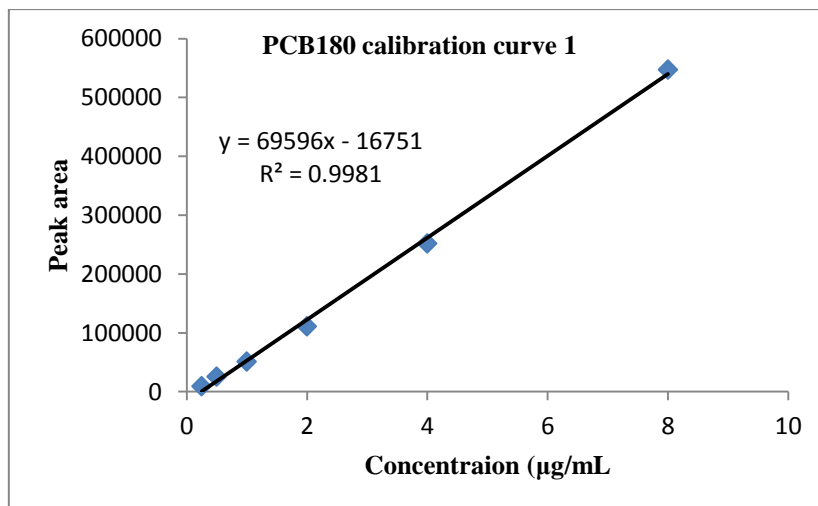
conc. (µg/mL)	peak area
0.25	9071
0.5	26062
1	50172
2	110089
4	251140
8	547132

PCB180 calibration curve 2

$y = 69570x - 17009$
$R^2 = 0.9979$
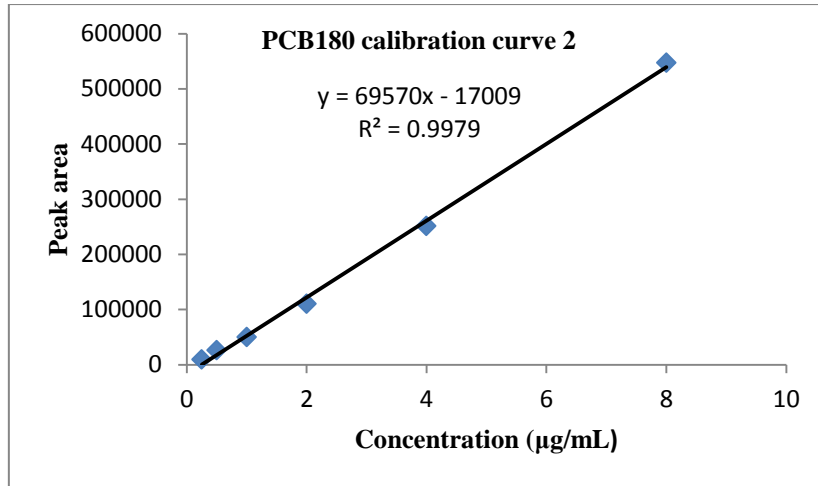
conc. (µg/mL)	peak area
0.25	8989
0.5	24677
1	49454
2	111907
4	249635
8	546506

PCB180 Calibration curve 3

$y = 69518x - 17290$
$R^2 = 0.998$
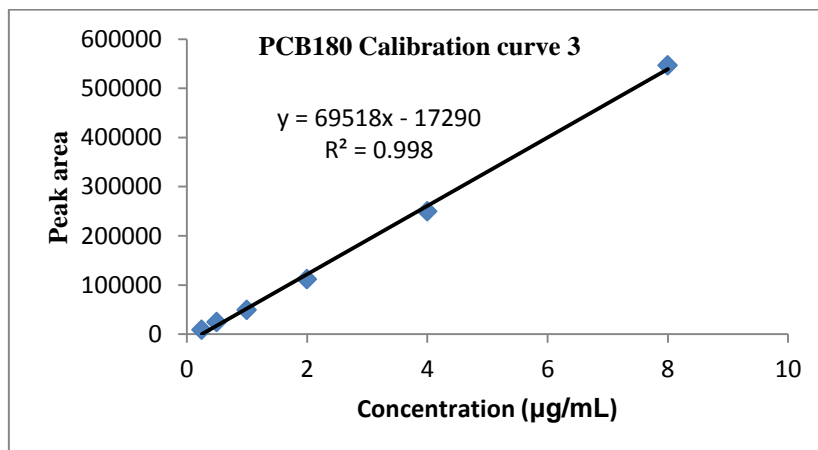
Run	slope	intercept	R^2
1	69596	-16751	0.9981
2	69570	-17009	0.9981
3	69518	-17290	0.9979
Mean	69561.33	-17016.67	0.9980

Overall equation: y = 69561.33x - 17016.67

Solving equation by replacing "**y**" by three peak areas of PCB180 obtained by running, for example, Inanda Dam inlet winter water extract three times in the GC-MS system, we obtain:

x_1 = 0.76243525 µg/mL x_2 = 0.76301028 µg/mL x_3 = 0.78310765 µg/mL

Since 1 L (1000 mL) of water was extracted and the extract concentrated to 2 mL, if we consider: C_{ex} = the concentration of PCB180 in the Inanda Dam inlet winter water extract in ng/mL.

V_{ex} = The Inanda Dam inlet concentrated extract volume in mL.

V_s = The Inanda Dam inlet water sample volume in mL.

$C_{PCB180,water}$ = Concentration of PCB180 in water of Inanda Dam inlet in ng/mL

Therefore: $C_{1PCB180,water} = \dfrac{C_{ex} * Vex}{V_s}$

$$= \frac{\frac{(0.76243525 * 1000)ng}{mL} * 2mL}{1000\ mL}$$

$$= 1.5248705\ ng/mL$$

$C_{2PCB180,water} = \dfrac{C_{ex} * Vex}{V_s}$

$$= \frac{\frac{(0.76301028 * 1000)ng}{mL} * 2mL}{1000\ mL}$$

$$= 1.52602056\ ng/mL$$

$C_{3PCB180,water} = \dfrac{C_{ex} * Vex}{V_s}$

$$= \frac{\frac{(0.78310765 * 1000)ng}{mL} * 2mL}{1000\ mL}$$

$$= 1.5662153\ ng/mL$$

The standard deviation of the three concentrations was calculated, using Microsoft excel and was found to be 0.02.

The final concentration was given by calculation of the mean of $C_{1PCB180,water}$, $C_{2PCB180,water}$ and $C_{3PCB180,water}$.

$$C_{PCB180,water} = \frac{C_{1PCB180,water} + C_{2PCB180,water} + C_{3PCB180,water}}{3}$$

$$= \frac{1.5248705\frac{ng}{mL} + 1.52602056\frac{ng}{mL} + 1.5662153\frac{ng}{mL}}{3}$$

$$= 1.53903545 \, ng/mL$$

Finally the concentration of the congener PCB180 in Inanda Dam inlet water, during winter, was 1.54 ±0.02 ng/mL.

B.2 Example of OCP calibration curves: *o,p'*-DDE and calculation of its concentration in soil/sediment samples.

conc. (µg/mL)	peak area
0.25	9807
0.5	34813
1	76825
2	129863
4	333226
8	658199

o,p'-DDE calibration curve 1

$y = 83985x - 13339$
$R^2 = 0.9974$
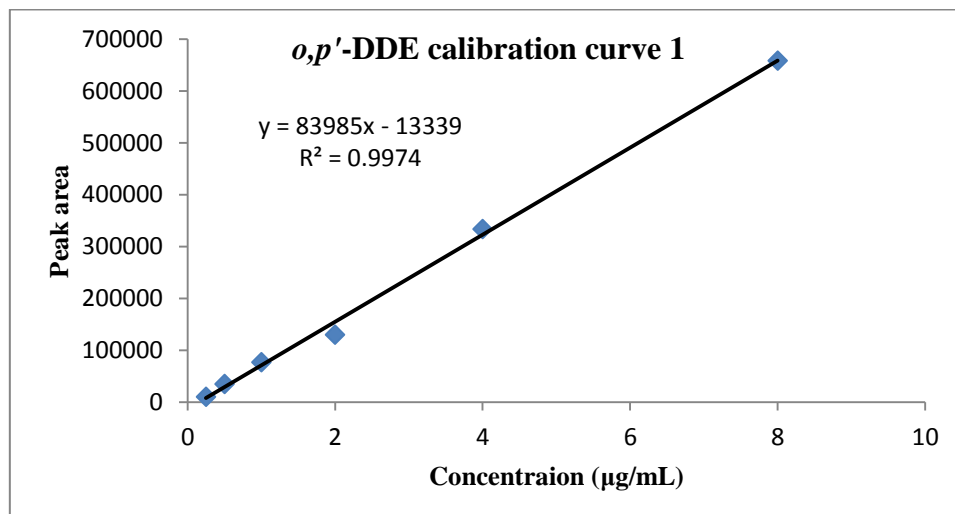
conc. (µg/mL)	peak area
0.25	9719
0.5	33621
1	75400
2	133030
4	332102
8	636256

o,p'-DDE calibration curve 2

$y = 81338x - 10157$

$R^2 = 0.9976$
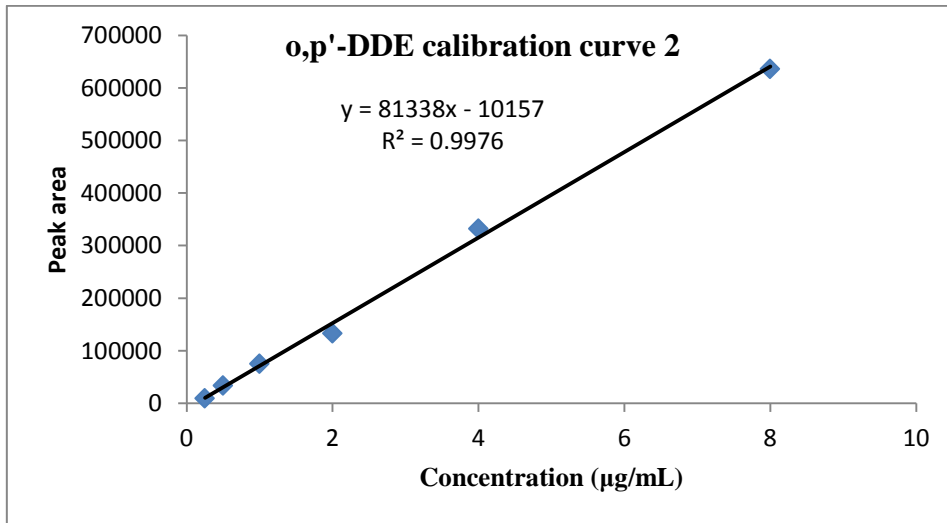
conc. (µg/mL)	peak area
0.25	10593
0.5	34425
1	79105
2	132940
4	335102
8	657142
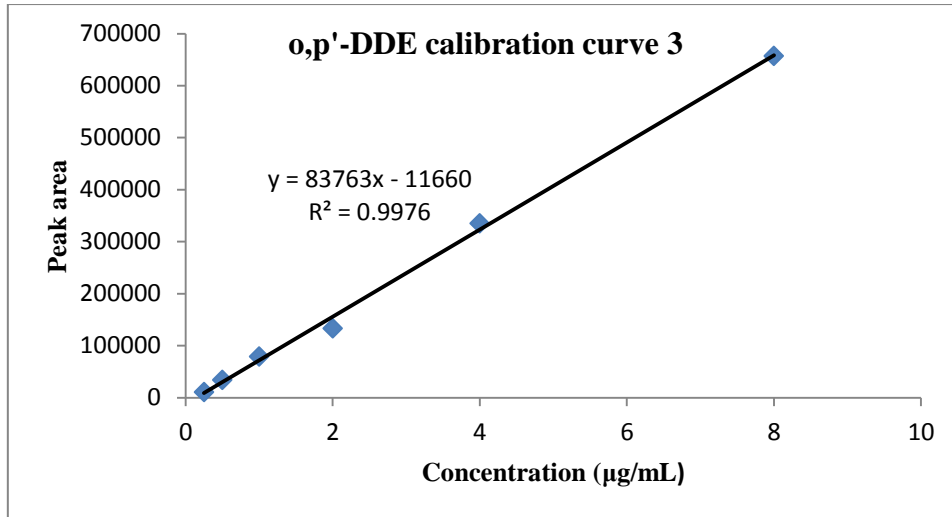
run	slope	intercept	R^2
1	83985	-13339	0.9974
2	81338	-10157	0.9976
3	83763	-11660	0.9976
Mean	83028.67	-11718.67	0.9975

Overall equation: y = 83028.67x - 11718.67

Solving equation by replacing "y" by three peak areas of *o,p*-DDE obtained by running, for example, Midmar Dam inlet spring river bank soil extract three times in the GC-MS system, we obtain:

x₁ = 0.66054778 µg/mL   **x₂** = 0.56058231 µg/mL   **x₃** = 0.75516570 µg/mL

Since 60 g of soil was extracted and the extract concentrated to 2 mL, if we consider:

C_{ex} = the concentration of *o,p*-DDE in the Midmar Dam outlet spring river bank soil concentrated extract in ng/mL,

V_{ex} = the extract volume in mL,

W_S = the sample weight (dry weight) in g,

$C_{o,p'-DDE,soil}$ = Concentration of *o,p*'-DDE in soil of Midmar Dam outlet in ng/mL,

Therefore: Therefore: $C_{1o,p-DDE,soil} = \dfrac{C_{ex*Vex}}{W_S}$

$$= \frac{\frac{(0.66054778 * 1000)ng}{mL} * 2mL}{60\ g}$$

$$= 22.0182593\ ng/g$$

$$C_{2o,p-DDE,soil} = \frac{C_{ex*Vex}}{W_S}$$

$$= \frac{\frac{(0.56058231 * 1000)ng}{mL} * 2mL}{60\ g}$$

$$= 18.686077\ ng/g$$

$$C_{3o,p-DDE,soil} = \frac{C_{ex*Vex}}{W_S}$$

$$= \frac{\frac{(0.75516570 * 1000)ng}{mL} * 2mL}{60\ g}$$

$$= 25.17219\ ng/g$$

The standard deviation of the three concentrations was calculated using Microsoft excel and was obtained to be 3.24

The mean of the three different concentrations, $C_{1o,p-DDE,soil}$, $C_{2o,p-DDE,soil}$ and $C_{3o,p-DDE,soil}$, were calculated to obtain the final concentration:

$$C_{o,p-DDE,soil} = \frac{C_{1o,p-DDE,soil} + C_{2o,p-DDE,soil} + C_{3o,p-DDE,soil}}{3}$$

$$= \frac{22.0182593\frac{ng}{g} + 18.686077\frac{ng}{g} + 25.17219\frac{ng}{g}}{3}$$

$$= 21.9588421\ ng/g$$

Finally the concentration of the *o,p'*-DDE in Midmar Dam outlet river bank soil, during spring, was 21.96 ±3.24 ng/g, dw.

APPENDIX C: GRAPHS OF CONCENTRATIONS OF ANALYTES

C.1. A-Concentrations of individual PCB congeners in water at each site for winter water samples. B- Total concentrations of PCBs at each site in winter water samples
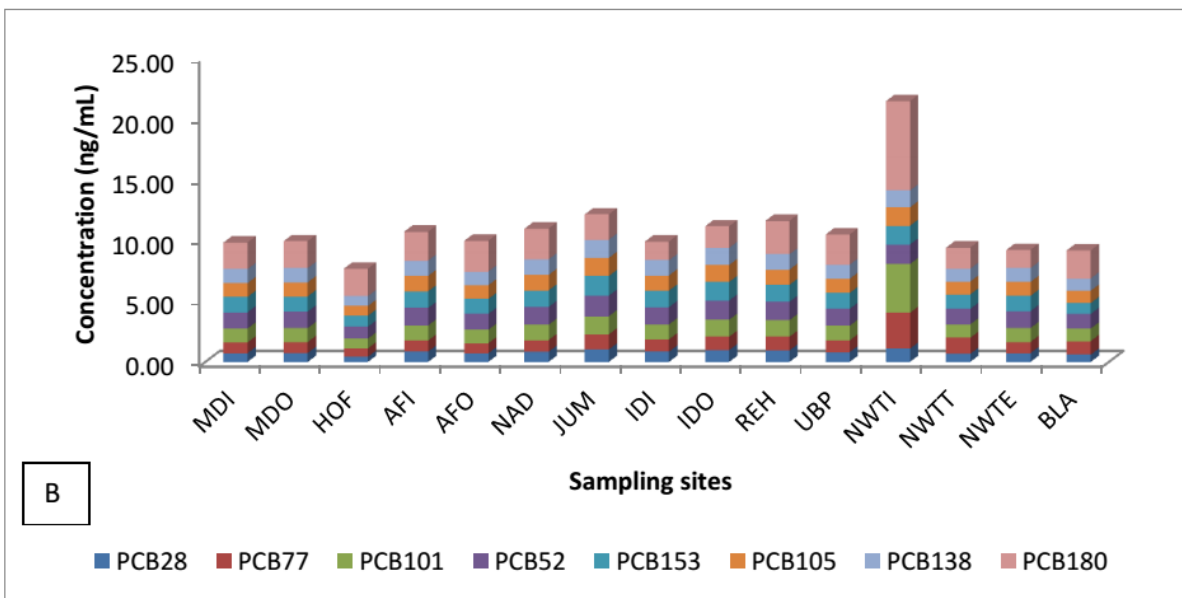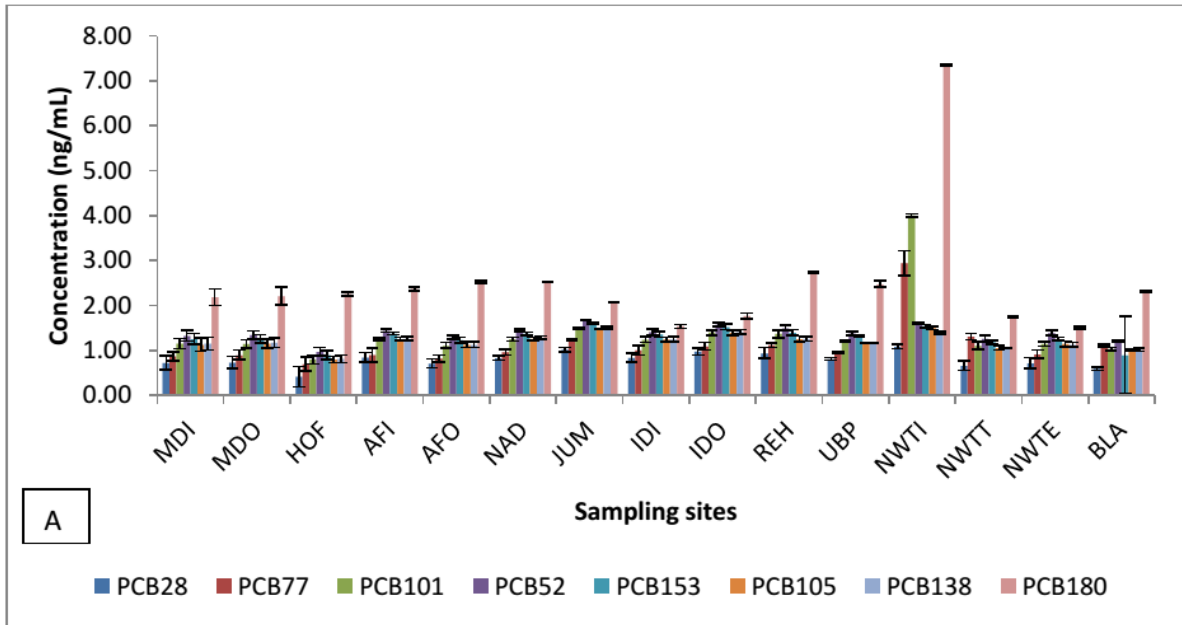
C.2. A- Concentrations of individual PCB congeners in pore water at each site for winter water samples. B- Total concentrations of PCBs at each site in winter pore water samples
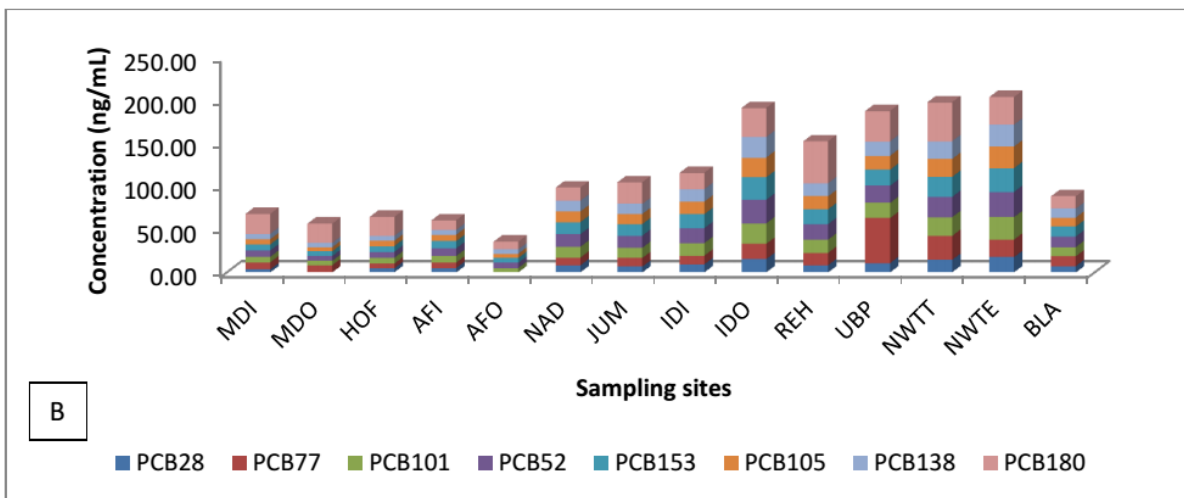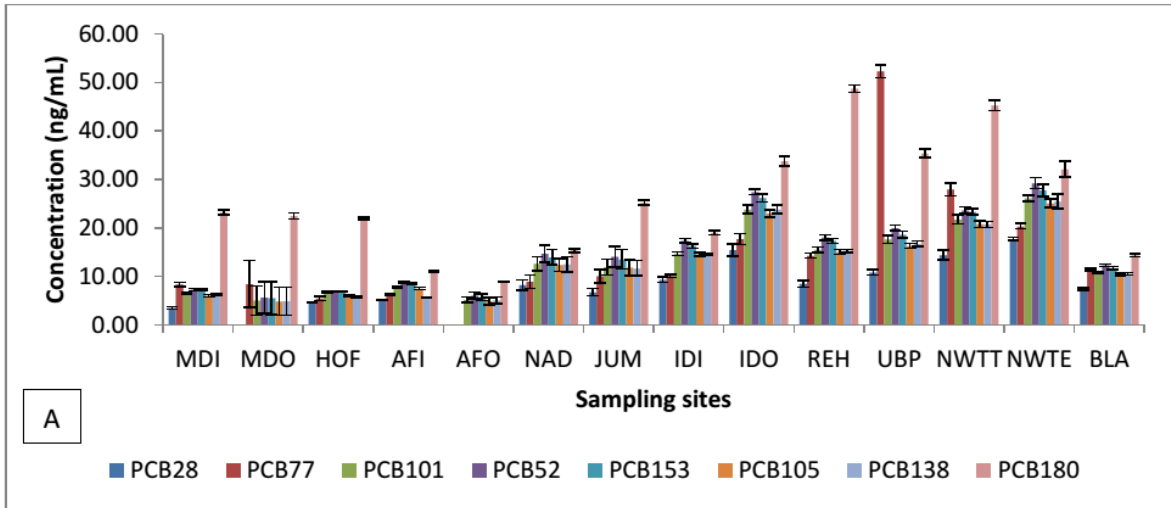
C.3. A-Concentrations of individual PCB sediment at each site for winter water samples. B- Total concentrations of PCBs at each site in winter pore water samples

C.4 Total average concentrations in each matrix for winter samples

APPENDIX D: INDIVIDUAL PCB CONCENTRATIONS IN SUMMER, AUTUMN AND SPRING

D.1 Individual PCB concentrations in summer surface water samples

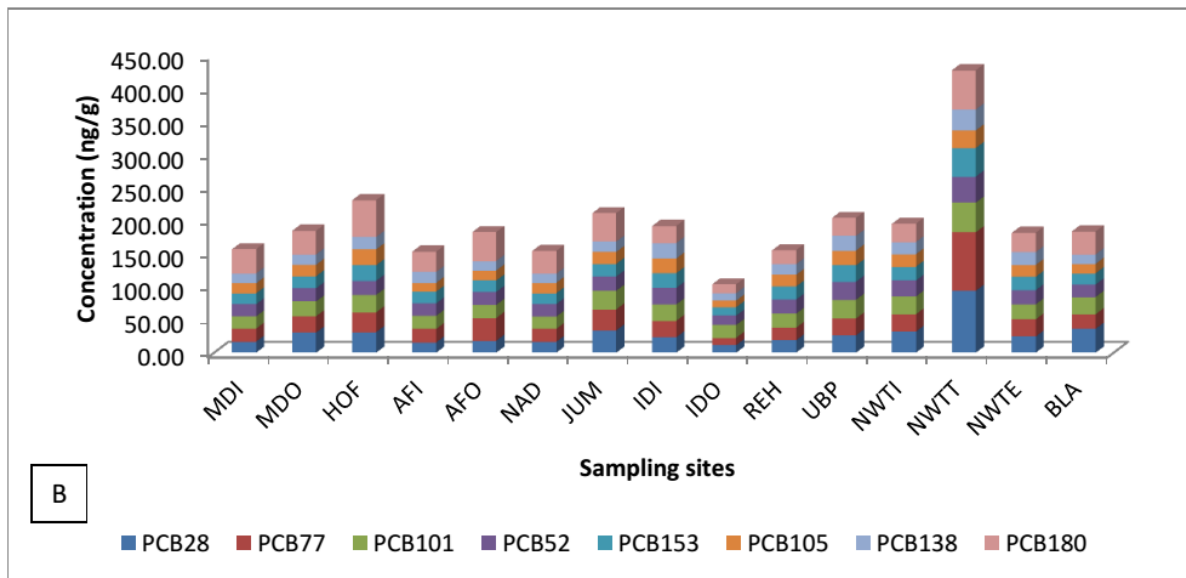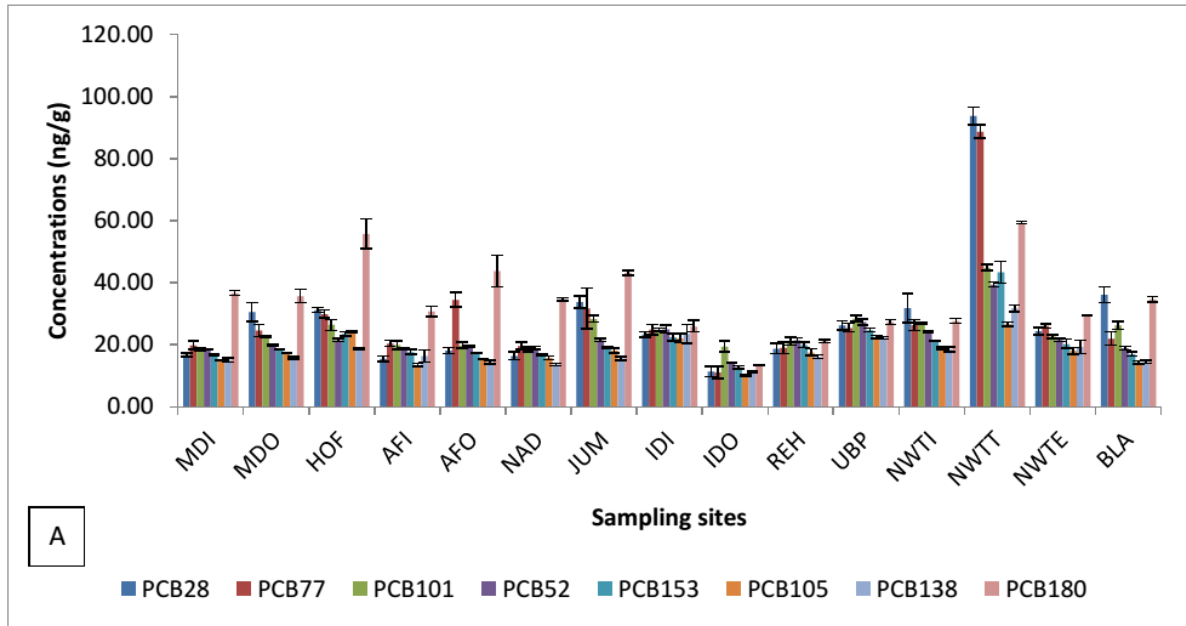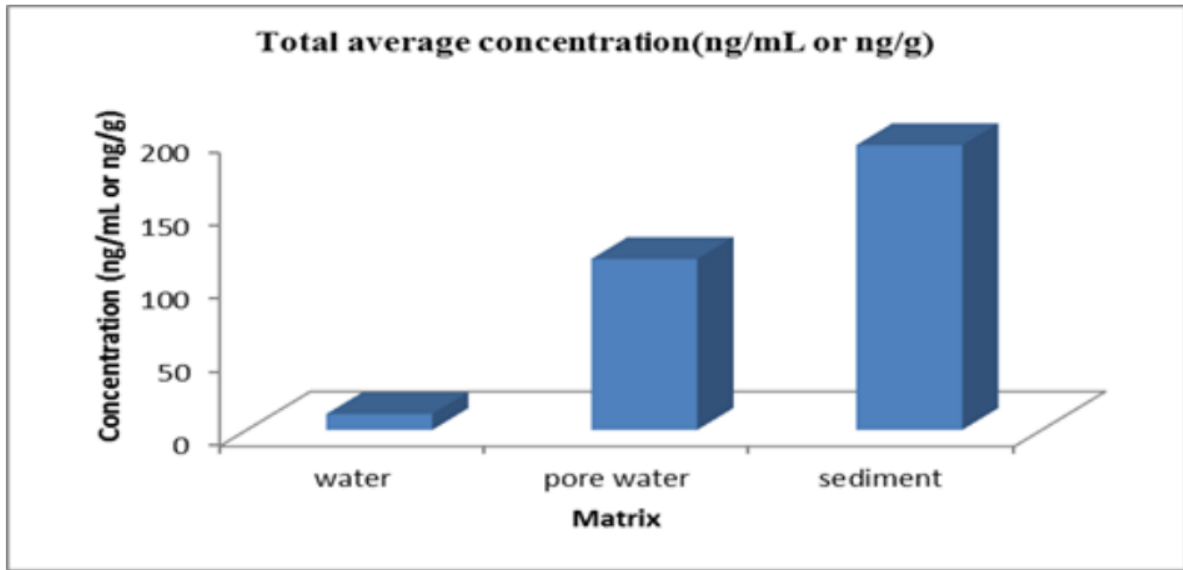| Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
				concentration (ng/mL)					
MDI	0.19±0.19	0.22±0.02	0.42±0.03	0.48±0.03	0.49±0.07	0.34±0.03	0.37±0.02	0.83±0.14	3.34±0.37
MDO	0.58±0.58	0.57±0.02	0.76±0.06	1.09±0.04	0.96±0.04	0.74±0.06	0.75±0.04	1.36±0.10	6.80±0.42
HOF	0.39±0.39	0.47±0.11	0.26±0.27	0.84±0.12	0.70±0.07	0.51±0.03	0.55±0.02	2.44±0.04	6.16±0.69
AFI	0.53±0.53	0.63±0.03	0.79±0.02	0.93±0.10	0.82±0.02	0.68±0.03	0.71±0.02	1.18±0.04	6.26±0.30
AFO	0.33±0.33	0.39±0.02	0.56±0.02	0.63±0.02	0.61±0.01	0.48±0.02	0.54±0.02	0.84±0.03	4.38±0.18
NAD	0.41±0.41	0.55±0.14	0.68±0.13	0.74±0.09	0.90±0.11	0.58±0.10	0.63±0.10	1.03±0.04	5.52±0.86
JUM	0.64±0.64	0.72±0.02	0.87±0.04	1.04±0.14	0.90±0.03	0.75±0.04	0.80±0.03	1.11±0.06	6.84±0.42
IDI	0.56±0.56	0.66±0.06	0.82±0.13	0.87±012	0.98±0.02	0.71±0.09	0.77±0.11	1.12±0.11	6.50±0.81
IDO	0.63±0.63	0.71±0.25	0.88±017	1.25±0.41	0.96±0.15	0.76±0.13	0.80±0.15	1.18±0.12	7.18±1.59
REH	0.33±0.33	0.51±0.13	0.59±0.10	1.03±0.14	0.83±0.08	0.50±0.07	0.54±0.09	1.12±0.03	5.45±0.77
UBP	0.32±0.32	0.39±0.05	0.55±0.04	0.73±0.12	0.61±0.04	0.46±0.05	0.48±0.02	0.84±0.06	4.38±0.41
NWTI	0.39±0.39	0.45±0.03	0.56±0.02	0.62±0.03	0.63±0.07	0.51±0.07	0.52±0.07	1.03±0.04	4.71±0.38
NWTT	0.44±0.44	0.51±0.14	0.64±0.07	0.66±0.03	0.55±0.15	0.50±0.08	0.56±0.09	0.56±0.12	4.42±0.82
NWTE	0.61±0.61	0.65±0.08	0.77±0.04	0.83±0.04	0.83±0.06	0.63±0.02	0.66±0.03	1.08±0.05	6.06±0.41
BLA	0.67±0.67	0.84±0.20	0.90±0.18	0.93±0.15	1.10±0.15	0.77±0.14	0.82±0.15	1.15±0.18	7.18±1.36
∑PCB	7.00±1.40	8.26±1.34	10.04±1.32	12.69±1.58	11.89±0.07	8.92±0.96	9.49±0.97	16.88±1.15	85.18±9.79
min	0.19±0.03	0.22±0.02	0.26±0.02	0.48±0.02	0.49±0.01	0.34±0.02	0.37±0.02	0.56±0.03	3.34±018
mean	0.47±0.09	0.55±0.09	0.67±0.09	0.85±0.11	0.79±0.07	0.59±0.06	0.63±0.06	1.13±0.08	5.68±0.65
max	0.670.21	0.84±0.26	0.90±0.27	1.25±0.41	1.10±0.15	0.77±0.14	0.82±0.15	2.44±0.18	7.18±1.59

D.2 Individual PCB concentrations in summer surface pore water samples

Site	Concentration (ng/mL)								
	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	2.84±0.17	3.30±0.08	4.19±0.15	3.85±0.21	3.97±0.11	3.07±0.11	3.59±0.26	7.04±1.84	31.85±2.94
MDO	1.32±0.67	1.55±0.86	1.97±1.08	1.91±1.09	1.91±1.09	1.41±0.76	1.54±0.84	8.06±0.15	19.65±6.55
HOF	0.95±0.11	0.11±0.06	2.34±0.47	2.04±0.30	2.04±0.34	1.24±0.24	1.48±0.16	9.78±0.59	19.99±2.27
AFI	2.09±0.02	3.11±0.38	4.32±0.35	3.40±0.19	3.24±0.08	2.33±0.05	4.53±0.22	9.64±0.12	32.65±1.40
AFO	0.86±0.09	1.04±0.17	1.83±0.22	2.06±0.16	1.88±0.23	1.18±0.08	1.51±0.18	3.87±0.14	14.23±1.26
NAD	3.24±0.55	3.77±0.74	5.41±0.77	5.51±0.91	5.24±0.66	4.01±0.65	4.55±0.65	6.94±0.15	38.67±5.08
JUM	4.57±0.42	5.13±0.76	7.25±0.81	7.03±0.93	6.90±0.76	5.40±0.55	5.96±0.59	12.66±0.69	54.92±5.49
IDI	2.74±0.36	3.23±0.50	6.45±0.55	6.80±0.66	6.46±0.52	4.74±0.37	5.30±0.46	15.70±0.49	51.41±3.91
IDO	1.78±0.43	3.90±0.32	6.53±0.17	7.83±0.42	6.99±0.35	4.55±0.35	5.50±0.34	13.36±0.34	50.43±2.72
REH	3.82±0.40	5.90±0.58	7.89±0.38	8.59±0.62	8.19±0.44	6.17±0.37	6.70±0.38	12.87±0.51	60.14±3.69
UBP	2.20±0.13	3.83±0.11	6.09±0.17	6.55±0.28	6.45±0.18	4.40±0.17	5.06±0.05	11.45±0.18	46.04±1.26
NWTT	2.10±0.14	2.11±0.43	5.99±0.14	6.61±0.16	5.95±0.07	3.81±0.16	4.47±0.30	13.46±0.18	44.51±1.59
NWTE	0.93±0.16	0.99±0.73	5.16±0.48	5.85±0.27	5.13±0.33	2.99±0.26	3.99±0.34	14.93±0.30	39.97±2.87
BLA	1.64±0.43	1.48±0.13	3.18±0.36	3.55±0.27	3.18±0.22	1.93±0.26	2.44±0.37	7.11±0.36	24.51±2.40
∑PCB	31.09±4.06	39.46±5.86	68.61±	71.56±6.47	67.55±5.39	47.23±4.37	56.61±5.13	146.86±6.02	528.97±43.44
min	0.86±0.02	0.11±0.06	1.83±	1.91±0.16	1.88±0.07	1.18±0.05	1.48±0.05	3.87±0.12	14.23±1.26
mean	2.22±0.29	2.82±0.42	4.90±	5.11±0.46	4.82±0.39	3.37±0.31	4.04±0.37	10.49±0.43	37.78±3.10
max	4.57±0.67	5.90±0.86	7.89±	8.59±1.09	8.19±1.09	6.17±0.76	6.70±0.84	15.70±1.84	60.14±6.55

D.3 Individual PCB concentrations in summer surface sediment samples

	Concentration (ng/g)								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	8.75±1.35	6.57±2.26	7.66±0.30	13.50±2.26	18.05±3.63	7.45±1.80	13.05±1.23	29.41±2.55	104.44±15.39
MDO	5.74±0.43	5.42±0.73	5.58±0.40	11.22±0.98	12.25±1.33	9.02±0.66	8.82±0.37	30.53±2.14	88.60±7.04
HOF	5.08±0.84	3.16±0.60	4.12±0.72	9.93±1.18	12.03±0.76	9.54±0.24	8.33±1.15	37.92±1.09	90.13±6.57
AFI	9.50±0.74	6.72±1.24	8.11±2.75	13.61±0.97	18.33±3.55	15.02±0.44	14.64±1.72	59.21±3.23	145.14±14.65
AFO	14.39±3.77	4.99±1.47	9.69±2.18	18.09±2.05	19.03±2.75	15.36±2.36	14.86±2.10	26.56±1.27	122.98±17.95
NAD	2.07±0.52	3.30±0.52	2.69±0.22	7.30±0.23	8.17±0.44	4.46±0.17	4.88±0.55	13.96±0.49	46.83±3.15
JUM	1.30±0.52	5.62±0.72	3.46±0.68	6.31±0.17	6.95±0.54	3.82±0.58	4.09±0.47	13.24±3.18	44.79±7.34
IDI	0.74±1.11	5.32±0.56	3.03±0.53	6.05±0.57	5.24±0.55	2.99±0.31	3.28±0.56	13.68±2.50	40.32±6.19
IDO	5.00±0.63	3.45±0.86	4.22±1.05	9.76±0.99	10.86±1.05	7.37±0.88	7.52±0.96	19.34±1.85	67.52±8.78
REH	5.05±1.15	2.42±0.23	3.74±0.47	5.80±0.58	15.69±1.63	6.19±0.48	6.09±0.72	13.85±1.87	58.83±6.44
UBP	4.46±0.46	1.28±0.28	2.87±0.48	9.38±1.50	13.24±2.08	7.49±0.76	7.53±0.46	18.00±0.16	64.27±6.28
NWTI	27.65±0.57	4.67±0.24	16.16±3.76	2.20±1.15	54.13±3.78	0.57±0.48	34.16±2.00	73.58±2.20	213.10±14.98
NWTT	25.38±0.38	16.12±0.38	20.75±0.60	27.97±0.13	34.61±2.55	13.73±1.92	47.71±2.25	71.95±3.20	258.22±12.18
NWTE	18.31±1.15	14.01±1.22	16.16±1.49	17.41±2.19	14.80±1.27	11.68±0.58	31.07±3.70	48.58±0.47	172.03±12.45
BLA	5.51±1.53	2.89±0.20	4.20±3.98	15.64±3.52	9.96±2.54	9.70±2.68	19.19±2.27	35.62±2.93	102.70±20.70
∑PCB	138.94±16.20	85.96±11.50	112.45±19.62	174.17±18.48	253.33±28.45	124.41±14.34	225.21±22.50	505.44±29.12	1619.91±160.20
min	0.74±0.43	1.28±0.20	2.69±0.22	2.20±0.13	5.24±0.44	0.57±0.17	3.28±0.37	13.24±0.16	40.32±3.15
mean	9.26±1.08	5.73±0.77	7.50±1.31	11.61±1.23	16.89±1.90	8.29±0.96	15.01±1.50	33.70±1.94	107.99±10.68
max	27.65±3.77	16.12±2.26	20.75±3.98	27.97±3.52	54.13±3.78	15.36±2.68	47.71±4.27	73.58±3.23	258.22±20.70

D.4 Individual PCB concentrations in summer surface soil samples

				Concentration (ng/mL)					
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	1.39±0.57	0.81±1.16	6.72±0.95	14.40±0.81	9.73±1.09	5.87±1.16	5.36±1.18	15.16±2.18	59.45±9.09
MDO	2.41±1.44	3.13±1.30	8.45±1.02	18.04±1.89	9.72±1.25	7.36±1.31	7.09±1.66	14.58±1.72	70.77±11.58
HOF	5.07±2.31	3.86±2.34	9.83±2.22	19.90±3.36	11.38±2.50	8.75±2.18	8.77±2.44	18.64±2.15	86.20±19.51
AFI	nd	nd	5.58±0.75	13.04±0.91	6.75±0.91	4.16±0.49	3.43±0.80	11.99±0.98	44.95±6.61
AFO	4.11±2.21	3.41±1.75	8.20±1.76	16.93±1.73	10.41±1.66	7.27±1.49	6.92±1.29	15.33±2.27	72.58±14.14
NAD	3.74±1.75	3.34±1.32	9.30±1.55	16.52±2.44	10.36±1.67	7.87±1.36	7.84±1.72	14.80±1.82	73.77±13.63
JUM	3.72±1.40	2.47±1.44	7.94±1.67	15.72±1.71	9.49±1.94	7.06±1.81	7.05±1.33	19.16±0.89	72.63±12.18
IDI	2.15±1.27	1.80±1.47	6.79±1.41	14.51±1.25	7.98±1.54	5.93±1.37	5.54±1.15	18.85±1.79	63.54±11.24
IDO	5.97±2.61	6.21±2.26	11.50±2.28	21.14±2.87	12.75±2.25	10.08±1.83	10.46±2.03	25.25±2.71	103.36±18.84
REH	1.94±1.60	nd	4.74±1.02	11.93±1.44	6.18±1.25	3.74±1.21	3.46±1.02	26.53±2.35	58.53±11.21
UBP	5.15±1.79	5.70±2.11	12.58±2.54	22.14±2.86	15.03±2.50	10.34±2.71	10.76±2.61	29.16±3.81	110.85±20.93
NWTT	7.33±2.24	7.03±0.47	11.92±0.60	55.29±2.57	59.53±2.32	23.07±0.17	34.23±1.90	77.32±1.18	275.74±11.45
NWTE	nd	0.08±2.35	3.13±2.46	16.90±1.02	2.81±1.20	12.08±1.02	21.81±4.82	74.66±9.59	131.47±23.95
BLA	nd	nd	4.88±1.33	18.61±3.47	6.61±0.88	6.76±1.43	3.46±1.30	56.18±4.82	96.50±15.39
∑PCB	42.98±22.69	37.84±21.20	111.57±21.57	275.08±28.32	178.71±22.94	120.35±19.53	136.18±25.25	417.62±38.26	1320.33±199.76
min	nd	nd	3.13±0.60	11.93±0.81	2.81±0.88	3.74±0.17	3.43±0.80	11.99±0.89	44.95±6.61
mean	3.07±1.62	2.70±1.51	7.97±1.54	19.65±2.02	12.77±1.64	8.60±1.40	9.73±1.80	29.83±2.73	94.31±14.27
max	7.33±2.61	7.03±2.35	12.58±2.54	55.29±3.47	59.53±2.50	23.07±2.71	34.23±4.82	77.32±9.59	275.74±23.95

nd = not detected

D.5 Individual PCB concentrations in autumn surface water samples

	Concentrations of PCBs in water (ng/mL)								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	1.82±0.02	0.93±0.06	0.81±0.03	0.25±0.06	0.42±0.30	0.23±0.02	0.01±0.03	1.51±0.24	5.98±0.76
MDO	0.76±0.11	0.41±0.02	0.78±0.02	0.32±0.05	0.39±0.03	0.35±0.02	0.13±0.02	3.20±0.04	6.35±0.31
HOF	1.56±0.06	0.65±0.13	0.87±0.05	0.13±0.27	0.31±0.01	0.33±0.05	0.11±0.02	1.14±0.13	5.11±0.73
AFI	1.32±0.02	0.62±0.05	0.62±0.02	0.10±0.04	0.16±0.04	0.15±0.02	nd	0.60±0.04	3.58±0.28
AFO	0.45±0.06	0.23±0.04	0.60±0.03	0.18±0.04	0.21±0.02	0.22±0.03	0.01±0.03	0.76±0.03	2.64±0.29
NAD	1.16±0.04	0.56±0.04	0.65±0.01	0.15±0.01	0.21±0.03	0.18±0.03	nd	1.16±0.04	4.07±0.20
JUM	2.65±0.02	0.96±0.44	0.87±0.02	0.22±0.05	0.32±0.08	nd	0.01±0.02	0.49±0.13	5.52±0.95
IDI	1.57±0.03	0.45±0.03	0.70±0.02	0.11±0.01	0.15±0.02	0.15±0.18	nd	0.69±0.17	3.82±0.32
IDO	1.12±0.04	0.55±0.02	0.48±0.00	nd	0.02±0.01	nd	nd	0.24±0.12	2.43±0.27
REH	1.44±0.03	0.67±0.02	0.76±0.02	0.23±0.02	0.28±0.02	0.26±0.02	0.02±0.03	3.02±0.04	6.68±0.21
UBP	1.65±0.02	0.74±0.04	0.74±0.03	0.19±0.04	0.18±0.03	0.21±0.03	0.01±0.03	1.22±0.06	4.94±0.28
NWTI	2.46±0.09	1.20±0.15	1.19±0.09	0.73±0.43	0.59±0.14	0.52±0.10	0.54±0.09	1.51±0.08	8.73±1.18
NWTT	2.89±0.17	0.51±0.22	0.92±0.07	0.75±0.01	0.52±0.08	0.22±0.09	0.08±0.05	1.45±0.44	7.35±1.14
NWTE	1.98±0.07	0.59±0.02	0.83±0.07	0.22±0.07	0.33±0.03	0.38±0.11	0.15±0.09	0.88±0.13	5.36±0.59
BLA	2.80±0.07	0.93±0.17	0.98±0.05	0.25±0.02	0.35±0.03	0.30±0.24	0.08±0.05	1.52±0.02	7.21±0.66
∑PCB	25.64±0.84	10.00±1.47	11.81±0.54	3.84±1.15	4.45±0.89	3.49±0.99	1.17±0.57	19.37±1.72	79.77±8.16
min	0.45±0.02	0.23±0.02	0.48±0.00	nd	0.02±0.01	nd	nd	0.24±0.02	2.43±0.20
mean	1.71±0.06	0.67±0.10	0.79±0.04	0.26±0.08	0.30±0.06	0.23±0.07	0.08±0.04	1.29±0.11	5.32±0.54
max	2.89±0.17	1.20±0.44	1.19±0.09	0.75±0.43	0.59±0.30	0.52±0.24	0.54±0.09	3.20±0.44	8.73±1.18

nd = not detected

D.6 Individual PCB concentrations in autumn pore water samples

Site	Concentrations of PCBs in pore water (ng/mL)								
	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	12.83±1.04	6.93±1.17	5.49±0.99	1.29±1.30	1.89±0.92	1.25±0.99	0.03±0.16	5.80±1.37	35.51±7.95
MDO	10.88±1.04	4.67±1.65	3.50±0.98	1.28±0.22	1.12±0.16	0.99±0.30	0.35±0.22	5.21±0.57	27.99±5.14
HOF	6.71±0.83	2.95±0.87	3.68±0.88	1.08±0.88	1.49±0.12	1.02±0.74	0.50±0.36	5.88±1.27	23.32±5.95
AFI	6.78±0.63	3.70±0.49	4.12±0.89	1.07±0.64	1.71±0.45	1.32±1.05	0.20±0.21	6.61±2.30	25.51±6.65
AFO	6.64±0.53	2.96±0.41	3.24±0.22	0.99±0.68	1.20±0.09	1.05±0.97	0.28±0.21	7.09±0.98	23.45±4.09
NAD	14.32±2.27	4.35±0.90	5.28±0.79	0.66±0.47	4.96±1.31	1.00±1.37	1.06±0.69	10.31±1.09	41.95±8.90
JUM	14.53±1.07	1.89±1.02	3.42±1.05	0.63±1.34	2.13±0.13	1.23±1.50	0.09±0.65	1.11±4.48	25.03±11.24
IDI	16.10±1.66	7.62±1.27	10.39±2.02	3.02±1.66	3.34±0.89	3.17±2.11	1.27±0.39	13.77±1.65	58.67±11.65
IDO	19.52±1.63	11.70±2.16	13.54±2.57	2.74±2.52	6.97±5.28	4.05±3.02	0.43±0.12	17.71±2.52	76.65±19.83
REH	13.86±1.51	5.95±1.61	11.38±2.39	3.13±1.72	4.03±0.22	3.26±2.32	0.96±0.40	16.31±5.02	58.89±15.19
UBP	12.43±1.59	5.66±0.67	11.14±1.53	3.55±1.80	4.58±0.68	3.71±1.93	1.33±1.23	17.90±1.91	60.31±11.34
NWTT	9.83±1.11	9.34±1.06	13.38±2.22	5.54±2.31	6.40±0.09	5.21±1.66	3.14±0.57	10.07±0.78	62.91±9.80
NWTE	10.46±1.12	10.88±1.25	11.92±3.42	1.88±0.78	6.37±0.56	3.39±0.97	2.86±0.68	10.68±2.28	58.45±11.06
BLA	6.10±1.98	4.34±0.59	6.57±0.72	2.65±1.00	3.54±0.25	3.21±1.42	2.10±0.42	12.44±1.28	40.96±7.65
∑PCB	160.99±18.01	82.95±15.11	107.06±20.66	29.51±17.33	49.75±11.17	33.85±20.34	14.60±6.30	140.89±27.51	619.61±136.44
min	6.10±0.53	1.89±0.41	3.24±0.22	0.63±0.22	1.12±0.09	0.99±0.30	0.03±0.12	1.11±0.57	23.32±4.09
mean	11.50±1.29	5.92±1.08	7.65±1.48	2.11±1.24	3.55±0.80	2.42±1.45	1.04±0.45	10.06±1.97	44.26±9.75
max	19.52±2.27	11.70±2.16	13.54±3.42	5.54±2.52	6.97±1.28	5.21±1.02	3.14±1.23	17.90±5.02	76.65±19.83

D.7 Individual PCB concentrations in autumn sediment samples

Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
				Concentrations of PCBs in sediment (ng/g)					
MDI	52.44±0.71	17.37±0.56	23.52±0.93	11.76±0.89	4.64±1.45	13.82±2.93	6.98±1.36	19.23±3.36	149.77±12.20
MDO	55.33±2.12	20.89±0.81	20.91±2.12	8.36±1.40	7.51±3.82	10.31±0.86	7.76±0.90	21.34±1.39	152.41±13.43
HOF	50.77±1.02	15.59±2.34	18.61±2.83	7.31±2.22	7.73±3.16	10.34±2.02	7.93±2.23	19.78±0.73	138.06±16.54
AFI	50.94±1.99	14.03±1.13	22.04±1.50	11.09±0.41	6.99±1.61	13.68±1.23	6.07±0.50	72.62±3.55	197.46±11.92
AFO	42.18±0.26	11.45±1.91	16.43±0.29	5.05±0.45	7.25±1.17	6.34±1.41	0.10±0.03	17.29±3.98	106.09±9.84
NAD	42.79±0.84	8.21±5.30	14.72±0.27	3.07±0.38	5.37±1.06	4.41±0.29	2.78±0.41	21.89±2.50	103.27±11.05
JUM	45.95±1.49	14.53±0.84	15.58±0.83	5.96±1.51	5.64±1.88	5.62±0.10	2.25±0.03	24.64±6.99	120.17±13.67
IDI	44.13±2.39	13.59±4.19	14.81±0.25	3.96±0.84	5.39±0.93	5.05±0.56	1.53±0.04	19.99±3.72	108.45±12.92
IDO	41.05±0.73	30.82±3.10	12.12±1.79	2.53±1.48	3.34±0.89	3.44±0.30	1.92±0.66	23.17±0.42	118.40±9.37
REH	42.88±0.13	14.32±2.28	14.46±0.51	4.09±1.26	3.48±1.25	4.05±0.24	2.01±0.34	19.00±2.78	104.28±8.79
UBP	49.17±0.59	18.61±2.97	16.12±1.03	7.11±1.27	5.91±1.54	6.89±1.25	0.51±1.02	26.48±7.08	130.79±16.76
NWTI	72.07±2.42	17.82±5.59	22.01±0.45	11.61±0.48	13.02±2.38	11.68±0.30	9.72±1.58	32.60±0.48	190.54±13.68
NWTT	61.13±2.71	9.70±1.02	17.13±0.55	5.44±0.06	8.13±2.12	7.63±0.99	3.34±1.05	90.25±0.88	202.74±9.39
NWTE	50.69±1.36	13.19±2.44	18.20±0.38	5.94±0.83	7.07±0.59	6.48±0.49	1.19±0.58	63.04±11.38	165.79±18.05
BLA	82.15±9.11	97.40±3.48	23.55±0.55	7.23±0.93	10.06±2.33	14.77±1.63	8.68±3.33	67.06±0.87	310.89±22.23
∑PCB	783.66±27.88	317.52±37.97	270.24±14.28	100.52±14.42	101.51±26.16	124.50±14.59	62.77±14.40	538.36±50.12	2299.09±199.83
min	41.05±0.13	8.21±0.56	12.12±0.25	2.53±0.06	3.34±0.59	3.44±0.10	0.10±0.03	17.29±0.42	103.27±8.79
mean	52.24±1.86	21.17±2.53	18.02±0.95	6.70±0.96	6.77±1.74	8.30±0.97	4.18±1.67	35.89±3.34	153.27±13.32
max	82.15±9.11	97.40±5.59	23.55±2.83	11.76±2.22	13.02±3.82	14.77±2.93	9.72±1.58	90.25±11.38	310.89±22.23

D.8 Individual PCB concentrations in autumn soil samples

	Concentrations of PCBs in soil (ng/g)								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	46.51±1.54	7.10±3.96	18.60±2.24	5.76±2.35	2.38±3.60	6.80±1.04	0.75±1.66	40.07±0.39	127.97±16.79
MDO	55.03±1.94	20.01±1.16	22.26±1.75	10.60±4.64	9.80±3.49	11.35±3.20	2.55±2.30	58.16±5.43	189.76±23.91
HOF	59.55±0.56	22.30±1.26	26.93±1.15	12.60±2.02	13.09±1.03	18.44±1.70	12.53±4.74	56.09±0.84	221.54±13.30
AFI	57.61±2.12	29.73±0.44	29.10±2.21	15.68±1.28	14.89±3.26	17.57±1.76	11.03±0.63	66.96±4.10	242.56±15.81
AFO	69.87±1.14	34.72±6.87	25.30±2.07	11.75±2.17	11.52±3.55	10.18±2.00	5.58±1.72	64.93±2.93	233.85±22.45
NAD	46.37±0.74	19.69±0.45	17.89±1.46	6.30±0.12	8.42±0.93	7.86±0.55	0.49±1.01	67.45±8.99	174.47±14.25
JUM	44.85±2.23	17.92±0.33	22.53±1.65	10.78±1.67	13.62±0.19	11.46±1.35	7.80±1.17	51.57±2.69	180.52±11.28
IDI	51.73±0.34	15.74±0.94	24.43±1.24	13.05±0.64	13.77±0.41	13.84±1.24	5.39±0.81	67.07±2.96	205.03±8.58
IDO	37.88±1.31	18.30±0.67	16.41±1.00	5.93±0.06	6.75±0.35	5.95±0.61	0.77±0.73	67.10±0.22	159.09±4.95
REH	52.10±0.62	21.74±0.34	24.02±0.81	9.50±2.58	9.90±1.61	9.37±1.24	4.01±1.18	65.08±4.33	195.72±12.70
UBP	79.37±1.81	36.12±0.60	38.08±1.69	22.63±1.63	20.88±1.74	21.46±2.24	14.88±2.48	78.43±9.73	311.83±21.93
NWTT	57.23±0.60	16.77±1.01	27.40±1.07	11.15±1.13	13.96±1.86	14.20±0.70	5.49±1.24	58.26±6.40	204.47±14.01
NWTE	50.14±3.68	16.19±1.40	26.31±1.25	10.85±1.12	14.22±1.47	13.22±1.06	7.29±0.97	77.08±6.17	215.30±17.12
BLA	80.40±7.93	28.17±1.90	60.61±7.18	24.43±3.37	40.73±5.87	28.92±6.95	7.20±0.74	68.14±10.64	338.61±44.57
∑PCB	788.65±26.57	304.49±21.35	379.88±26.76	170.99±24.76	193.92±29.36	190.63±25.63	85.77±21.37	886.40±65.83	3000.73±241.64
min	37.88±0.34	7.10±0.33	16.41±0.81	5.76±0.06	2.38±0.19	5.95±0.55	0.49±0.63	40.07±0.22	127.97±4.95
mean	56.33±1.90	21.75±1.53	27.13±1.91	12.21±1.77	13.85±2.10	13.62±1.83	6.13±1.53	63.31±4.70	214.34±17.26
max	80.40±7.93	36.12±6.87	60.61±7.18	24.43±4.64	40.73±5.87	28.92±6.95	14.88±4.74	78.43±10.64	338.61±44.57

D.9 Individual PCB concentrations in spring surface water samples

Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
					Concentration (ng/mL)				
MDI	0.53±0.06	0.61±0.07	0.67±0.07	0.68±0.06	0.59±0.05	0.46±0.05	0.51±0.06	0.81±0.11	4.84±0.51
MDO	0.48±0.06	0.55±0.07	0.60±0.06	0.62±0.05	0.53±0.04	0.41±0.03	0.43±0.03	0.68±0.05	4.31±0.39
HOF	0.44±0.06	0.54±0.06	0.59±0.06	0.61±0.06	0.53±0.04	0.39±0.05	0.43±0.05	0.67±0.05	4.20±0.44
AFI	0.45±0.06	0.52±0.03	0.56±0.02	0.57±0.01	0.49±0.01	0.37±0.03	0.39±0.02	0.61±0.01	3.96±0.19
AFO	0.44±0.05	0.51±0.03	0.56±0.03	0.58±0.02	0.49±0.02	0.37±0.01	0.40±0.03	0.63±0.03	3.98±0.23
NAD	0.70±0.05	0.78±0.04	0.83±0.04	0.84±0.04	0.73±0.03	0.62±0.03	0.62±0.03	0.87±0.03	5.99±0.29
JUM	0.55±0.04	0.63±0.03	0.67±0.04	0.69±0.05	0.60±0.05	0.48±0.03	0.51±0.03	0.68±0.04	4.80±0.30
IDI	0.53±0.04	0.58±0.02	0.64±0.03	0.66±0.02	0.57±0.03	0.45±0.02	0.47±0.03	0.65±0.03	4.56±0.22
IDO	0.57±0.03	0.71±0.03	0.68±0.03	0.69±0.02	0.60±0.03	0.48±0.02	0.50±0.02	0.69±0.02	4.91±0.20
REH	0.50±0.02	0.62±0.02	0.62±0.04	0.65±0.02	0.56±0.03	0.43±0.02	0.46±0.02	0.84±0.02	4.68±0.20
UBP	0.44±0.04	0.54±0.04	0.56±0.04	0.58±0.04	0.51±0.04	0.37±0.03	0.40±0.04	0.64±0.04	4.05±0.31
NWTI	0.44±0.05	0.98±0.07	0.54±0.04	0.57±0.02	0.49±0.04	0.38±0.04	0.39±0.04	1.26±0.03	5.03±0.34
NWTT	0.39±0.04	0.53±0.05	0.54±0.04	0.54±0.04	0.47±0.04	0.34±0.04	0.38±0.04	0.67±0.05	3.87±0.33
NWTE	0.44±0.04	0.55±0.05	0.55±0.05	0.57±0.04	0.55±0.02	0.38±0.04	0.39±0.04	0.76±0.05	4.19±0.33
BLA	0.31±0.05	0.42±0.06	0.46±0.05	0.48±0.03	0.41±0.05	0.29±0.04	0.36±0.02	0.59±0.04	3.32±0.34
∑PCB	7.21±0.70	9.06±0.67	9.05±0.64	9.33±0.53	8.12±0.52	6.24±0.48	6.65±0.49	11.04±0.59	66.69±4.63
min	0.31±0.02	0.42±0.02	0.46±0.02	0.48±0.01	0.41±0.01	0.29±0.01	0.36±0.02	0.59±0.01	3.32±0.19
mean	0.48±0.05	0.60±0.04	0.60±0.04	0.62±0.04	0.54±0.03	0.42±0.03	0.44±0.03	0.74±0.04	4.45±0.31
max	0.70±0.06	0.98±0.07	0.83±0.07	0.84±0.06	0.73±0.05	0.62±0.05	0.62±0.06	1.26±0.11	5.99±0.51

D.10 Individual PCB concentrations in spring pore water samples

				Concentration (ng/mL)					
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	4.75±0.39	7.19±0.28	5.88±0.33	5.89±0.43	5.35±0.38	4.34±0.32	4.64±0.23	6.61±0.30	44.64±2.66
MDO	5.57±0.59	8.70±0.57	6.74±0.56	6.61±0.47	6.14±0.45	5.07±0.48	5.31±0.48	7.87±0.42	52.02±4.02
HOF	2.49±0.28	4.10±0.38	3.31±0.34	3.29±0.27	2.98±0.31	2.29±0.27	2.52±0.25	7.07±0.33	28.04±2.42
AFI	8.44±0.71	9.76±0.75	9.19±0.63	9.00±0.62	8.48±0.58	7.37±0.52	7.54±0.52	9.65±0.48	69.41±4.83
AFO	6.09±0.85	12.02±1.26	7.50±0.75	7.53±0.59	6.90±0.66	5.59±0.54	5.90±0.51	10.43±0.54	61.95±5.70
NAD	5.68±0.82	6.83±0.76	7.17±0.81	7.34±0.67	6.57±0.71	5.23±0.57	5.46±0.63	8.28±0.62	52.57±5.59
JUM	6.64±1.42	8.13±1.27	8.91±1.17	9.02±0.88	8.00±0.84	6.60±0.98	6.85±0.95	10.94±0.79	65.08±8.31
IDI	9.86±1.38	11.20±1.26	11.85±1.23	11.83±1.24	10.81±1.14	8.79±0.99	9.18±1.04	12.72±1.08	86.25±9.36
IDO	6.03±1.03	7.43±1.07	8.78±0.84	9.21±0.63	7.92±0.74	5.67±0.75	6.21±0.80	9.98±0.54	61.25±6.39
REH	6.36±0.76	16.54±1.25	8.47±0.67	8.23±0.55	7.54±0.67	6.01±0.57	6.28±0.48	12.93±0.52	72.37±5.48
UBP	5.53±0.89	38.44±2.50	7.76±0.62	7.73±0.62	6.93±0.57	5.26±0.51	5.58±0.42	44.13±1.36	121.37±7.48
NWTT	9.07±0.81	59.40±3.85	11.59±0.63	11.15±0.71	10.56±0.69	8.40±0.45	8.65±0.45	62.24±2.15	181.06±9.74
NWTE	11.21±0.90	58.87±5.38	13.30±0.77	11.93±0.47	9.50±4.70	9.74±0.65	9.84±0.69	54.07±4.39	178.46±17.96
BLA	6.12±0.38	45.93±4.72	8.08±0.35	7.38±0.17	7.24±0.46	2.83±0.15	5.86±0.36	43.95±3.40	127.39±9.99
∑PCB	11.21±11.22	59.40±25.31	13.30±9.70	11.93±8.31	10.81±12.91	9.74±7.75	9.84±7.82	62.24±16.90	181.06±99.92
min	2.49±0.28	4.10±0.28	3.31±0.33	3.29±0.17	2.98±0.31	2.29±0.15	2.52±0.23	6.61±0.30	28.04±2.42
mean	6.70±0.80	21.04±1.81	8.47±0.69	8.30±0.59	7.49±0.92	5.94±0.55	6.42±0.56	21.49±1.21	85.85±7.14
max	11.21±1.42	59.40±5.38	13.30±1.23	11.93±1.24	10.81±4.70	9.74±0.99	9.84±1.04	62.24±4.39	181.06±17.96

D.11 Individual PCB concentrations in spring sediment samples

	Concentration (ng/g)								
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	19.73±5.17	17.96±1.76	21.49±1.72	10.67±3.74	20.66±1.93	23.36±2.81	16.51±3.99	33.46±0.24	163.83±21.35
MDO	17.41±2.41	16.74±2.04	16.19±1.80	16.16±1.34	16.14±2.02	14.30±1.86	13.84±1.59	39.56±4.58	150.34±17.65
HOF	18.53±4.24	21.74±3.63	20.38±2.02	15.95±0.65	19.40±2.10	18.97±0.37	15.50±0.31	45.07±0.46	175.55±13.79
AFI	12.81±0.82	7.24±2.29	13.23±2.93	14.55±0.68	14.41±1.29	15.59±8.07	17.40±4.91	42.09±0.70	137.32±21.68
AFO	10.27±1.94	8.52±3.03	11.72±1.57	12.17±2.66	12.57±3.69	14.15±0.71	8.09±0.75	43.23±0.43	120.70±14.79
NAD	9.57±1.50	9.15±1.68	9.86±1.48	11.68±1.50	11.02±0.72	8.87±2.06	9.46±0.50	24.99±3.19	94.61±12.64
JUM	14.28±4.31	9.95±0.06	12.35±1.51	11.79±0.16	11.37±0.11	8.71±0.10	12.38±2.63	16.50±0.33	97.33±9.20
IDI	18.49±0.17	13.70±0.72	15.55±0.81	16.44±0.79	14.80±0.81	12.57±0.73	13.56±0.92	21.79±0.51	126.91±5.47
IDO	6.92±1.56	5.12±1.60	7.40±1.12	8.47±0.69	7.97±1.26	5.89±0.91	6.36±0.84	13.59±0.58	61.72±8.55
REH	13.03±2.40	14.53±0.48	20.91±2.59	23.13±2.88	15.54±1.61	21.18±1.05	14.16±1.81	23.04±0.67	145.54±13.48
UBP	12.39±3.78	16.03±4.62	14.73±1.38	14.73±2.38	9.55±1.51	12.82±2.25	19.09±7.66	45.17±0.53	144.49±24.10
NWTI	27.78±0.79	65.32±3.47	36.37±1.37	18.03±1.33	19.73±2.66	18.64±6.06	29.60±2.09	55.93±4.08	271.40±21.86
NWTT	84.46±4.43	57.68±7.31	75.24±15.92	60.81±11.32	76.76±8.40	49.08±9.14	51.67±4.39	71.60±5.02	527.29±65.92
NWTE	89.26±8.96	57.68±2.41	50.71±3.25	55.39±0.73	55.13±2.67	36.80±3.55	46.33±2.72	59.05±7.57	450.35±31.85
BLA	11.84±2.15	4.26±2.06	22.31±0.83	12.88±0.97	11.00±4.13	17.02±8.55	17.05±4.77	77.03±6.70	173.38±30.14
∑PCB	366.76±44.63	325.61±37.16	348.42±40.30	302.86±31.81	316.04±34.93	277.95±48.20	291.00±39.88	612.11±35.59	2840.75±312.49
min	6.92±0.17	4.26±0.06	7.40±0.81	8.47±0.16	7.97±0.11	5.89±0.10	6.36±0.31	13.59±0.24	61.72±5.47
mean	24.45±2.98	21.71±2.48	23.23±2.69	20.19±2.12	21.07±2.33	18.53±3.21	19.40±2.66	40.81±2.37	189.38±20.83
max	89.26±8.96	65.32±7.31	75.24±15.92	60.81±11.32	76.76±8.40	49.08±9.14	51.67±7.66	77.03±7.57	527.29±65.92

D.12 Individual PCB concentrations in spring soil samples

				Concentration (ng/g)					
Site	PCB28	PCB77	PCB101	PCB52	PCB153	PCB105	PCB138	PCB180	∑PCB
MDI	14.26±1.02	19.51±0.92	18.53±0.97	29.48±0.07	19.89±1.10	18.05±0.80	21.89±2.01	27.65±1.33	169.26±8.22
MDO	8.28±0.51	12.01±0.45	13.09±0.45	21.88±0.04	13.69±0.52	12.08±0.48	11.66±0.28	24.80±1.89	117.50±4.62
HOF	14.87±0.09	16.65±2.98	22.83±0.23	31.08±2.00	21.91±0.25	21.81±0.71	18.80±2.38	83.48±2.55	231.42±11.14
AFI	10.85±1.05	10.40±0.93	21.00±3.01	34.63±0.08	14.48±2.32	17.51±4.26	44.67±7.69	63.36±1.03	216.90±20.37
AFO	8.71±0.40	10.86±1.03	14.37±0.27	23.19±0.45	14.69±1.28	12.56±0.61	13.39±1.06	51.07±4.13	148.83±9.24
NAD	13.25±0.71	16.09±0.81	17.56±0.56	29.38±0.07	18.49±1.42	16.29±1.21	17.00±1.22	22.26±1.63	150.31±7.62
JUM	6.10±0.33	7.69±0.74	10.17±0.33	18.65±0.29	10.95±0.31	8.81±0.20	8.80±0.42	15.04±1.51	86.21±4.14
IDI	6.23±0.29	8.57±0.23	10.15±0.41	19.03±0.04	9.97±0.47	8.30±0.53	8.52±0.44	20.46±0.73	91.23±3.12
IDO	4.64±0.56	7.24±0.20	8.81±0.20	16.37±0.25	9.27±0.21	7.28±0.29	7.67±0.45	17.71±1.15	79.00±3.32
REH	11.73±0.47	9.53±1.59	11.16±0.48	17.68±0.79	9.51±0.38	9.60±0.86	10.27±0.38	77.78±1.94	157.26±6.89
UBP	5.63±0.27	7.47±0.25	13.73±2.11	20.18±0.01	12.04±1.49	9.31±0.43	12.67±1.94	44.61±4.61	125.65±11.11
NWTT	28.74±1.40	51.04±6.07	37.60±1.49	26.65±3.30	39.85±2.57	21.61±0.68	30.50±0.73	85.35±1.94	321.33±18.17
NWTE	6.81±1.30	10.26±1.06	14.50±0.83	20.90±0.16	12.59±0.72	11.07±0.87	14.08±2.68	73.31±4.31	163.51±11.94
BLA	6.18±0.16	5.45±1.79	9.83±0.30	22.13±1.15	15.02±2.02	9.73±0.73	9.84±1.12	59.21±3.39	137.40±10.66
∑PCB	146.28±8.55	192.78±19.00	223.32±11.62	331.22±8.72	222.34±15.07	184.01±12.66	229.76±22.81	666.08±32.14	2195.80±130.58
min	4.64±0.09	5.45±0.20	8.81±0.20	16.37±0.01	9.27±0.21	7.28±0.20	7.67±0.28	15.04±0.73	79.00±3.12
mean	10.45±0.61	13.77±1.36	15.95±0.83	23.66±0.62	15.88±1.08	13.14±0.90	16.41±1.63	47.58±2.30	156.84±9.33
max	28.74±1.40	51.04±6.07	37.60±3.01	34.63±3.30	39.85±2.57	21.81±4.26	44.67±7.69	85.35±4.61	321.33±20.37

APPENDIX E: INDIVIDUAL CONCENTRATIONS OF OCPs IN SUMMER, AUTUMN AND SPRING

E.1 Individual OCP concentrations in summer surface water samples

	Concentration (ng/mL)										
Site	HCB	HCH	heptachlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCP
MDI	nd	nd	nd	0.61±0.09	0.53±0.05	0.70±0.05	0.99±0.42	0.56±0.01	0.72±0.06	nd	4.10±0.68
MDO	nd	1.00±0.03	0.58±0.06	1.45±0.15	2.14±0.04	1.58±0.06	2.23±0.03	0.71±0.04	2.20±0.13	0.92±0.04	12.81±0.58
HOF	nd	nd	nd	0.64±0.05	nd	1.08±0.10	2.07±0.12	0.55±0.09	0.76±0.05	0.49±0.54	5.58±0.95
AFI	nd	nd	0.21±0.02	0.90±0.03	0.84±0.06	1.07±0.03	1.73±0.10	0.72±0.04	0.95±0.03	nd	6.42±0.30
AFO	nd	nd	nd	0.74±0.02	0.77±0.02	0.90±0.03	1.53±0.06	0.62±0.04	0.88±0.03	nd	5.44±0.20
NAD	nd	nd	0.20±0.04	0.96±0.10	0.93±0.10	1.09±0.11	1.75±0.10	0.98±0.07	1.03±0.06	0.76±0.47	7.70±1.03
TUM	1.57±0.03	2.16±0.08	1.47±0.03	1.25±0.14	0.89±0.05	1.07±0.04	2.27±0.06	1.39±0.08	0.99±0.02	0.70±0.05	13.77±0.56
IDI	nd	nd	nd	0.65±0.04	0.63±0.01	1.45±0.09	2.62±0.09	0.49±0.05	0.78±0.03	nd	6.61±0.31
IDO	nd	nd	nd	0.70±0.05	0.70±0.01	0.84±0.04	1.46±0.02	0.53±0.04	0.81±0.01	nd	5.04±0.18
REH	nd	0.51±0.17	0.31±0.10	1.13±0.17	1.13±0.21	1.34±0.22	2.08±0.25	0.84±0.19	1.14±0.16	1.31±0.26	9.79±1.73
UBP	nd	0.55±0.34	0.32±0.14	1.44±0.36	1.44±0.31	1.36±1.16	2.65±4.62	1.15±0.36	1.18±0.10	1.68±0.91	11.76±8.29
NWTI	nd	1.66±0.08	1.02±0.02	1.56±0.01	2.01±0.07	2.68±0.04	3.02±0.04	1.92±0.06	2.39±0.03	nd	16.26±0.34
NWTT	nd	0.24±0.70	nd	0.89±0.12	2.06±0.67	2.17±0.69	2.75±0.69	1.30±0.55	1.35±0.18	1.04±0.40	11.80±4.01
NWTE	nd	nd	0.40±0.11	1.38±1.33	0.74±0.11	1.99±0.17	2.45±1.49	1.23±1.24	0.72±0.03	1.08±0.62	9.98±5.10
BLA	nd	nd	0.46±0.16	1.01±0.25	1.01±0.24	1.23±0.23	1.88±0.32	0.90±0.14	1.03±0.20	0.52±0.16	8.05±1.71
∑OCP	1.57±0.03	6.13±1.40	4.96±0.68	15.31±2.93	15.82±1.93	20.55±3.06	31.46±8.40	13.90±3.00	16.92±1.10	8.49±3.45	135.11±25.98
min	nd	nd	nd	0.61±0.09	nd	0.70±0.05	0.99±0.42	0.49±0.05	0.72±0.03	nd	4.10±0.68
mean	0.10±0.01	0.41±0.09	0.33±0.05	1.02±0.20	1.05±0.13	1.37±0.20	2.10±0.56	0.93±0.20	1.13±0.07	0.57±0.23	9.01±1.73
max	1.57±0.03	2.16±0.08	1.47±0.03	1.56±0.01	2.14±0.04	2.68±0.04	3.02±0.04	1.92±0.06	2.39±0.03	1.68±0.91	16.26±0.34

nd= not detected

E.2 Individual OCP concentrations in summer pore water samples

Site						Concentration (ng/mL)					
	HCB	**HCH**	Heptachlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'DDD/Dieldrin	endrin	p,p'DDD/o,p'DDT	mirex	∑OCPs
MDI	nd	nd	2.02±0.66	5.76±0.19	4.92±0.11	5.39±0.50	9.00±0.32	5.66±0.56	nd	1.40±1.46	34.14±3.81
MDO	1.79±1.46	3.66±1.32	3.67±0.09	7.78±0.92	4.96±0.62	6.20±0.45	10.26±0.58	nd	5.23±0.15	1.27±0.45	44.83±6.96
HOF	nd	nd	nd	4.16±0.48	2.28±0.38	3.38±0.18	5.88±0.14	6.01±0.81	nd	5.79±1.45	27.50±3.42
AFI	nd	0.94±1.51	3.65±0.24	8.15±1.32	4.30±0.36	4.55±0.18	9.66±0.35	4.37±1.04	nd	0.52±0.16	36.14±5.15
AFO	nd	nd	2.02±1.01	6.42±0.17	4.43±2.82	7.58±0.46	13.96±0.45	4.63±1.22	7.00±0.47	1.72±0.40	47.76±7.00
NAD	nd	nd	nd	6.75±0.20	6.49±0.47	7.46±0.44	13.70±0.48	6.43±0.70	7.25±0.29	1.01±0.11	49.09±2.70
TUM	nd	nd	nd	10.87±1.04	7.66±0.47	9.57±0.35	17.25±1.22	5.87±1.98	9.45±0.20	1.18±0.35	61.85±5.62
IDI	nd	nd	nd	9.27±0.88	9.16±0.46	10.71±0.38	19.03±0.40	5.95±1.43	10.23±0.28	2.57±0.25	66.94±4.08
IDO	nd	nd	nd	10.27±0.41	9.65±0.14	11.92±0.12	22.42±1.31	8.21±0.23	11.94±0.51	1.45±0.18	75.86±2.90
REH	nd	nd	nd	8.60±0.34	8.13±0.85	9.36±0.52	16.61±0.51	5.51±0.21	9.13±0.40	1.76±0.18	59.10±2.99
UBP	nd	nd	nd	7.98±1.16	6.74±0.27	7.96±0.27	14.50±1.09	6.40±1.22	8.29±0.23	nd	51.89±4.24
NWTT	nd	nd	nd	7.88±0.61	8.23±0.49	10.13±0.41	17.91±1.45	6.82±1.11	9.57±0.49	0.89±0.36	61.43±4.91
NWTE	nd	nd	nd	9.66±0.95	8.37±0.20	9.54±0.19	16.83±0.49	6.98±1.17	9.49±0.29	1.91±0.38	62.78±3.68
BLA	nd	nd	nd	7.75±1.27	5.36±0.37	6.49±0.17	12.28±1.25	4.60±0.68	6.98±0.13	nd	43.46±3.86
∑OCPs	1.79±1.46	4.60±2.84	11.35±2.00	111.30±9.94	90.70±8.01	110.24±4.62	199.30±10.02	77.45±12.34	94.56±3.45	21.48±5.73	722.78±61.31
min	nd	nd	nd	4.160±0.48	2.28±0.38	3.380±0.18	5.882±0.14	nd	nd	nd	27.50±3.42
mean	0.128±0.20	0.329±0.38	0.811±0.27	7.950±1.32	6.479±1.07	7.87±0.62	14.236±1.34	5.532±1.65	6.75±0.46	1.534±0.76	51.63±8.17
max	1.792±1.46	3.661±1.32	3.67±0.09	10.873±1.04	9.65±0.14	11.92±0.12	22.42±1.31	8.21±0.23	11.94±0.51	5.79±1.45	75.86±2.90

nd= not detected

E.3 Individual OCP concentrations in summer sediment samples

	Concentration (ng/g)										
Site	HCB	HCH	Heptachlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCP
MDI	2.08±1.59	nd	12.73±2.08	18.29±3.48	10.17±2.43	12.12±0.29	18.53±3.01	20.87±3.92	14.50±2.06	nd	109.27±18.85
MDO	nd	2.15±2.61	14.35±3.11	10.28±4.67	9.41±2.93	14.11±0.79	16.18±2.17	15.08±3.40	12.89±0.63	6.91±1.05	101.35±20.32
HOF	nd	9.58±4.73	27.35±3.14	29.68±2.77	9.00±1.79	19.84±0.97	14.77±2.34	32.05±3.45	19.77±1.69	nd	162.05±20.89
AFI	4.40±2.83	4.88±1.64	21.90±2.55	17.50±1.89	10.46±0.70	14.76±0.32	21.14±2.17	16.52±4.35	16.86±0.84	5.47±0.55	133.8817.28
AFO	nd	nd	16.97±1.82	31.55±2.67	11.96±0.36	11.79±0.23	15.06±1.29	24.12±4.00	12.24±0.33	7.09±2.54	130.79±10.70
NAD	2.84±1.40	2.15±1.43	29.55±2.99	19.65±1.93	13.35±1.08	16.52±0.91	22.42±3.26	18.68±0.89	16.11±0.01	8.30±2.36	149.56±13.91
TUM	2.39±0.93	4.20±1.88	17.37±3.74	7.61±0.04	6.09±1.51	8.77±0.46	13.70±2.43	17.97±2.55	10.59±0.72	2.26±3.36	90.96±14.25
IDI	2.03±1.00	8.15±1.55	17.99±2.79	nd	8.14±1.99	11.10±0.79	14.13±1.61	18.10±3.97	11.30±0.89	nd	90.93±13.69
IDO	3.53±0.88	4.14±1.85	19.92±0.54	8.09±1.76	9.29±2.35	12.00±0.21	16.90±3.62	18.50±3.03	11.69±1.03	nd	104.05±15.26
REH	3.99±0.53	10.41±1.27	23.90±4.37	3.82±0.95	10.41±2.44	14.03±0.75	15.08±1.00	17.02±3.36	12.32±1.38	7.29±1.95	118.26±16.05
UBP	8.00±0.12	23.82±1.78	33.61±4.28	7.99±1.73	11.25±1.76	16.71±1.78	16.65±0.43	24.46±3.58	14.79±2.65	6.62±3.71	163.90±18.11
NWTI	12.02±1.40	55.54±4.93	130.19±4.34	15.00±0.86	9.53±1.13	23.62±0.45	26.75±0.65	24.54±2.05	44.97±4.00	15.51±3.01	357.67±19.80
NWTT	21.38±0.84	72.78±5.93	146.82±3.77	58.33±2.73	15.09±3.12	27.18±2.46	21.71±3.27	24.49±4.52	30.79±2.91	26.41±3.00	444.99±29.55
NWTE	15.58±1.25	58.54±2.44	98.36±6.67	34.72±0.74	12.61±0.48	15.49±3.09	19.42±3.59	17.93±2.42	17.43±1.92	40.90±0.22	330.98±22.61
BLA	6.14±1.97	52.71±2.08	51.05±7.01	33.61±3.12	16.89±3.95	12.24±2.21	19.02±0.70	32.87±4.12	15.45±3.85	33.23±3.19	273.22±29.02
∑OCP	84.38±14.72	309.04±34.13	662.06±53.19	296.12±29.34	163.64±28.03	230.29±15.70	271.45±31.55	323.20±49.60	261.69±24.91	159.99±26.13	2761.86±280.29
min	nd	nd	12.73±2.08	nd	6.09±1.51	8.77±0.46	13.70±2.43	15.08±3.40	10.59±0.72	nd	90.93±13.69
mean	5.63±0.98	20.60±2.28	44.14±3.55	19.74±1.96	10.91±1.87	15.35±1.05	18.10±2.10	21.55±3.31	17.45±1.66	10.67±1.74	184.12±18.69
max	21.38±0.84	72.78±5.93	146.82±3.77	58.33±2.73	16.89±3.95	27.18±2.46	26.75±0.65	32.87±4.12	44.97±4.00	40.90±0.22	444.99±29.55

nd= not detected

E.4 Individual OCP concentrations in summer soil samples

Site	HCB	HCH	Heptachlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCPs
					Concentration (ng/g)						
MDI	nd	nd	8.90±2.63	12.85±0.86	21.53±3.00	16.59±3.61	19.58±0.91	21.40±3.58	12.69±0.57	nd	113.54±15.16
MDO	nd	nd	8.75±2.84	13.95±0.98	12.32±0.71	16.04±0.84	18.64±2.76	16.71±1.48	14.41±0.50	nd	100.82±10.11
HOF	6.63±0.58	nd	6.85±3.70	24.00±3.03	10.27±1.18	17.02±0.97	23.37±0.54	16.03±0.18	14.67±1.03	4.00±1.32	122.84±12.53
AFI	0.87±0.79	nd	4.33±0.83	22.55±1.31	11.02±0.99	17.81±1.15	25.80±1.28	38.96±3.68	14.98±0.38	5.50±2.64	141.82±13.05
AFO	nd	nd	7.98±0.72	12.94±0.22	10.06±0.56	14.00±1.49	21.31±0.30	29.96±3.01	11.86±0.86	nd	108.11±7.16
NAD	nd	nd	7.51±1.27	17.97±2.93	13.29±1.82	19.59±2.68	27.79±2.43	24.10±3.60	15.33±1.96	nd	125.59±16.69
TUM	nd	nd	7.42±0.28	8.37±2.86	8.09±0.70	13.04±0.62	25.81±1.27	11.30±0.60	17.91±1.65	nd	91.94±7.98
IDI	nd	nd	8.62±1.47	3.54±0.88	7.16±0.45	11.59±0.59	27.15±0.82	26.96±3.22	11.36±0.23	nd	96.38±7.66
IDO	nd	nd	6.92±1.32	8.48±0.43	8.04±0.63	13.61±0.49	27.71±0.59	14.75±2.74	12.77±0.51	nd	92.29±6.73
REH	nd	nd	10.83±0.07	9.54±1.39	7.87±1.71	14.80±0.64	20.92±0.89	21.36±1.52	12.65±0.21	5.34±0.41	103.32±6.83
UBP	8.08±2.70	nd	13.32±2.78	9.91±2.44	13.15±0.71	30.54±3.82	25.40±0.87	43.10±2.98	15.21±0.24	nd	158.72±16.53
NWTT	32.23±0.37	nd	12.97±2.89	76.54±1.32	29.89±0.62	33.09±3.30	21.98±3.09	45.49±3.70	15.83±0.34	6.36±1.31	274.38±16.95
NWTE	14.46±1.65	nd	19.72±3.28	62.19±2.02	27.63±3.68	21.31±1.76	32.25±2.08	34.38±1.05	13.56±2.12	nd	225.50±17.64
BLA	8.49±0.80	nd	6.08±1.87	19.04±4.00	16.32±1.29	14.10±2.92	27.49±3.45	19.91±2.09	12.82±1.53	10.15±1.15	134.41±19.11
∑OCPs	70.77±6.90	nd	130.22±25.95	301.88±24.69	196.63±18.06	253.12±24.87	345.20±21.27	364.42±37.43	196.05±12.13	31.36±6.83	1889.66±174.12
min	nd	nd	4.33±0.83	3.54±0.88	7.16±0.45	11.59±0.59	18.64±2.76	11.30±0.60	11.36±0.23	nd	91.94±7.98
mean	5.06±0.92	nd	9.30±3.46	21.56±3.29	14.05±2.41	18.08±3.32	24.66±2.84	26.03±4.99	14.00±1.62	2.24±1.31	134.98±23.22
max	32.23±0.37	nd	19.72±3.28	76.54±1.32	29.89±0.62	33.09±3.30	32.25±2.08	45.49±3.70	17.91±1.65	10.15±	274.38±16.95

nd= not detected

E.5 Individual OCP concentrations in autumn surface water samples

					Concentration (ng/mL)						
Site	HCB	HCH	Hpchlor	Aldrin	o, p'-DDE	p,p'-DDE	o, p'-DDD/Dieldrin	Endrin	p,p'-DDD/o,p-DDT	Mirex	∑OCPs
MDI	nd	2.22±0.15	0.60±0.58	nd	0.99±0.27	0.32±0.06	0.77±0.05	0.53±0.01	nd	nd	5.42±1.13
MDO	nd	2.08±0.17	0.87±0.02	nd	0.92±0.10	0.54±0.01	0.74±0.15	0.49±0.45	0.51±0.12	nd	6.15±1.03
HOF	nd	1.81±0.22	1.06±0.16	nd	0.82±0.11	0.52±0.04	0.67±0.12	0.67±0.23	nd	nd	5.55±0.88
AFI	nd	2.78±0.21	nd	nd	0.98±0.13	0.84±0.17	0.69±0.26	nd	0.50±0.10	nd	5.79±0.88
AFO	nd	1.90±0.04	nd	nd	0.96±0.13	0.62±0.06	0.78±0.12	nd	0.49±0.14	nd	4.75±0.49
NAD	nd	2.45±0.27	nd	nd	0.90±0.20	0.85±0.23	0.80±0.35	nd	0.27±0.26	nd	5.27±1.30
JUM	nd	2.38±0.13	nd	nd	1.02±0.04	0.58±0.07	0.82±0.15	nd	0.54±0.12	nd	5.35±0.51
IDI	nd	2.75±0.19	0.98±0.21	nd	1.08±0.03	0.66±0.01	0.87±0.07	nd	nd	nd	6.34±0.51
IDO	nd	1.92±0.01	2.52±0.33	nd	0.95±0.11	0.52±0.05	0.80±0.02	nd	nd	nd	6.70±0.51
REH	nd	2.35±0.10	0.79±0.19	nd	0.95±0.06	0.67±0.03	0.92±0.13	1.01±0.01	nd	nd	6.70±1.51
NWTI	nd	3.37±0.08	1.95±0.17	nd	1.01±0.07	0.54±0.04	0.86±0.05	0.00±0.36	nd	nd	7.73±0.77
UBP	2.90±0.30	4.70±0.32	2.65±0.03	1.09±0.24	1.38±0.02	0.45±0.36	0.76±0.17	0.70±0.00	0.64±0.08	nd	15.28±1.52
NWTT	2.13±0.08	4.76±0.58	1.92±0.92	0.06±0.32	0.78±1.22	0.42±0.30	0.76±0.36	0.68±0.43	nd	nd	11.50±4.21
NWTE	nd	2.80±0.23	1.11±0.06	0.61±1.00	1.06±0.03	0.74±0.06	1.12±0.16	0.56±0.40	nd	nd	7.99±1.94
BLA	3.09±0.21	4.05±0.91	2.15±0.13	0.40±0.11	1.01±0.10	0.85±0.30	1.06±0.08	0.64±0.28	0.44±0.01	nd	13.68±2.14
∑OCPs	8.12±0.58	42.32±3.60	16.60±2.80	2.16±1.67	14.80±2.63	9.11±1.79	12.43±2.23	5.29±2.18	3.39±0.84	nd	114.22±19.32
min	nd	1.81±0.22	nd	nd	0.78±1.22	0.32±0.06	0.67±0.12	nd	nd	nd	4.75±0.49
Mean	0.54±0.04	2.82±0.24	1.11±0.19	0.14±0.11	0.99±0.18	0.61±0.12	0.83±0.15	0.35±0.15	0.23±0.06	nd	7.61±1.29
max	3.09±0.21	4.76±0.58	2.65±0.03	1.09±0.24	1.38±0.02	0.85±0.23	1.12±0.16	1.01±0.01	0.64±0.08	nd	15.28±1.52

nd= not detected

E.6 Individual OCP concentrations in autumn pore water samples

					Concentration (ng/mL)						
Site	HCB	HCH	Heptachlor	Aldrin	o,p'-DDE	p,p'-DDE	o, p'-DDD/Dieldrin	Endrin	p,p'-DDD/o,p-DDT	Mirex	∑OCPs
MDI	5.94±0.07	16.58±1.17	4.77±0.47	nd	9.66± 0.95	4.23±0.47	8.57±0.40	0.77±0.44	4.00±0.63	4.39±2.73	58.91±7.33
MDO	6.38±3.78	14.18±3.34	3.24±1.79	nd	5.68± 3.27	4.26±2.51	5.41±3.19	0.57±0.15	2.04±0.94	2.79±2.13	44.54±21.09
HOF	3.07±1.02	7.55±2.86	2.69±0.79	nd	3.95± 1.62	4.17±1.94	4.21±1.45	0.19±0.22	1.65±0.53	5.02±2.05	32.49±12.49
AFI	5.09±0.14	12.71±0.17	1.42±0.52	nd	5.70± 0.70	5.53±0.38	6.38±0.44	0.57±0.73	1.58±0.39	nd	38.97±3.48
AFO	4.68±0.86	15.40±1.69	2.43±0.58	nd	7.43± 0.80	5.67±0.52	7.55±0.65	0.19±0.25	3.53±0.57	nd	46.88±5.91
NAD	4.70±0.86	15.43±1.69	2.45±0.58	nd	7.48± 0.80	5.71±0.52	7.57±0.65	0.21±0.31	3.54±0.57	nd	47.09±5.98
JUM	14.62±2.75	48.27±2.35	8.97±1.64	0.04±0.28	8.39± 0.94	7.04±0.79	11.55±0.46	1.49±2.19	5.87±0.92	nd	106.25±12.31
IDI	11.15±0.16	30.44±1.18	7.68±1.12	nd	15.83±1.11	17.31±0.30	29.05±1.00	1.50±1.24	6.37±0.48	nd	119.33±6.60
IDO	17.39±0.82	42.07±2.00	9.18±0.67	nd	25.71± 1.68	19.58±3.31	26.96±2.59	3.88±0.97	11.81±1.89	nd	156.59±13.94
REH	13.45±0.20	41.96±2.02	11.52±0.71	nd	19.81± 2.18	18.45±1.93	22.01±1.37	2.38±1.82	9.06±1.58	nd	138.64±11.80
UBP	19.33±2.66	36.43±2.47	7.11±1.47	nd	39.35± 3.00	21.67±4.63	34.37±2.21	6.49±3.79	14.86±1.19	13.65±3.01	193.26±24.44
NWTT	14.40±0.71	33.37±1.59	12.05±1.05	nd	19.04± 1.73	15.85±2.72	28.57±1.98	1.58±1.35	7.89±1.36	13.66±1.01	146.40±13.50
NWTE	14.41±0.28	33.39±0.58	12.09±0.34	nd	19.08± 0.90	15.98±1.07	28.61±2.04	1.61±1.03	7.93±1.69	13.69±2.03	146.79±9.96
BLA	10.10±0.43	17.59±0.04	3.25±0.32	nd	9.53± 1.32	11.70±0.72	12.76±1.13	1.58±0.16	4.74±1.14	8.46±0.54	79.70±5.80
∑OCPs	144.71±14.75	365.38±	88.84±12.05	0.04±0.28	196.63±20.98	157.16±21.82	233.56±19.54	23.02±14.66	84.85±13.88	61.65±13.51	1355.84±154.63
min	3.07±1.02	7.55±2.86	1.42±0.52	nd	3.95±1.62	4.17±1.94	4.21±1.45	0.19±0.22	1.58±0.53	nd	32.49±12.49
Mean	10.34±1.05	26.10±1.65	6.35±0.86	0.00	14.05±1.50	11.23±1.56	16.68±1.40	1.64±1.05	6.06±0.99	4.40±0.97	96.85±11.04
max	19.33±2.66	48.27±2.35	12.09±0.34	0.04±0.02	39.35±3.00	21.67±4.63	34.37±	6.49±3.79	14.86±1.19	13.69±2.03	193.26±24.44

nd= not detected

E.7 Individual OCP concentrations in autumn sediment samples

	Concentration (ng/g)										
Site	HCB	HCH	Hpchlor	Aldrin	o,p'-DDE	p,p'-DDE	o, p'-DDD/Dieldrin	Endrin	p,p'-DDD/o,p-DDT	Mirex	∑OCPs
MDI	33.97±1.91	60.19±3.37	24.10±1.20	nd	22.31±2.66	12.50±2.14	29.92±1.96	72.47±3.42	15.11±2.30	nd	270.58±18.97
MDO	37.54±0.97	73.41±5.19	12.41±0.92	nd	20.69±0.21	11.49±0.81	33.68±1.39	62.46±2.80	15.72±1.77	nd	267.39±14.07
HOF	33.81±3.02	95.67±4.38	11.77±1.84	nd	16.68±2.25	16.71±6.54	33.35±2.79	62.13±3.39	20.53±0.54	nd	290.66±24.76
AFI	33.95±3.17	96.61±2.58	11.19±1.06	nd	23.85±0.93	18.43±2.96	32.08±1.28	74.96±2.63	21.66±3.35	9.38±2.38	322.11±20.35
AFO	20.54±1.88	62.69±3.73	9.87±2.49	nd	21.17±0.80	14.11±1.25	34.20±1.69	53.64±2.26	12.45±3.70	16.90±2.84	245.58±20.65
NAD	41.70±3.01	88.54±4.49	6.98±1.27	nd	31.32±3.91	17.23±5.23	34.49±1.72	22.88±2.11	15.09±1.37	22.68±4.25	280.92±27.35
JUM	32.01±3.47	90.11±3.23	12.86±2.51	nd	25.20±4.90	26.43±0.41	39.53±2.01	37.50±2.27	14.05±1.17	11.24±2.75	288.94±22.73
IDI	37.67±1.36	84.06±3.36	18.08±2.58	nd	20.17±1.25	10.27±1.89	27.56±0.45	73.31±4.25	15.18±2.08	11.36±1.75	297.67±18.97
IDO	39.91±3.94	75.32±3.26	22.47±1.26	nd	20.54±0.99	12.13±1.09	30.85±1.87	34.61±3.04	13.43±1.55	nd	249.26±17.00
REH	39.38±1.59	66.17±3.17	7.41±2.16	nd	21.51±1.67	11.82±0.38	29.40±1.12	36.60±3.28	13.07±1.52	15.25±3.04	240.61±17.93
NWTI	53.38±0.77	69.45±2.41	11.95±4.01	4.88±0.30	22.41±4.67	11.54±0.78	31.02±0.71	31.62±2.58	12.07±1.25	7.68±0.84	256.02±18.32
UBP	55.85±1.61	116.61±3.47	13.55±3.34	2.20±1.52	20.32±1.76	15.50±0.46	35.69±1.54	176.34±1.05	12.49±1.55	15.06±0.30	463.59±16.60
NWTT	84.49±3.78	110.10±3.25	21.29±2.10	6.97±1.58	38.91±4.29	17.60±2.02	41.17±2.74	186.55±0.91	24.32±1.68	16.01±1.10	547.42±23.46
NWTE	63.58±2.44	95.92±3.98	11.03±3.96	3.09±1.54	18.51±2.58	15.37±1.86	30.02±2.02	77.26±3.13	13.98±1.88	16.87±3.00	345.63±26.37
BLA	52.66±3.37	108.38±4.27	16.36±4.06	6.30±0.52	23.03±3.97	22.45±6.46	41.24±4.99	81.69±11.79	30.41±0.09	18.72±3.01	401.23±42.53
∑OCPs	660.46±36.29	1293.20±54.15	211.31±34.76	23.44±5.46	346.64±36.85	233.57±34.29	504.21±28.28	1084.03±48.90	249.57±25.80	161.16±25.26	4767.58±330.06
min	20.54±1.88	60.19±3.37	6.98±1.27	nd	16.68±2.25	10.27±1.89	27.56±0.45	22.88±2.11	12.07±1.25	nd	240.61±17.93
Mean	44.03±2.42	86.21±3.61	14.09±2.32	1.56±0.36	23.11±2.46	15.57±2.29	33.61±1.89	72.27±3.26	16.64±1.72	10.74±1.68	317.84±22.00
max	84.49±3.78	116.61±	24.10±1.20	6.97±1.58	38.91±4.29	26.43±0.41	41.24±4.99	186.55±0.91	30.41±0.09	22.68±4.25	547.42±23.46

nd= not detected

E.8 Individual OCP concentrations in autumn soil samples

Site	HCB	HCH	Hpchlor	Aldrin	o, p'-DDE	p,p'-DDE	o, p'-DDD/Dieldrin	Endrin	p,p'-DDD/o,p-DDT	Mirex	∑OCPs
					Concentration (ng/g)						
MDI	40.57±1.95	72.06±4.69	9.68±4.69	nd	23.86±4.64	11.11±2.89	34.52±5.25	88.74±3.29	18.37±4.99	8.70±2.54	307.61±33.73
MDO	48.91±3.02	79.78±1.64	13.55±1.64	1.41±4.12	23.57±3.45	12.40±1.20	33.12±4.42	53.34±5.20	15.47±1.87	26.34±3.01	307.89±30.54
HOF	72.14±2.29	99.01±1.37	20.12±1.37	5.07±2.80	29.97±3.06	18.72±0.36	37.46±2.14	73.75±1.46	18.52±1.31	22.22±5.87	396.94±23.91
AFI	74.16±3.87	104.22±3.31	25.51±3.31	8.62±2.56	46.83±2.21	20.32±2.98	53.37±5.02	84.70±1.59	25.63±3.14	20.86±2.59	464.22±29.86
AFO	61.98±4.25	102.61±3.23	26.71±3.23	3.87±5.11	32.48±6.32	24.77±1.54	61.93±1.71	74.52±4.02	24.84±3.12	10.53±1.49	424.23±37.96
NAD	35.16±4.01	100.98±2.47	17.79±2.47	4.06±3.87	23.56±1.30	30.50±1.05	48.54±1.29	81.57±3.38	16.59±1.45	28.07±3.63	386.83±28.69
JUM	26.77±1.63	66.89±4.37	6.37±4.37	nd	24.88±2.85	20.73±2.61	46.62±3.05	123.69±3.96	28.20±0.58	34.55±4.87	378.70±29.67
IDI	29.03±3.44	73.71±2.02	6.30±2.02	nd	22.51±0.67	16.38±0.93	35.17±3.70	142.83±2.11	16.58±1.34	15.28±5.90	357.79±21.34
IDO	32.27±2.92	78.85±4.56	11.61±4.56	12.81±2.29	44.12±4.90	31.29±4.25	64.28±1.58	151.40±4.00	21.05±1.53	31.58±2.29	479.27±32.35
REH	39.05±2.52	90.42±5.64	5.91±5.64	nd	32.88±3.28	36.66±1.16	52.52±4.05	122.26±5.04	12.44±1.91	25.88±2.98	418.02±29.56
UBP	80.38±4.91	129.52±2.09	31.84±2.09	11.24±3.36	60.90±2.21	28.86±3.27	53.38±4.86	158.51±2.31	25.52±4.33	27.65±7.09	607.80±37.48
NWTT	84.99±4.95	139.73±6.08	24.33±6.08	16.07±1.01	68.07±1.97	51.52±5.13	56.69±3.98	147.35±5.28	32.58±3.59	50.11±2.98	671.45±40.04
NWTE	50.60±1.85	80.44±3.08	17.19±3.08	11.94±1.71	27.42±4.43	15.48±3.35	38.87±5.44	58.75±3.98	16.55±4.51	32.04±3.45	349.27±36.69
BLA	33.42±1.10	55.17±2.87	14.60±2.87	14.99±0.85	84.59±3.91	37.86±3.20	50.84±1.58	59.59±0.22	20.87±0.14	44.24±1.18	416.17±15.73
∑OCPs	709.42±42.71	1273.38±47.43	231.51±47.43	90.09±27.69	545.65±45.21	356.60±33.92	667.31±48.06	1421.00±45.84	293.21±33.81	378.03±49.87	5966.20±427.55
min	26.77±1.63	55.17±2.87	5.91±5.64	nd	22.51±0.67	11.11±2.89	33.12±4.42	53.34±5.20	12.44±1.91	8.70±2.54	307.61±30.54
Mean	50.67±3.05	90.96±3.39	16.54±3.39	6.43±1.98	38.97±3.23	25.47±2.42	47.67±3.43	101.50±3.27	20.94±2.41	27.00±3.56	426.16±30.54
max	84.99±4.95	139.73±6.08	31.84±2.09	16.07±1.01	84.59±3.91	51.52±5.13	64.28±1.58	158.51±2.31	32.58±3.59	50.11±2.98	671.45±40.04

nd = not detected

E.9 Individual OCP concentrations in spring surface water samples

					Concentration (ng/mL)						
Site	HCB	HCH	Hpchlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCPs
MDI	nd	nd	0.37±0.15	0.62±0.10	0.68±0.06	0.78±0.02	1.40±0.10	1.36±0.64	1.08±0.51	0.47±0.02	6.76±1.60
MDO	nd	nd	0.27±0.12	0.63±0.03	0.60±0.06	0.70±0.04	1.29±0.11	1.13±0.50	0.76±0.05	nd	5.38±0.91
HOF	nd	nd	0.33±0.07	0.76±0.01	0.78±0.03	0.87±0.04	1.44±0.07	1.26±0.08	0.82±0.02	nd	6.26±0.32
AFI	nd	nd	0.25±0.05	0.67±0.04	0.70±0.04	0.76±0.04	1.38±0.13	1.02±0.09	0.75±0.02	nd	5.53±0.41
AFO	nd	nd	0.23±0.05	0.67±0.03	0.67±0.06	0.76±0.05	1.34±0.08	1.08±0.04	0.73±0.04	nd	5.47±0.35
NAD	nd	nd	0.23±0.01	0.70±0.07	0.68±0.04	0.77±0.03	1.39±0.06	0.93±0.11	0.76±0.04	nd	5.47±0.36
JUM	0.02±0.00	nd	0.32±0.03	0.85±0.02	0.88±0.07	0.92±0.02	1.59±0.08	1.08±0.08	0.86±0.03	nd	6.53±0.33
IDI	nd	nd	0.23±0.02	0.72±0.05	0.73±0.04	0.82±0.01	1.47±0.06	0.94±0.01	0.79±0.04	nd	5.69±0.23
IDO	nd	nd	0.29±0.02	0.82±0.05	0.84±0.03	0.91±0.01	1.37±0.42	0.98±0.05	0.84±0.03	nd	6.04±0.61
REH	nd	nd	0.28±0.03	1.61±0.04	0.93±0.06	1.01±0.05	1.69±0.06	1.08±0.11	0.92±0.03	nd	7.53±0.38
UBP	nd	nd	0.23±0.03	1.52±0.03	0.77±0.05	0.83±0.01	1.47±0.06	1.13±0.12	0.78±0.02	nd	6.72±0.32
NWTI	nd	nd	0.30±0.02	1.50±0.07	0.82±0.03	0.87±0.04	1.44±0.07	1.09±0.09	0.82±0.02	nd	6.84±0.35
NWTT	nd	nd	0.24±0.02	0.91±0.04	0.58±0.03	0.70±0.03	1.22±0.04	0.84±0.11	0.70±0.02	2.63±0.31	7.82±0.61
NWTE	4.86±0.06	nd	0.36±0.01	0.80±0.06	0.73±0.04	0.91±0.03	1.37±0.02	1.93±0.33	0.97±0.05	nd	11.92±0.60
BLA	0.58±0.02	nd	0.27±0.03	1.11±0.05	0.66±0.01	0.77±0.02	1.35±0.04	0.95±0.11	0.77±0.02	nd	6.47±0.30
∑OCPs	5.46±	nd	4.20±0.67	13.89±0.68	11.04±0.66	12.39±0.46	21.21±1.39	16.81±2.48	12.34±0.96	3.09±0.33	100.44±7.69
min	nd	nd	0.23±0.05	0.62±0.10	0.58±0.03	0.70±0.04	1.22±0.04	0.84±0.11	0.70±0.02	nd	5.38±0.91
mean	0.36±0.07	nd	0.28±0.04	0.93±0.05	0.74±0.04	0.83±0.03	1.41±0.09	1.12±0.17	0.82±0.06	0.47±0.02	6.70±0.51
max	4.86±0.00	nd	0.37±0.15	1.61±0.04	0.93±0.06	1.01±0.05	1.69±0.06	1.93±0.33	1.08±0.51	2.63±0.31	11.92±0.60

nd= not detected

E.10 Individual OCP concentrations in spring pore water samples

Site	HCB	HCH	Hpchlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	Endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCPs
					Concentration (ng/mL)						
MDI	nd	nd	nd	4.13±0.06	5.66±0.05	7.02±0.05	8.96±0.06	nd	4.64±0.12	1.13±0.17	31.56±0.51
MDO	nd	nd	nd	2.41±0.88	3.47±1.02	4.02±0.91	5.44±0.89	nd	nd	0.77±0.70	16.12±4.39
HOF	2.00±0.20	1.47±0.56	3.77±0.32	7.10±0.11	6.60±0.05	7.43±0.09	7.05±0.06	nd	5.86±0.05	4.84±0.88	46.12±2.31
AFI	nd	1.13±0.72	1.55±0.36	5.39±0.23	5.94±0.16	6.89±0.01	8.91±0.09	nd	5.06±0.06	1.02±0.31	35.89±1.34
AFO	nd	nd	nd	3.53±0.18	4.40±0.35	5.17±0.16	7.03±0.18	nd	nd	0.47±0.23	20.60±1.10
NAD	nd	1.31±0.75	2.58±0.36	7.05±0.17	9.38±0.13	11.56±0.12	15.14±0.16	nd	8.28±0.21	1.77±0.43	57.08±2.34
TUM	nd	nd	2.44±0.44	6.05±0.14	8.61±0.11	11.94±0.15	15.43±0.22	8.42±0.28	7.85±0.23	1.72±1.16	62.46±2.74
IDI	nd	2.96±0.25	3.03±0.09	9.81±0.09	12.73±0.05	15.65±0.07	20.65±0.10	7.13±0.25	10.93±0.02	3.34±0.26	86.23±1.18
IDO	nd	0.95±0.11	3.09±0.48	10.56±0.13	16.06±0.05	19.43±0.06	26.59±0.06	4.67±0.66	14.00±0.08	2.26±0.17	97.60±2.45
REH	nd	1.96±0.65	3.63±0.79	9.55±0.15	13.54±0.08	16.72±0.05	22.49±0.06	5.20±0.22	11.48±0.16	3.25±0.18	87.81±2.34
UBP	nd	0.76±0.02	3.47±0.39	10.40±0.12	13.18±0.10	16.62±0.02	21.71±0.12	12.96±0.07	11.03±0.09	4.02±0.47	94.16±1.42
NWTT	2.20±0.89	2.53±0.09	4.21±0.75	14.82±0.04	16.12±0.05	19.61±0.11	25.40±0.02	5.96±0.08	13.88±0.11	5.04±0.29	109.77±2.42
NWTE	nd	0.80±0.01	4.46±0.49	9.74±0.02	15.99±0.09	19.77±0.05	25.22±0.04	10.92±0.19	12.50±0.11	2.95±0.18	102.35±1.27
BLA	nd	1.63±0.49	nd	5.69±0.05	8.05±0.10	10.08±0.11	12.85±0.03	nd	6.80±0.11	2.00±0.46	47.09±1.35
∑OCPs	4.21±1.09	15.51±3.76	32.24±4.48	106.22±2.38	139.75±2.38	171.92±1.96	222.87±2.10	55.25±1.75	112.31±1.35	34.58±5.92	894.84±27.17
min	nd	nd	nd	2.41±0.88	3.47±1.02	4.02±0.91	5.44±0.89	nd	nd	0.47±0.70	16.12±4.39
mean	0.30±0.08	1.11±0.27	2.30±0.32	7.59±0.17	9.98±0.17	12.28±0.14	15.92±0.15	3.95±0.13	8.02±0.10	2.47±0.42	63.92±1.94
max	2.20±0.89	2.96±0.65	4.46±0.49	14.82±0.04	16.12±0.05	19.77±0.05	26.59±0.06	12.96±0.07	14.00±0.08	5.04±0.29	109.77±2.42

nd= not detected

E.11 Individual OCP concentrations in spring sediment samples

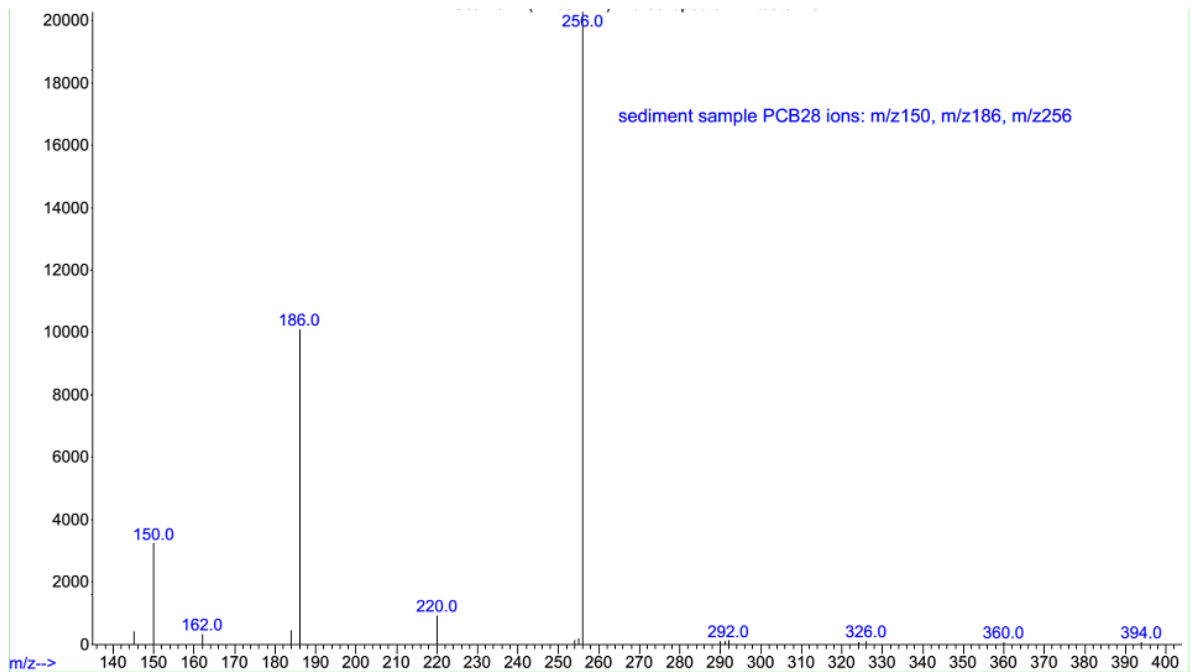| Site	HCB	HCH	Hpchlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'-DDT	mirex	∑OCPs
					Concentration (ng/g)						
MDI	21.13±2.16	33.88±3.51	37.20±2.68	nd	26.70±4.43	30.86±0.96	35.46±4.82	18.07±1.63	25.01±1.60	10.47±2.61	238.78±24.40
MDO	14.67±2.21	56.57±3.17	45.85±3.28	2.38±1.30	19.21±3.07	20.71±4.24	30.40±3.63	27.32±3.61	20.71±2.99	6.31±0.41	244.14±27.91
HOF	23.52±0.53	87.31±2.27	11.98±2.05	15.66±1.53	37.29±6.85	55.47±5.36	37.76±4.98	23.19±3.76	17.30±2.56	4.40±1.09	313.89±30.97
AFI	5.02±1.97	63.53±3.66	32.26±2.58	12.56±1.60	39.12±2.02	26.18±2.20	44.32±6.54	14.55±1.25	24.28±3.22	8.83±1.32	270.66±26.36
AFO	4.52±5.29	51.20±3.12	52.92±4.26	15.60±3.68	22.31±5.30	22.23±4.34	22.45±3.00	17.69±4.05	17.85±6.42	19.41±2.37	246.17±41.83
NAD	nd	3.72±1.60	17.10±4.27	17.69±4.11	17.30±1.18	18.35±1.71	24.10±2.01	27.29±2.09	19.68±1.79	23.68±2.21	168.92±20.98
TUM	10.01±2.22	24.10±2.29	24.80±1.71	6.60±2.84	19.21±0.45	20.98±1.13	25.21±1.05	31.67±5.01	21.04±0.68	9.81±2.44	193.45±19.82
IDI	9.88±1.41	99.90±2.52	28.31±5.98	nd	19.89±1.17	21.05±0.24	23.50±1.01	23.32±4.91	18.52±2.51	8.13±3.05	252.49±22.79
IDO	6.30±1.34	12.39±1.91	31.14±6.32	16.65±1.99	20.35±1.79	21.47±1.44	26.60±0.88	28.07±5.11	20.18±2.83	7.68±0.57	190.83±24.19
REH	6.02±0.60	13.85±0.71	34.36±4.40	19.36±2.73	18.58±5.06	30.19±5.88	23.73±4.55	19.44±2.03	21.21±4.77	18.63±1.63	205.38±32.35
UBP	24.15±1.88	26.66±3.29	46.82±2.81	66.78±2.67	33.39±2.65	42.07±3.25	42.46±3.21	32.40±6.75	26.36±5.05	25.52±2.48	366.62±34.04
NWTI	38.97±4.05	159.02±2.02	41.39±0.32	80.73±4.21	51.74±4.91	37.19±3.09	33.33±0.62	19.77±1.52	28.69±2.18	27.52±0.45	518.35±23.38
NWTT	37.85±0.92	276.39±2.98	58.63±2.89	93.04±4.22	67.24±0.48	32.11±1.13	24.25±1.50	32.96±1.53	34.34±2.54	27.89±0.59	684.68±18.76
NWTE	29.75±0.79	176.79±2.53	44.22±1.51	71.13±3.28	63.56±5.84	33.50±2.64	23.51±1.33	19.99±1.11	38.59±0.54	19.29±0.59	520.32±20.16
BLA	7.10±0.37	59.82±0.83	32.47±1.49	40.96±3.49	29.16±2.39	26.52±0.83	38.53±6.84	26.26±1.35	36.19±2.47	13.11±1.20	310.12±21.27
∑OCPs	238.89±25.73	1145.12±36.42	539.46±46.55	459.12±37.66	485.07±47.59	438.90±38.45	455.61±45.98	362.00±45.71	369.95±42.12	230.68±23.02	4724.80±389.22
min	nd	3.72±1.60	11.98±2.05	nd	17.30±	18.35±1.71	22.45±3.00	14.55±1.25	17.30±	4.40±1.09	168.92±20.98
mean	15.93±1.72	76.34±2.43	35.96±3.10	30.61±2.51	32.34±3.17	29.26±2.56	30.37±3.07	24.13±3.05	24.66±2.81	15.38±1.53	314.99±25.95
max	38.97±4.05	276.39±2.98	58.63±2.89	93.04±4.22	67.24±0.48	55.47±5.36	44.32±6.54	32.96±1.53	38.59±0.54	27.89±0.59	684.68±18.76

nd = not detected

E.12 Individual OCP concentrations in spring soil samples

							Concentration(ng/g)				
Site	HCB	HCH	Hpchlor	aldrin	o,p'-DDE	p,p'-DDE	o,p'-DDD/Dieldrin	endrin	p,p'-DDD/o,p'DDT	mirex	∑OCPs
MDI	5.68±1.60	31.26±0.45	17.99±2.11	10.26±0.84	16.77±4.36	22.09±2.80	25.96±3.39	20.71±6.21	29.73±3.83	6.50±1.54	186.96±27.13
MDO	2.88±1.52	18.78±1.28	18.72±1.53	7.58±5.52	21.96±3.24	17.27±2.49	23.27±1.34	50.41±2.01	16.15±2.91	8.95±2.61	185.96±24.45
HOF	3.43±0.26	91.96±4.60	16.12±0.57	16.10±3.31	59.16±2.94	29.45±2.67	22.67±0.06	37.30±2.58	26.31±0.71	3.97±3.68	306.47±21.38
AFI	0.54±0.59	28.93±6.96	24.68±2.20	13.02±3.44	26.90±6.02	22.86±3.14	25.10±1.67	62.33±3.68	20.88±1.67	22.01±2.90	247.25±32.27
AFO	nd	6.94±0.51	13.37±1.94	11.61±2.54	15.67±2.70	15.58±4.64	21.95±1.12	39.59±2.01	17.05±2.44	23.96±2.07	165.72±2.07
NAD	6.57±2.86	4.21±0.35	17.41±0.53	19.99±2.66	23.11±4.33	25.13±3.60	32.04±2.67	48.82±4.87	23.49±3.02	25.94±0.62	226.70±25.51
TUM	3.57±1.91	16.69±0.82	9.56±1.51	5.48±2.13	14.85±2.10	17.81±1.94	23.39±1.15	31.10±2.30	17.47±1.69	4.02±1.00	143.94±16.57
IDI	nd	15.59±0.85	9.72±0.63	8.77±3.05	12.04±2.40	14.50±3.11	18.15±0.90	32.41±3.62	14.22±1.72	5.28±1.27	130.67±17.55
IDO	nd	4.11±0.65	10.73±0.31	13.47±1.74	13.50±2.13	16.77±2.65	23.74±2.50	27.92±6.45	17.98±1.62	8.22±2.17	136.43±20.22
REH	nd	21.02±2.21	22.79±1.58	15.63±1.58	15.02±3.78	24.97±6.09	21.50±1.46	19.26±2.07	18.77±3.58	11.42±5.26	170.39±27.61
UBP	5.58±2.64	32.71±1.32	22.73±2.23	17.92±4.44	16.71±2.92	17.33±4.10	26.70±4.01	29.03±4.03	15.16±2.47	25.80±6.09	209.67±34.25
NWTT	15.51±1.35	14.61±3.35	26.44±0.78	26.21±1.69	24.03±0.73	30.56±3.45	22.22±2.40	91.04±2.98	25.98±1.91	40.06±6.55	316.65±25.18
NWTE	8.95±2.34	84.31±3.00	14.79±5.81	21.59±9.48	12.25±1.12	15.73±1.40	25.72±0.52	60.69±2.24	18.95±3.29	23.44±5.97	286.43±35.17
BLA	10.56±3.99	47.27±1.06	22.58±5.25	21.48±5.37	23.62±3.69	15.14±1.97	28.65±0.39	35.64±6.68	45.90±3.69	28.69±2.98	279.51±35.05
∑OCPs	63.27±19.07	418.39±27.41	247.64±26.98	209.10±47.76	295.59±42.47	285.18±44.06	341.05±23.59	586.24±51.72	308.04±34.54	238.25±44.71	2992.75±344.42
min	nd	4.11±0.65	9.56±1.51	5.48±2.13	12.04±2.40	14.50±3.11	18.15±0.90	19.26±2.07	14.22±1.72	3.97±3.68	130.67±17.55
mean	4.52±1.73	29.88±1.96	17.69±1.93	14.94±3.41	21.11±3.03	20.37±3.15	24.36±1.69	41.87±3.69	22.00±2.47	17.02±3.19	213.77±24.60
max	15.51±1.35	91.96±4.60	26.44±0.78	26.21±1.69	59.16±2.94	30.56±3.45	32.04±2.67	91.04±2.98	45.90±2.47	40.06±6.55	316.65±25.18

APPENDIX F: MASS SPECTRUM SHOWING MONITORED IONS

F.1 Example of PCB (PCB28) ions monitored in SIM mode

F. 2 Example of OCP (HCH) ions monitored in SIM mode

Scan 155 (6.932 min): ocpstd4ppm1.D\data.ms

HCH standard ions: m/z147, m/z183, m/z219

Scan 155 (6.932 min): wurpw11ocprun2.D\data.ms

sediment sample HCH ions: m/z147, m/z183, m/z219